PEROXYCARBOXYLIC ACID-BASED
POLYELECTROLYTE CAPSULE SYSTEM
HAVING A LONG SHELF LIFE

Inventors: Peter Schmiedel, Duesseldorf (DE); Heribert Kaiser, Duesseldorf (DE); Wolfgang von Rybinski, Duesseldorf (DE); Bernhard Orlich, Barcelona (ES); Matteo Buzzacchi, Flero (IT)

Correspondence Address:
DANN DORFMAN HERRELL AND SKILLMAN
A PROFESSIONAL CