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(57) Washing method comprising at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in the tub of washing water and of a detergent comprising at least one the so called "stimuli-responsive" surfactants, a main wash obtained by the interaction of a mixture of washing water and detergent with the one or more products for removing the dirt from

the one or more products and creating a water suspension of "surfactants-dirt" aggregates, and one or more rinses of the one or more products contained into the tub by rinsing water. The washing method comprises at least the application, to the water suspension of "surfactants-dirt" aggregates and/or to the rinsing water, of one or more stimuli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way.



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Description

[0001] The present invention refers to a washing method and a washing machine implementing the method.

[0002] Nowadays washing machines, e.g. laundry washers and dishwashers, typically comprise an outer casing, provided with a loading/unloading door, containing a washing tub in which the products to wash (e.g. clothes, textiles, dishes, etc) are placed during the washing cycle; in the case of the laundry washers a perforated drum is also rotatably installed in the tub for holding and shaking the laundry to be washed.

[0003] Commonly used washing machines comprise also means to introduce and distribute a detergent in the washing tub (and also in the drum in the case of the laundry machines), means to introduce and distribute the washing and the rinsing water in the washing tub, means for heating the washing water, and discharge means for evacuating the washing water after the wash and after the rinse.

[0004] These washing machines of known type comprise also interface means for allowing the user to select a washing program and to set and/or to display some washing parameters (e.g. the washing water's temperature, the washing time, etc).

[0005] The washing cycle carried out in these kinds of washing machine includes at least a main wash, achieved by the pouring of the washing water and detergent in the tub, for washing the products contained in it.

[0006] After the main wash, the mixture of dirty washing water and detergent is normally drained out of the washing machine, and discharged into the sewer conduit.

[0007] The washing cycle includes also, after the main wash, the rinse of the products contained in the tub with clean water, followed by the drain of the latter.

[0008] The water and the detergent utilized in the washing cycle can be used only one time, and must be discharged during and/or at the end of the cycle; this generates two kind of problems, one related to the consumption of water and detergent, and the other related to the introduction in the environment of the dirty water-detergent mixture, that could be a source of pollution.

[0009] The detergents commonly used in the above mentioned washing machines are complex products containing some different compounds (e.g. surfactants, builders, bleach, enzymes, soil release compounds, fragrances, etc); the surfactants have the main role in the dirt removal.

[0010] The common surfactants currently used in washing machines are molecules with a hydrophilic head and a hydrophobic chain; the hydrophobic chain has the role to interact with and to remove the dirt from the product to wash (e.g. textiles or dishes), while the role of the hydrophilic head is to enhance the solubility in water.

[0011] When these surfactants are melted in water, they produce a foam that interacts with the dirt, removing it from the products to wash.

[0012] The aggregates of surfactants and dirt particles

(named "micelles") are stable in water as a water suspension.

[0013] After the main wash, the water suspension of "surfactants-dirt" aggregates is drained out of the washing machine.

[0014] The use of these kinds of surfactants in the washing machines typically creates some problems connected with the fact that the surfactants, once they are added to water, are difficult to remove, and consequently the water suspension of "surfactants-dirt" introduced in the environment after the wash could be a source of environmental pollution.

[0015] This problem is further aggravated by the fact that surfactants may be harmful, or even toxic, under certain circumstances, e.g. when interacting with lipid membranes or denaturing proteins.

[0016] Furthermore, sometimes some residuals of surfactants can remain on the washed products, with the risk that they can produce allergic reactions and/or skin irritations in the people coming in contact to them.

[0017] Nowadays some molecules called "stimuli-responsive" or "intelligent" surfactants are also known; these molecules are similar to the above-mentioned surfactants, but with the further characteristic to change their properties (e.g. their solubility in water) on the basis of an external stimulus.

[0018] The stimulus can be physical (e.g. changes of the temperature, light, pressure, mechanical stress, electrical or electromagnetic stimuli, etc), or chemical (changes of the pH value, chemical reactions, salt addition, presence of metal ions, etc).

[0019] The changes in the properties of the surfactants can be irreversible or reversible; in the first case, the stimulus breaks (or weakens) one or more chemical bonds in the molecule of the surfactant, with the result of the loosening of the hydrophobic-hydrophilic properties (these kinds of surfactants are called "cleavable surfactants").

[0020] In the second case, the stimulus can be used to switch the properties of the surfactant (or of a part of it) in the reversible way (in this case the surfactants are named "on demand surfactants").

[0021] The aim of the present invention is to obtain a washing method and a washing machine implementing the method that allow washing the desired products with a low environmental impact.

[0022] Within this aim, another object of the invention is to achieve the wash of the desired products reducing the waste of detergent and of washing/ rinsing water.

[0023] An additional object of the invention is to reduce the risk of allergic reactions and skin irritations for the people coming in contact to the washed products.

[0024] Another object of the invention is to increase the washing performances.

[0025] It is therefore an object of the present invention to solve the above- noted problems, thereby doing away with the drawbacks of the cited prior art.

[0026] The Applicant has found that by the application of one or more appropriate stimuli to the "stimuli-respon-

sive" surfactants in one or more pre-established points of the washing cycle, it is possible to modify selectively some properties of the surfactants particles in a way that reduce or eliminate the above-mentioned problems.

[0027] In particular, the above-mentioned aim and objects, as well as others that will become better apparent hereinafter, are achieved by a washing method comprising at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in the tub of washing water and of a detergent comprising at least one the so called "stimuli-responsive" surfactants, a main wash obtained by the interaction of a mixture of the washing water and detergent with the one or more products for removing the dirt from these products and creating a water suspension of "surfactants-dirt" aggregates, and one or more rinses of the one or more products contained into the tub by rinsing water; the method comprises at least the application, to the water suspension of "surfactants-dirt" aggregates and/or to the rinsing water, of one or more stimuli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way.

[0028] Preferably, if the one or more stimuli are applied to the rinsing water, after the application of the one or more stimuli, the rising water is recycled for a further rinse, directly or after being stored in storage means, sited internally or externally to the washing machine.

[0029] The one or more stimuli may be applied to the water suspension of "surfactants-dirt" aggregates and/or to the rinsing water while it is passing through a discharge conduct coming out of the tub and/or inside storage means sited internally or externally to the washing machine, and/or inside a further discharge conduct coming out of the storage means.

[0030] In a different possible embodiment of the present invention, the method comprises at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in the tub of washing water and detergent comprising at least one of the so called "stimuli-responsive" surfactants, a main wash obtained by the interaction of a mixture of the washing water and the detergent with the one or more products for removing the dirt from these one or more products and creating a water suspension of "surfactants-dirt" aggregates, and the discharge of the water suspension of "surfactants-dirt" aggregates from the tub, it comprises at least the further following steps:

- a. application to the water suspension of "surfactants-dirt" aggregates, after discharge from the tub, of one or more stimuli suitable for changing in a reversible way the solubility properties of the surfactants, so as to obtain a phase separation among the surfactants particles and the dirty water;
- b. removal of the surfactants particles from the dirty water;
- c. draining of the dirty water, deprived of the sur-

factants particles; and

- d. recycling of the surfactants particles for a further washing cycle.

[0031] Preferably, the method comprises the step of keeping the changed solubility properties of the surfactants particles during the step of removal of the surfactants particles from the dirty water, so as to maintain the phase separation among the surfactants and the dirty water, and the further step of suppressing the one or more stimuli or to submit the surfactants particles to one or more reverse-stimuli to restore the original solubility properties.

[0032] Before being reused in the further washing cycle, the surfactants particles previously used in the main wash may be stored in a storage device placed internally or externally to the washing machine.

[0033] In another possible embodiment, the method comprises at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in the tub of washing water and detergent comprising at least one of the so called "stimuli-responsive" surfactants, a main wash obtained by the interaction of a foam, made of a mixture of washing water and detergent, with the one or more products for removing the dirt from these one or more products and to create a water suspension of "surfactants-dirt" aggregates; in this embodiment the method comprises at least the further following steps:

- a. monitoring if the amount of foam in the tub is within a prefixed range; and
- b. if the amount of the foam is outside this prefixed range, application to the mixture of washing water and detergent of one or more stimuli suitable for changing the one or more "stimuli-responsive" surfactants properties, so as to modify the amount of foam.

[0034] The step of monitoring if the amount of the foam in the tub is within a prefixed range may comprise monitoring if one or more properties of the "stimuli-responsive" surfactants affecting the amount of foam are within predetermined ranges.

[0035] According to a further aspect thereof, the present invention relates to a washing machine comprising at least an outer casing, a washing tub in which products to wash are loaded to be submitted to a washing cycle, and a liquid feeding device to introduce into the tub washing water and a detergent containing one or more "stimuli-responsive" surfactants into the tub, for creating a water/detergent mixture interacting with the products for removing the dirt from these one or more products and creating a water suspension of "surfactants-dirt" aggregates, the liquid feeding device being also suitable to introduce into the tub rinsing water; in this embodiment the machine comprises a stimulation device for the application to the water suspension of "surfactants-dirt" aggregates and/or to the rinsing water, of one or more stim-

uli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way.

[0036] The stimulation device may be associated with the tub or with a recirculation circuit connected with the tub for draining the rinsing water from the tub after each rinse, and for re-introducing the rinsing water in the tub after the application to it of the one or more stimuli by the stimulation device.

[0037] In a different embodiment, the washing machine comprises at least an outer casing, a washing tub in which products to wash are loaded to be submitted to a washing cycle, and a liquid feeding device to introduce into the tub washing water and a detergent containing one or more "stimuli-responsive" surfactants into the tub, for creating a water/detergent mixture interacting with the products for removing the dirt from these products and creating a water suspension of "surfactants-dirt" aggregates, the liquid feeding device being also suitable to introduce into the tub rinsing water; in this embodiment the washing machine comprises at least a stimulation device for the application to the water suspension of "surfactants-dirt" aggregates of one or more stimuli suitable for changing in a reversible way the solubility properties of the surfactants, so that to obtain a phase separation among the surfactants particles and the dirty water, a surfactant removal device for removing the surfactants particles from the dirty water, a draining line for draining the dirty water, deprived of the surfactants particles, and a recycling line for recycling the surfactants particles for a further washing cycle.

[0038] The surfactant removal device may comprise a filter, and/or a centrifuge, and/or a decanter, or a septum made of a material able to attract the surfactant particles only if their chemical/physical properties are changed consequently to the application of the one or more stimuli.

[0039] The recycling line may comprise a storage device placed internally or externally to the washing machine.

[0040] In a still different embodiment, the washing machine comprises at least an outer casing, a washing tub in which products to wash are loaded to be submitted to a washing cycle, and a liquid feeding device to introduce into the tub washing water and a detergent containing one or more "stimuli-responsive" surfactants into the tub, for creating a water/detergent mixture generating a foam interacting with the products for removing the dirt from these products and creating a water suspension of "surfactants-dirt" aggregates, the liquid feeding device being also suitable to introduce into the tub rinsing water; in this embodiment the washing machine comprises a monitoring device for monitoring the amount of foam in the tub, and a stimulation device for the application to the water/"stimuli-responsive" surfactants mixture of one or more stimuli suitable for changing the "stimuli-responsive" surfactants properties, so as to modify the amount of foam, if the amount of foam in the tub is outside a prefixed range.

[0041] The monitoring device may comprise one or

more monitoring sensors, connected to the tub for revealing the amount of the foam, and operatively connected to an electronic control system for communicating to it an information related to the amount of foam, the electronic control system commanding the stimulation device and/or being operatively connected to an interface displaying device to display the amount of foam, so as to allow a user to activate the stimulation device.

[0042] Features and advantages of the present invention will anyway be more readily understood from the description that is given below by way of nonlimiting example with reference to the accompanying drawings, in which:

- **Figure 1** is a schematic view of a first embodiment of a washing machine according to the invention;
- **Figure 2** is a flow chart illustrating the steps of a first embodiment of the washing method according to the invention;
- **Figure 3** is a flow chart illustrating the steps of a second embodiment of a washing method according to the invention;
- **Figure 4** is a flow chart illustrating the steps of third embodiment of a washing method according to the invention;
- **Figure 5** is a flow chart illustrating the steps of a fourth embodiment of a washing method according to the invention;
- **Figure 6** is a flow chart illustrating the steps of a fifth embodiment of a washing method according to the invention;
- **Figure 7** is a flow chart illustrating the steps of a sixth embodiment of a washing method according to the invention.

[0043] It must be noticed that the washing method and the washing machine according to the invention that will be described in the following should be applied substantially to at any kind of washing machine, in particular to a laundry washer or to a dishwasher.

[0044] In **Figure 1** is schematically illustrated a first embodiment of a washing machine 1, particularly a laundry washer, according to the invention; the washing machine 1 comprises an outer casing 2, containing a washing tub 3, in which is rotatably installed a perforated drum 4, in which the products 5 to wash (in this case textiles, clothes, etc) can be loaded.

[0045] The washing machine 1 comprises a liquid feeding device to introduce into the tub 3 the washing water, a detergent containing one or more "stimuli-responsive" surfactants, and the rinsing water.

[0046] The liquid feeding device advantageously comprises an adduction conduct 6 fluidly connectable to the hydraulic system of the building in which the washing machine 1 is installed and ending into the tub 3, for the adduction of the clean water to the tub 3; the liquid feeding device further comprises an admission drawer 7 arranged along the adduction conduct 6, for housing a de-

tergent which is conveyed into the tub 3 by the water flowing in the adduction conduct 6.

[0047] The washing machine 1 comprises also a discharge conduct 8, for evacuating the washing water after the wash and/or after the rinse, fluidly connected to the tub 3 and advantageously provided with a pump 9 to drain the water from the bottom of the tub 3.

[0048] Advantageously the pump 9 can be also fluidly connected to a recirculation circuit 10, designed so as to recirculate into the top of the tub 3 some of the washing/rinsing water drawn from the bottom of the tub 3 by the pump 9, via the discharge conduct 8, during the wash or during the rinsing, so as to assure that the washing/rinsing water reaches all the products 5 placed in the tub 3.

[0049] The washing machine 1 comprises also an interface displaying device 11, cooperating with the electronic control system of the washing machine 1, not illustrated, for allowing the user to select a washing program and to set and/or to display some washing parameters (e.g. the washing water's temperature, the washing time, etc).

[0050] The washing machine 1 also comprises one or more stimulation devices 12 suitable to apply one or more stimuli to the "stimuli-responsive" surfactants contained in the detergent, as will be described in the following.

[0051] Advantageously the stimulation device 12 can be a device suitable to change the pH value, for example an electrolyser, which can be set both internally and externally to the washing machine; the electrolysis of the water produces an acid water solution and an alkaline water solution that can be used to change the pH of the washing bath.

[0052] The pH value could also be modified, for instance, by the addition of some suitable additives to the mixture of water and surfactants.

[0053] Alternatively the stimulation device 12 can be, for instance, a suitable source of light radiation or another electromagnetic radiation (internal or external to the washing machine).

[0054] The stimulation device 12 can also be a heater or another device suitable to modify the temperature of the water (internal or external to the washing machine).

[0055] Advantageously, the stimulation device 12 can be actuated by the electronic control system of the washing machine.

[0056] Advantageously the number and the position of the stimulation devices 12 could be the more pertinent, in relation to the various particular embodiments of the invention. In particular, depending on the embodiment, the appliance can comprise one, two, or even more stimulation devices 12. If the appliance comprises two or more stimulation devices, these can be of a same type or of different types, and can be arranged, according to the needs, in positions close to each other, so as to operate in the same area, or in different positions, as will be explained in more detail below.

[0057] In **Figure 2** is represented a flow chart schematizing the steps of a first embodiment of a washing

method according to the invention.

[0058] In this case, after loading the products to wash in the tub 3 of the washing machine 1 (as mentioned above, in the case of a laundry washer, the laundry to wash are loaded into the perforated drum 4 contained in the tub 3), by operating on the interface displaying device 11 it is possible to select the desired washing program (step 100) depending on the type and of the dirty-level of the products 5 to wash.

[0059] For instance, in the case of a laundry washer it is possible to select the desired washing temperature, the rotating speed of the perforated drum 5, the time of washing, etc.

[0060] Once the program has been selected and started, the washing water and of the detergent are adducted into the tub (step 105), and the main wash is then started (step 110); the main wash can be a typical main wash of known washing machines.

[0061] In the washing method according to the invention, the detergent could contain some different compounds, but in particular it must contain one or more of the "stimuli-responsive" surfactants mentioned below.

[0062] Advantageously the stimulus changing the properties of these "stimuli-responsive" surfactants can be physical (e.g. changes of the temperature, light, pressure, etc) and/or chemical (changes of the pH value, chemical reactions, salt addition, presence of metal ions, etc).

[0063] In the first embodiment illustrated in **Figure 2**, the changes in the properties of the "stimuli-responsive" surfactants are irreversible.

[0064] During the main wash (step 110), the "stimuli-responsive" surfactants interact with the washing water, creating a foam which interacts with and removes the dirt from the product to wash (e.g. textiles or dishes).

[0065] Some known examples of "stimuli-responsive" surfactants sensible to the pH variations, or to the presence of ions and salts, are the surfactants or the polymers supporting the surfactants based on molecules functionalized with carboxylic acids group, amminic groups, amidic groups, piridinic groups, benzoic acids groups, imidazole groups.

[0066] Other known "stimuli-responsive" surfactants sensible to the pH variations are, for example, weak polyacids as poly(acrylic acid) (PAAc), poly(methacrylic acid), derivatives of p-aminobenzene sulphonamide, Poly(N,N0-dimethyl aminoethyl methacrylate), Poly(vinyl imidazole), alginate polymers, polymethylmethacrylate based polymers (for example the product commercially known as EUDRAGIT), chitosanes, polymers based on piperazine as Poly(N-acryloyl-N0-alkylpiperazine) and peptide derived polymers.

[0067] Some known examples of "stimuli-responsive" surfactants sensible to light radiation are the surfactant molecules based on azobenzene groups (4-ethylazobenzene 49-(oxyethyl) trimethylammonium bromide (EZTABr), 4-alkylazobenzene-49-(oxy-2-hydroxypropyl) trimethylammonium methylsulfate (AZMS-0, AZMS-1,

AZMS-2, AZMS-4, and AZMS-8), spiropyran groups, stilbene derivatives, cinnamate groups, triarylmethane.

[0068] Some known examples of "stimuli-responsive" surfactants sensible to a redox stimulus (i.e. chemical reactions with exchanges of electrons) are polymeric molecules based viologens, paraphenylene diamine, ferrocenes and derived species, nicotinamide.

[0069] Some known examples of "stimuli-responsive" polymers supporting surfactant sensible to temperature are poly(N-isopropylacrylamide) (PNIPAAm), polyacids, polyacrylamide derivatives, N-acryloylpyrrolidine, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers (Pluronics, or Poloxamers) and derived substituted polymers, Poly(N-substituted acrylamide) derived polymers, (Poly(N-isopropylacrylamide), Poly(N,N'-diethylacrylamide), Poly(2-carboxyisopropylacrylamide), Poly(N-(L)-(1-hydroxymethyl) propylmethacrylamide)), Poly(N-acryloyl-N'-alkylpiperazine) derived polymers, Poly(N-vinylisobutylamide), Poly(vinyl methyl ether), Poly(N-vinylcaprolactam), Poly(dimethylaminoethyl methacrylate), poly(2-ethoxyethyl vinyl ether-b-2-hydroxyethyl vinyl ether)

[0070] Some known examples of "stimuli-responsive" surfactants sensible to a light radiation, in which the stimulus changes irreversibly the properties of the surfactant are the photo degradable phenylazosulfonates (sodium 4-alkylphenylazosulfonates) and derived molecules.

[0071] Advantageously the detergent could contain also one or more enzymes, of the known type, supported by a polymeric substratum that can change its properties (e.g. its solubility in water) consequently to an external stimulus, similarly to the above mentioned "stimuli-responsive" surfactants or supporting polymers; the role of these enzymes could be, for example, to improve the removal of the lipid particles from the products to wash.

[0072] Some known examples of enzymes usually contained in the detergent are amylase, mannanase, protease, cellulase, glycosidase, lipase.

[0073] After the main wash, the water suspension of "surfactants-dirt" aggregates is discharged from the tub (step 115) through the discharge conduct 8.

[0074] Possibly, the discharged water suspension of "surfactants-dirt" aggregates may be stored in first storage means (step 118), which can be, for example, a first storage tank, indicated with the reference number 13 in Figure 1 sited internally or externally to the washing machine 1.

[0075] Advantageously, as mentioned above, the washing machine 1 is provided with a stimulation device 12 suitable to apply to the water suspension of "surfactants-dirt" aggregates, after the main wash, one or more stimuli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way (step 120).

[0076] These stimuli can be applied when the water suspension of "surfactants-dirt" aggregates is flowing through the discharge conduct 8; in this case the stimu-

lation device 12 can be arranged along the discharge conduct 8.

[0077] Alternatively the stimulation device 12 can be associated with the storage tank 13, so as to apply the stimulus when the water suspension of "surfactants-dirt" aggregates is stored in the first storage tank 13.

[0078] As a further alternative, the stimulation device 12 can be arranged along a further discharge conduct 14 coming out from the storage tank 13, so as to apply the stimulus to the water flowing through the conduct 14.

[0079] In a still further alternative, two or more stimulation devices 12 can be arranged in the different positions indicated above, so as to enhance the stimulation effect.

[0080] After being submitted to these one or more stimuli (step 120), the water suspension of "surfactants-dirt" aggregates is drained out (step 125), and can be released into the environment with a reduced impact on the latter, because the surfactants molecules contained in that water have been broken by the stimulus, losing their polluting effect.

[0081] Anyway the stimulus or stimuli must be applied to the water suspension of "surfactants-dirt" aggregates when it has been drained from the tub 3, because if the application of the stimulus or stimuli takes place inside the tub 3, the breaking of the surfactants molecules would release again the dirt inside the tub 3.

[0082] The steps 115, 118, 120 and 125 overall form a step of the present embodiment, herein after called "irreversible stimulus at the end of main wash", and indicated with the reference number 130.

[0083] Alternatively to the application by an automatic stimulus device 12 as the ones previously described, the stimulus can also be triggered by the user, for instance by adding an appropriate additive to the water suspension of "surfactants-dirt" aggregates, advantageously when said water suspension of "surfactants-dirt" aggregate is stored in the first storage tank 13, for example through a suitable admission door (not illustrated) provided on said first storage tank 13.

[0084] In a following step of the washing method illustrated in Figure 2, the products to be washed, placed inside the tub 3 (or inside the drum 4 in the case of a laundry washer), are submitted to one or more rinses, made with clean water, for removing the residual particles of dirt and surfactants (step 135). In this case, after each rinse the rinsing water is drained out of the washing machine 1. Corresponding spin cycles are also typically applied.

[0085] In Figure 3 is illustrated a flow chart schematically representing a second embodiment of the washing method according to the invention.

[0086] After the program selection and start (step 100), the loading of water and surfactants into the tub (step 105) and the main wash (step 110), the water suspension of "surfactants-dirt" aggregates is drained with the application of the "irreversible stimulus at the end of main wash" (step 130), as previously described, or alternative-

ly it is drained without any stimulus, as in the traditional washing processes (step 140).

[0087] After draining of these water suspension, the products 5 to wash, stored in the tub 3 of the washing machine 1 (or in the drum 4 in the case of a laundry washer), are submitted to one or more rinses (step 135).

[0088] After each rinse (step 135), the rinsing water, containing a residual amount of "stimuli-responsive" surfactants, is submitted to one or more stimuli suitable for irreversibly breaking the "stimuli-responsive" surfactants residuals molecules (step 145).

[0089] After being submitted to these one or more stimuli, the rinse water can be drained (step 150) through the draining conduct 8, and can be released into the environment with a reduced impact on the latter, because the surfactants molecules contained in that water have been broken by the stimuli, losing their polluting effect.

[0090] Also in this case the application of said one or more stimuli can be advantageously obtained by a suitable internal washing machine device and/or directly by the user.

[0091] Advantageously said stimulation device 12 can be positioned so as to apply the stimulus directly into the tub 3, or in the discharge conduct 8 where the discharged rinsing water flows.

[0092] The rinsing water may be stored in second storage means (which could also coincide to the first storage means already described), which can be, for example, a second storage tank (not illustrated) sited internally or externally to the washing machine 1; in this case said one or more stimuli can be applied, instead of inside the discharge conduct 8, inside the second storage means, or inside a further discharge conduct (not illustrated) coming out of the latter.

[0093] A third embodiment of the washing method according to the invention is illustrated in **Figure 4**.

[0094] Up to the rinses (step 135), this embodiment coincides with the embodiment of Figure 3.

[0095] In this case, after each rinse (step 135) and after the submission of the rinsing water to one or more stimuli suitable for irreversibly breaking the "stimuli-responsive" surfactants residuals molecules (step 145), the rinsing water is advantageously recycled (step 155) for the next rinse (which can be done in the same washing cycle or in a further one).

[0096] In this case the tub 3 of the washing machine 1 is advantageously fluidly connected with a recirculation circuit, that can advantageously be the same recirculation circuit 10, previously described, used to assure that the washing/rinsing water reaches all the products 5 during the wash and the rinse, or which can also be a further specific circuit.

[0097] Advantageously, after the application of said one or more stimuli and before recirculation thereof, the rinsing water may be stored in third storage means (step 160), sited internally or externally to the washing machine, allowing storing said rinsing water for a further rinse; the third storage means can be advantageously a

third storage tank 15, arranged in series along the recirculation circuit 2, downstream the stimulation device 12.

[0098] Alternatively the rinsing water could be first stored in the third storage means, and then submitted to the stimulus; in this case the stimulation device 12 is associated to said third storage means.

[0099] Alternatively the stimulus can be advantageously applied also directly inside the tub 3 of the washing machine, during the rinse or after each rinse, by a stimulation device 12 associated with said tub 4.

[0100] The breaking of the residual "stimuli-responsive" surfactants molecules contained in the rinsing water allows to reduce the amount of residual "stimuli-responsive" surfactants molecules present in the products 5 to wash, reducing, as a consequence, the risk of allergic reactions and of skin irritations for the people coming in contact to the washed products.

[0101] Moreover, the possibility to reuse the rinsing water for more than one rinse allows to obtain a consistent water saving.

[0102] Also in this case the application of said one or more stimuli can be obtained by a suitable internal washing machine device and/or directly by the user.

[0103] The flow chart of another embodiment of the washing method according to the invention is illustrated in **Figure 5**; in this case, after the program selection (step 100), the water and surfactants loading (step 105), the main wash (step 110) and the discharge of the dirt water suspension of "surfactants-dirt" aggregates from the tub (step 115), the dirt water suspension of "surfactants-dirt" aggregates is canalized in a recycling line 17, fluidly connecting the discharge conduct 8 and the tub 4, where it is submitted to one or more stimuli suitable for changing the solubility properties of said surfactants, so as to obtain a phase separation among said surfactants and the water containing the dirt (step 165).

[0104] In this case the changes in the surfactants properties are reversible, so that this type of stimulus can be called "reversible stimulus".

[0105] Advantageously, also in this case the application of said one or more stimuli can be obtained by a suitable internal washing machine stimulation device 12, fluidly connected to the discharge conduct 8 and/or directly by the user.

[0106] Said surfactants must be kept in a stimulated condition (i.e. in a condition in which they are not soluble in water) during all the removal process of the surfactants particles from the dirty water, so as to maintain the phase separation among the surfactants and the dirty water.

[0107] Once the phase separation among the surfactants and the dirty water has been obtained, the washing method according to the invention provides for the removal of the surfactants particles from the dirty water (step 170), by using a surfactant removal device 16 for removing said surfactants particles from said dirty water, which can advantageously include, for example, an apposite filter, or a centrifuge, or a decanter (all of them not illustrated).

[0108] This surfactant removal device 16 can be fluidly connected in series with the stimulation device 12.

[0109] The dirty water, deprived of the surfactants, can therefore be drained out of the washing machine (step 175), while the surfactants particles can be recycled for the next washing cycle (step 180). This allows reducing the amount of detergent used for the washing procedure, and consequently to achieve a money saving and a reduced environmental impact.

[0110] During the washing program there is also one or more rinse (step 130), and one or more spin.

[0111] The step of recycling the surfactants particles (step 180) can include some sub-steps.

[0112] First, the surfactants particles can be stored in suitable forth store means (step 181) (placed internally or externally to the washing machine), for example in an apposite forth storage tank 18, so that they can be reused in the next washing cycle.

[0113] Before reusing the surfactants previously used in the main wash and submitted to said one or more stimuli, it is necessary to change their solubility properties in the opposite way (step 182), as to restore their dirt-removing properties.

[0114] If the stimulus applied to the surfactants to obtain the above-mentioned phase separation is, for example, a variation in the pH, it is necessary to apply one or more "reverse-stimuli" to the surfactants to restore the initial pH value, and consequently restoring their initial properties; in this case it must be used a suitable reverse-stimulation device 19 (internal or external to the washing machine, automatic or actuated directly by the user) to apply said one or more reverse stimuli; in the case of the pH variation, this reverse-stimulation device 19 can be, for example an electrolyser fluidly connected in series with the surfactants removal device 16, along the recycling line 17.

[0115] If the stimulus applied to the surfactants to change their solubility in water is, for example, a light radiation or an electromagnetic radiation, the interruption of the irradiation restores the former solubility of the surfactants; in this case it is not necessary to provide a specific device to apply to the surfactants one or more stimuli to restore their properties, but it is sufficient to interrupt the application of said one or more stimuli used to obtain the above-mentioned phase separation.

[0116] If the stimulus applied to the surfactants to change their solubility in water is, for example, a temperature increase, the restoration of the initial properties of the surfactants can be achieved advantageously by the natural cooling of the latter.

[0117] Advantageously the removal of the surfactants particles from the dirty water can also be obtained by using a suitable septum or filter made of a material able to attract the surfactant particles only if their chemical/physical properties are changed consequently to the application of said one or more stimuli.

[0118] When the dirty water containing the surfactant particles passes through the septum, the surfactant par-

ticles remain attached to the latter, while the dirty water can be drained out of the washing machine.

[0119] By suspending the application or said one or more stimuli, or by applying one or more "reverse stimuli" to the surfactant particles, the latter come off the septum, and can be recycled for the next washing cycle.

[0120] There are also known in the art some kind of surfactants that can change their properties in two different ways, subsequently to two different stimuli.

[0121] By using this kind of surfactants in the washing method according to the invention it is possible to obtain the phase separation between the surfactant particles and the dirty water by the application of a first stimulus, and successively removing the surfactants particles from the dirty water using a septum that can attract the surfactant particles only after the application to the latter of a second stimulus.

[0122] Once the original solubility properties of the surfactants has been restored, the surfactants could also be stored in fifth store means (placed internally or externally to the washing machine), for example in an apposite fifth storage tank 20, arranged along the recycling line 17 downstream the reverse-stimulation device 19, so that they can be reused in the next washing cycle.

[0123] Also in this case, a further step of the fourth embodiment of the washing method illustrated in Figure 5 provides for the submission of the products to wash, placed inside the tub 3, to one ore more rinses (step 135), each one made with clean water, for removing the residual particles of dirt and surfactants.

[0124] In this case, after each rinse, the rinsing water is drained out of the washing machine 1.

[0125] In Figure 6 is illustrated the flow chart of a fifth embodiment of the washing method according to the invention, which differs from the application disclosed with reference to Figure 5 only because the rinsing water is submitted, after each rinse (step 130), to the application of one or more further stimuli suited for irreversibly breaking the "stimuli-responsive" surfactants residuals molecules (step 145), in the same way of the embodiment of the washing method disclosed with reference to Figures 3 and 4.

[0126] Also in this case the application of said one or more further stimulus can be obtained by a stimulation device 12 internal to the washing machine and/or directly by the user.

[0127] In particular, the rinsig water submitted to irreversible stimulus can be directly drained and released into the environmental (step 150) as in the embodiment of Figure 3, or it can be stored in a tank (step 160) and reused for the same or the next rinse (step 155) as in the embodiment of Figure 4.

[0128] In Figure 7 is illustrated another embodiment of a washing method according to the invention, which allows modifying the washing performances during the main wash.

[0129] After loading the products 5 to wash in the tub 3 of the washing machine 1 (in the drum 4 in the case of

a laundry washer), and selecting the desired washing program (step 100), the washing water and the detergent (containing one or more of the above-mentioned "stimuli-responsive" surfactants) are added to the tub (step 105).

[0130] The "stimuli-responsive" surfactants, interacting with the washing water, generate foam which interacts and removes the dirt from the product 5 to wash (e.g. textiles or dishes) (step 183).

[0131] In this embodiment, the washing machine is provided with a device for continuously or periodically monitoring the amount of foam present in the tub, directly or through the measure of opportune properties of the "stimuli-responsive" surfactants affecting the amount of foam. The aim is to control the washing performances; in fact, for example in a laundry washer, if the quantity of foam is too low, the removal of the dirt could be ineffective, while if the quantity of the foam is too high, it can hinder the correct mechanical shaking of the fabric to wash, consequently reducing the mechanical washing effect (with the exception of some types of textile, for example the wool, for which a great amount of foam is preferable in order to reduce the mechanical shaking and reducing the felting) .

[0132] Advantageously said device for monitoring the amount of foam could comprise one or more first monitoring sensor (not illustrated), connected to the tub for revealing the amount of the foam present inside (step 184), and operatively connected to the electronic control system of the washing machine for communicating to it the suitable information related to the amount of foam (step 185).

[0133] Advantageously the monitor sensor could be, for example, a turbidity sensor, or an optical sensor, or a conductivity sensor, or a foam sensor comprising a pressure sensor operatively connected with the draining pump, etc.

[0134] The monitoring device is preferably set so as to check if the amount of foam in the tub is within a prefixed range.

[0135] If the amount of foam is outside said range, the electronic control system of the washing machine can advantageously command a suitable device (internal or external to the washing machine) that provides the application to the water/"stimuli-responsive" surfactants mixture of one or more stimuli suitable for changing the "stimuli-responsive" surfactants properties so as to increase or decrease the amount of the foam as desired (step 186).

[0136] Alternatively, in a further embodiment, the electronic control system of the washing machine could be operatively connected to the interface displaying device 11 of the washing machine 1 for displaying to the user the amount of foam, so as to allow him to selectively apply, manually, said one or more stimuli (for example adding some additives) to the water/"stimuli-responsive" surfactants mixture.

[0137] Once the main wash (here indicated as step

110') is come to the end, the washing method according to the invention can proceed with the direct discharge of the water suspension of "surfactants-dirt" aggregates, or with the application to the latter to one or more stimuli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way, as described with reference to Figure 2, and with the subsequent draining of the dirty water out of the washing machine with a reduced impact on the environment ("irreversible stimulus at the end of main wash" (step 130) described with reference to Figure 1).

[0138] Alternatively, as described with reference to the embodiment illustrated in Figures 5 and 6: the water suspension of "surfactants-dirt" aggregates can be submitted to one or more stimuli suitable for changing the solubility properties of said surfactants, so as to obtain a phase separation among said surfactants and the water containing the removed dirt (step 165); in this case it is possible to recycle the surfactants for the next washing cycle (step 180).

[0139] Also in this case a further step of the washing method according to the invention provides for submitting the products to wash, placed inside the tub, to one or more rinses (step 135), each one made with clean water, for removing the residuals of dirt and surfactants; in this case, after each rinse, the rinsing water is drained out of the washing machine.

[0140] Alternatively, after each rinse the rising water can be advantageously submitted to the application of one or more further stimuli suited for irreversibly breaking the "stimuli-responsive" surfactants residuals molecules, in the same way of the application of the washing method disclosed with reference to Figures 3 and 4.

[0141] Also in this case the application of said one or more further stimuli can be obtained by a suitable internal washing machine device and/ or directly by the user.

[0142] Once submitted to the further stimulus, the rinsing water can be recycled for a next rinse, as illustrated with reference to Figure 4, or can also be drained from the washing machine.

[0143] It is seen therefore how the invention has achieved the proposed aim and objects, there being provided a washing method and a washing machine implementing the method that allows washing the desired products, such as laundry or dishes, with a low environmental impact, because the breaking of the surfactants molecules before draining them out of the washing machines, reduces the forming of foam, the proliferation of bacteria, and the risks connected with the possible harmfulness or toxicity of the surfactants.

[0144] Furthermore the washing method and a washing machine implementing the method, allowing the recycle of the surfactants and/or of the water (both of the washing water and of the rinsing water), allows reducing the use of water and of detergent, which is advantageous both in terms of money saving and in terms of environmental impact.

[0145] In addition, the washing method and a washing

machine implementing the method according to the invention, allows to reduce the residual of detergent in the washed products after the wash by a washing machine, consequently reducing the risks of allergic reactions and skin irritations for the people coming in contact with the washed products.

[0146] Also, the possibility of controlling some parameters of the water/"stimuli-responsive" surfactants mixture during the main wash, allows controlling almost instantaneously the amount of foam inside the tub, which allows increasing the washing performances.

Claims

1. Washing method, comprising at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in said tub of washing water and of a detergent comprising at least one the so called "stimuli-responsive" surfactants, a main wash obtained by the interaction of a mixture of said washing water and detergent with said one or more products for removing the dirt from said one or more products and creating a water suspension of "surfactants-dirt" aggregates, and one or more rinses of said one or more products contained into said tub by rinsing water, **characterized in that** it comprises at least the application, to said water suspension of "surfactants-dirt" aggregates and/or to said rinsing water, of one or more stimuli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way.
2. Washing method according to claim 1, **characterized in that**, if said one or more stimuli are applied to the rinsing water, after said application of said one or more stimuli, said rising water is recycled for a further rinse, directly or after being stored in storage means, sited internally or externally to said washing machine.
3. Washing method according to claim 1, **characterized in that** said one or more stimuli are applied to said water suspension of "surfactants-dirt" aggregates and/or to said rinsing water while it is passing through a discharge conduct coming out of said tub and/or inside storage means sited internally or externally to said washing machine, and/or inside a further discharge conduct coming out of said storage means.
4. Washing method, comprising at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in said tub of washing water and detergent comprising at least one of the so called "stimuli-responsive" surfactants, a main wash ob-

tained by the interaction of a mixture of said washing water and detergent with said one or more products for removing the dirt from said one or more products and creating a water suspension of "surfactants-dirt" aggregates, and the discharge of said water suspension of "surfactants-dirt" aggregates from the tub, **characterized in that** it comprises at least the further following steps:

- a. application to said water suspension of "surfactants-dirt" aggregates, after discharge from said tub, of one or more stimuli suitable for changing in a reversible way the solubility properties of said surfactants, so as to obtain a phase separation among the surfactants particles and the dirty water;
- b. removal of said surfactants particles from said dirty water;
- c. draining of said dirty water, deprived of said surfactants particles; and
- d. recycling of said surfactants particles for a further washing cycle.
5. Washing method according to claim 4, **characterized in that** it comprises the step of keeping said changed solubility properties of said surfactants particles during the step of removal of said surfactants particles from said dirty water, so as to maintain the phase separation among said surfactants and said dirty water, and the further step of suppressing said one or more stimuli or to submit said surfactants particles to one or more reverse-stimuli to restore the original solubility properties.
6. Washing method according to claim 5, **characterized in that** before being reused in said further washing cycle, said surfactants particles previously used in said main wash are stored in a storage device placed internally or externally to said washing machine.
7. Washing method, comprising at least the loading of one or more products to wash in the tub of a washing machine, the selection of the desired washing program, the adduction in said tub of washing water and detergent comprising at least one of the so called "stimuli-responsive" surfactants, a main wash obtained by the interaction of a foam, made of a mixture of said washing water and detergent, with said one or more products for removing the dirt from said one or more products and to create a water suspension of "surfactants-dirt" aggregates, **characterized in that** it comprises at least the further following steps:
 - a. monitoring if the amount of said foam in said tub is within a prefixed range; and
 - b. if the amount of said foam is outside said prefixed range, application to said mixture of said

- washing water and detergent of one or more stimuli suitable for changing said one or more "stimuli-responsive" surfactants properties, so as modify the amount of said foam.
8. Washing method according to claim 7, **characterized in that** the step of monitoring if the amount of said foam in said tub is within a prefixed range, comprises monitoring if one or more properties of said "stimuli-responsive" surfactants affecting the amount of said foam are within predetermined ranges.
 9. Washing machine (1), comprising at least an outer casing (2), a washing tub (3) in which products (5) to wash are loaded to be submitted to a washing cycle, and a liquid feeding device (6, 7) to introduce into said tub washing water and a detergent containing one or more "stimuli-responsive" surfactants into said tub, for creating a water/detergent mixture interacting with said products for removing the dirt from said products and creating a water suspension of "surfactants-dirt" aggregates, said liquid feeding device being also suitable to introduce into said tub rinsing water, **characterized in that** it comprises a stimulation device (12) for the application to said water suspension of "surfactants-dirt" aggregates and/or to said rinsing water, of one or more stimuli suitable for breaking the "stimuli-responsive" surfactants molecules in an irreversible way.
 10. Washing machine according to claim 9, **characterized in that** said stimulation device (12) is associated with said tub or with a recirculation circuit (10) connected with said tub for draining said rinsing water from said tub (3) after each rinse, and for re-introducing said rinsing water in said tub (3) after the application to it of said one or more stimuli by said stimulation device.
 11. Washing machine (1), comprising at least an outer casing (2), a washing tub (3) in which products (5) to wash are loaded to be submitted to a washing cycle, and a liquid feeding device (6, 7) to introduce into said tub washing water and a detergent containing one or more "stimuli-responsive" surfactants into said tub, for creating a water/detergent mixture interacting with said products for removing the dirt from said products and creating a water suspension of "surfactants-dirt" aggregates, said liquid feeding device being also suitable to introduce into said tub rinsing water, **characterized in that** it comprises at least a stimulation device (12) for the application to said water suspension of "surfactants-dirt" aggregates of one or more stimuli suitable for changing in a reversible way the solubility properties of said surfactants, so that to obtain a phase separation among the surfactants particles and the dirty water, a surfactant removal device (16) for removing said surfactants particles from said dirty water, a draining line (8) for draining said dirty water, deprived of said surfactants particles, and a recycling line (18) for recycling said surfactants particles for a further washing cycle.
 12. Washing machine according to claim 11, **characterized in that** said surfactant removal device comprises a filter, and/or a centrifuge, and/or a decanter, or a septum made of a material able to attract said surfactant particles only if their chemical/physical properties are changed consequently to the application of said one or more stimuli.
 13. Washing machine according to claim 11 or 12, **characterized in that** said recycling line comprises a storage device placed internally or externally to said washing machine.
 14. Washing machine (1), comprising at least an outer casing (2), a washing tub (3) in which products (5) to wash are loaded to be submitted to a washing cycle, and a liquid feeding device (6, 7) to introduce into said tub washing water and a detergent containing one or more "stimuli-responsive" surfactants into said tub, for creating a water/detergent mixture generating a foam interacting with said products for removing the dirt from said products and creating a water suspension of "surfactants-dirt" aggregates, said liquid feeding device being also suitable to introduce into said tub rinsing water, **characterized in that** it comprises a monitoring device for monitoring the amount of said foam in the tub, and a stimulation device (12) for the application to said water/"stimuli-responsive" surfactants mixture of one or more stimuli suitable for changing the "stimuli-responsive" surfactants properties, so as modify the amount of said foam, if the amount of said foam in said tub is outside a prefixed range.
 15. Washing machine according to claim 14, **characterized in that** said monitoring device comprises one or more monitoring sensors, connected to the tub for revealing the amount of the foam, and operatively connected to an electronic control system for communicating to it an information related to said amount of said foam, said electronic control system commanding said stimulation device and/or being operatively connected to an interface displaying device to display the amount of foam, so as to allow a user to activate said stimulation device.

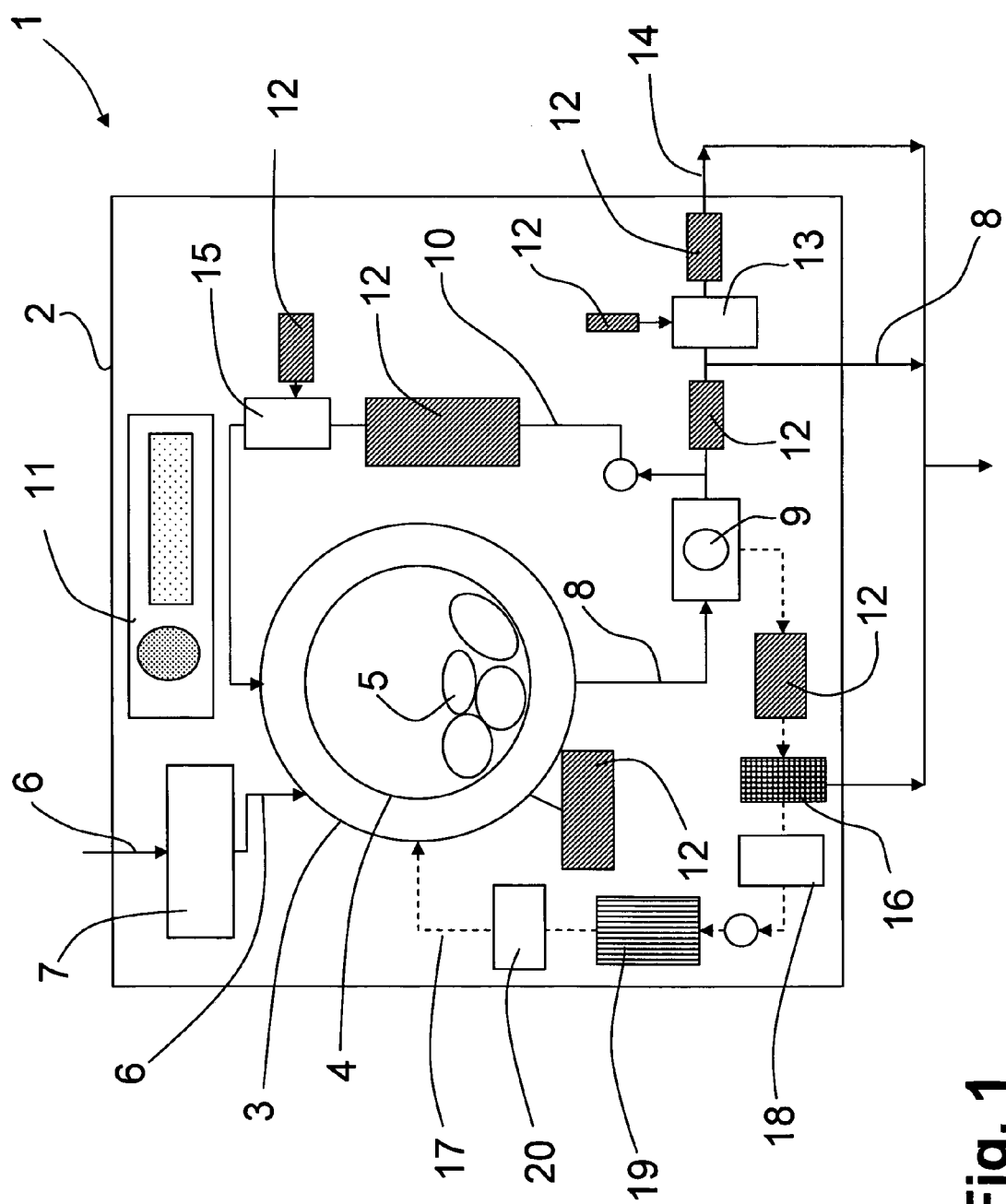
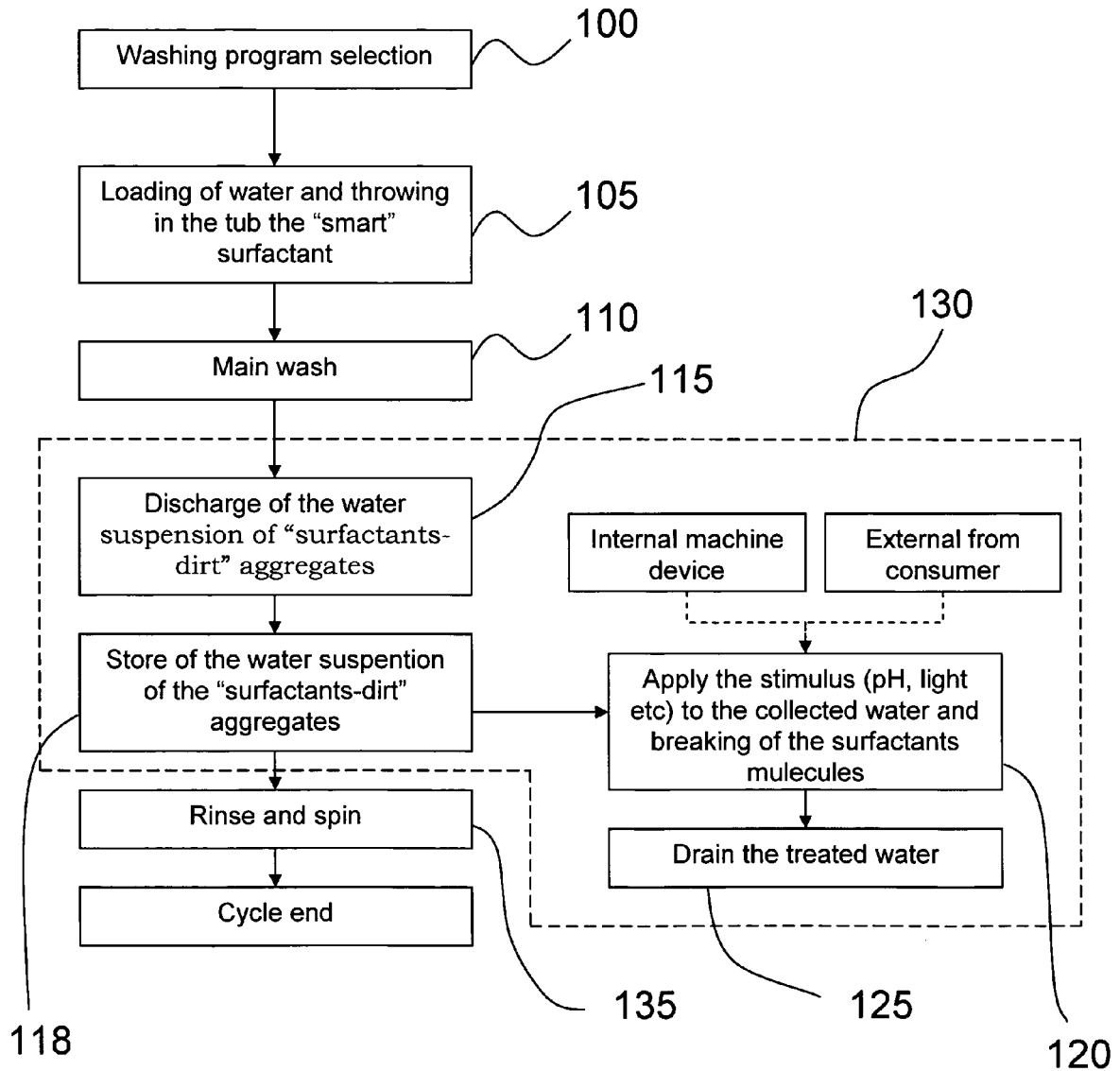
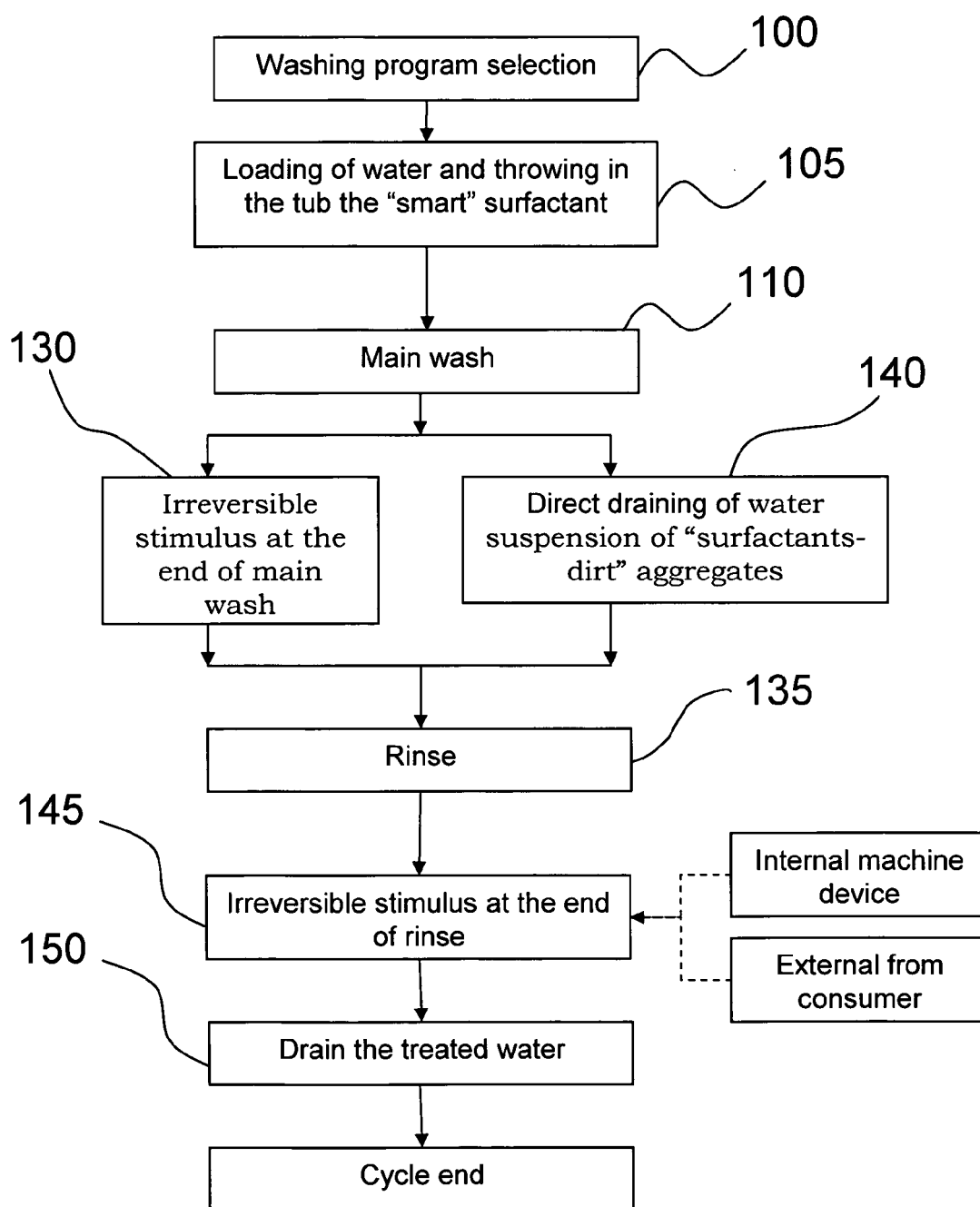
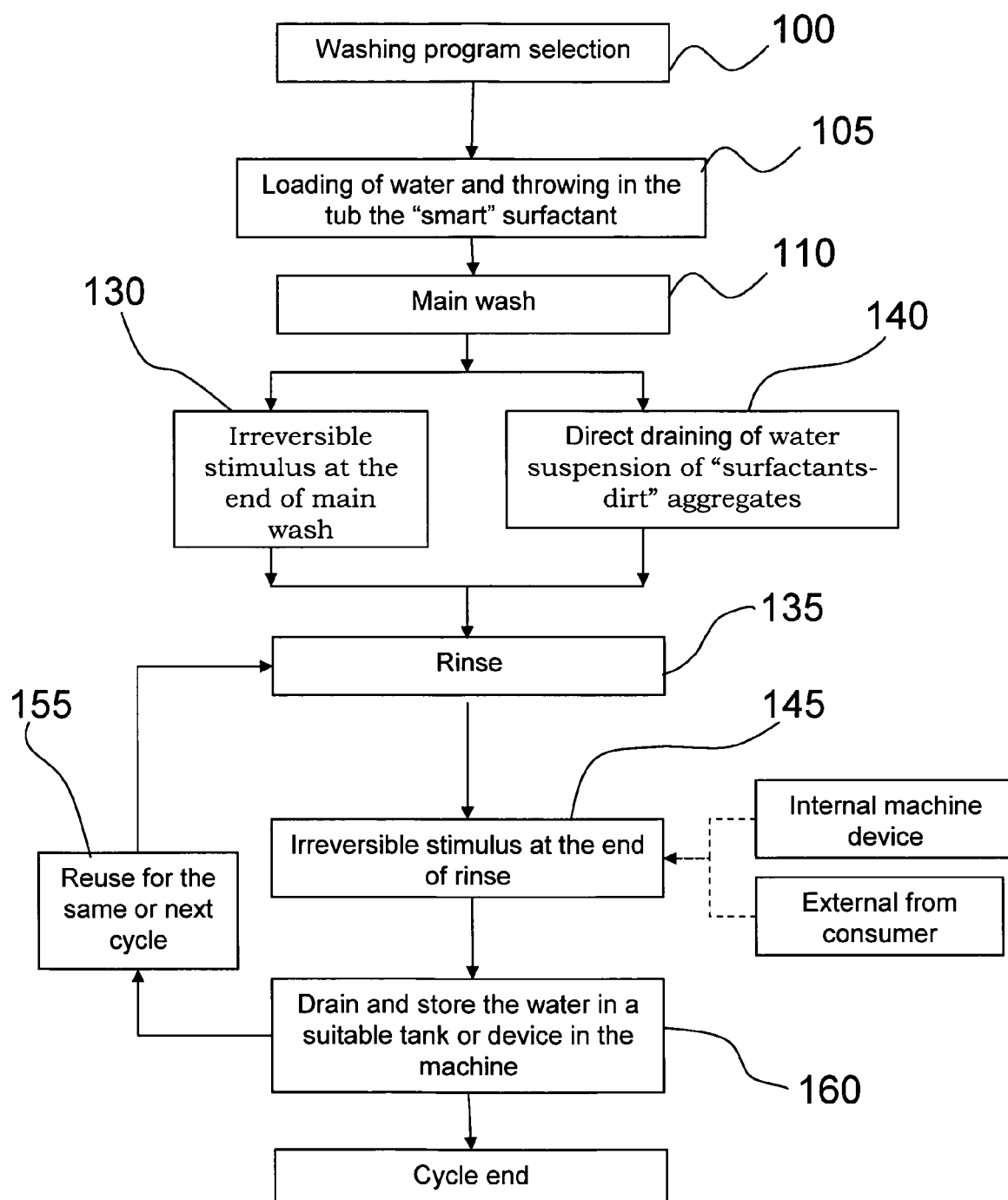


Fig. 1

**Fig. 2**

**Fig. 3**

**Fig. 4**

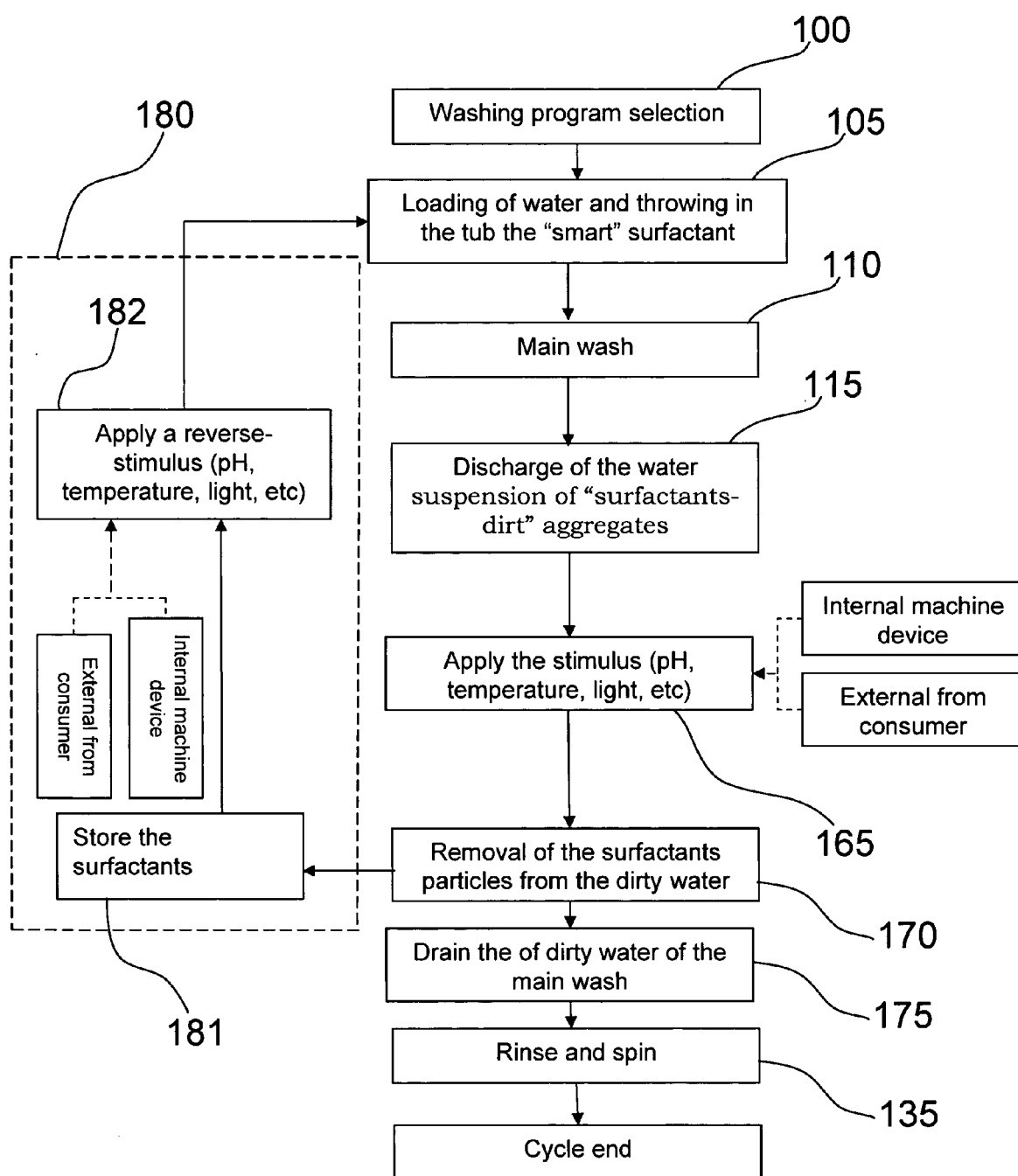


Fig. 5

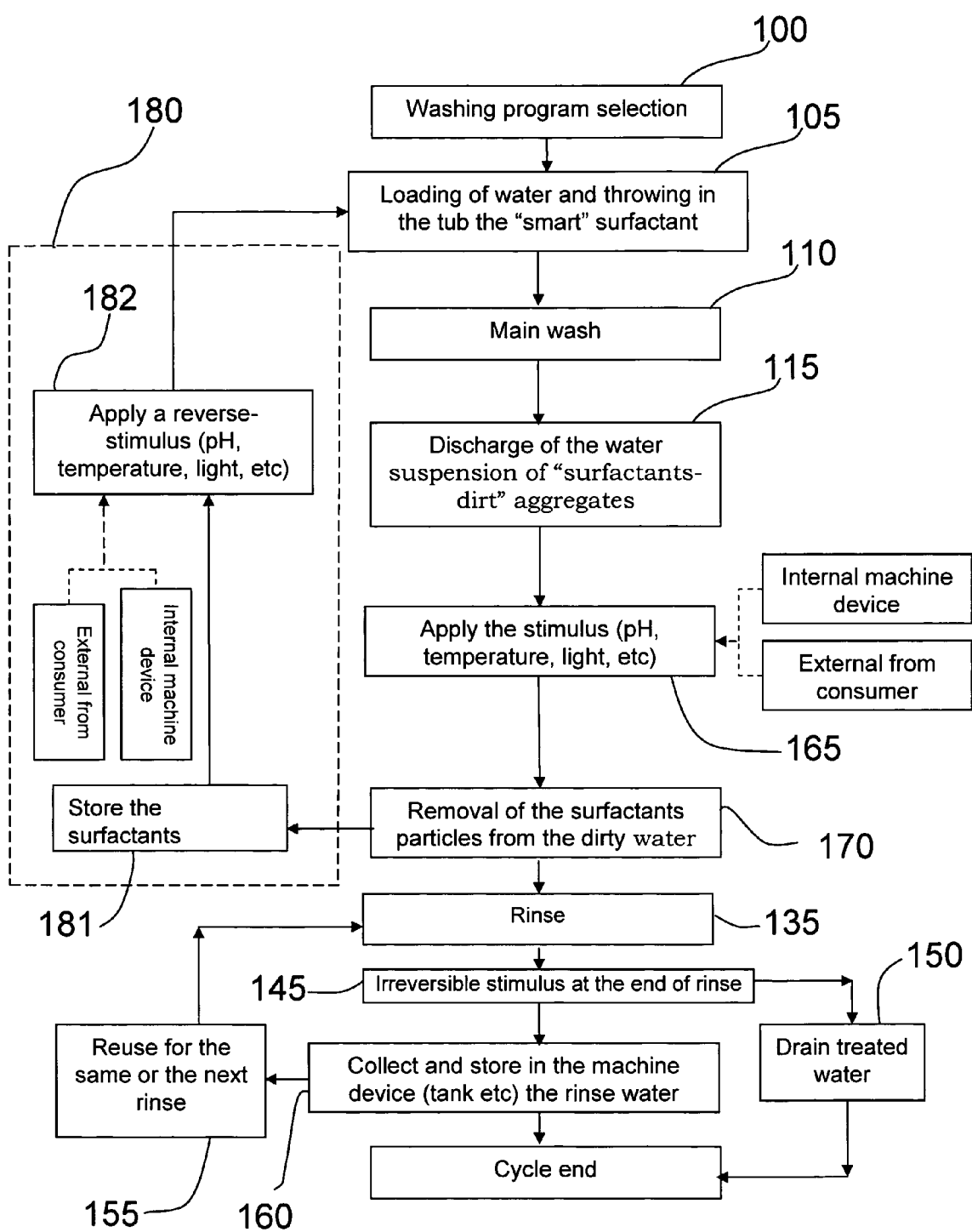


Fig. 6

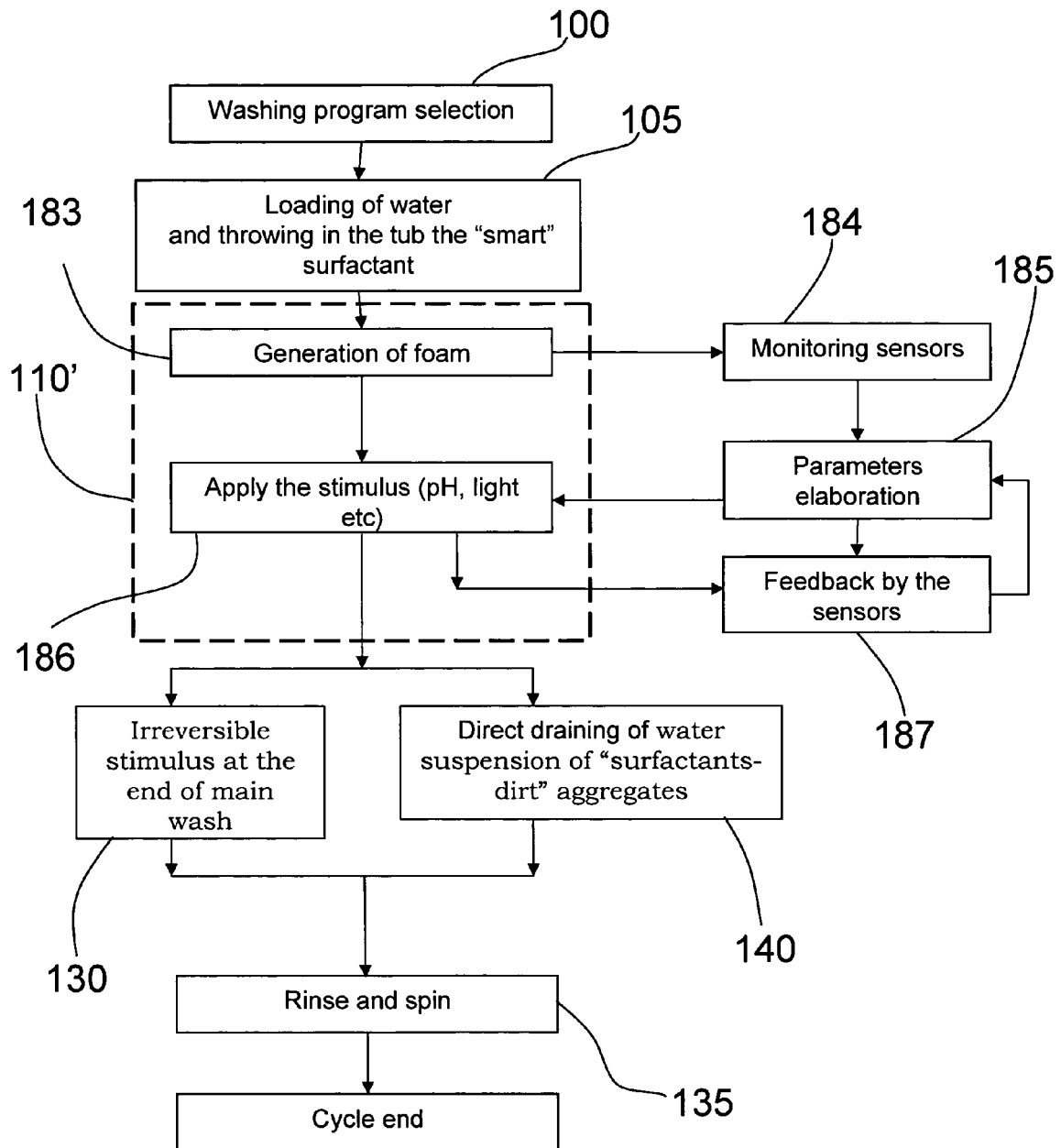


Fig. 7



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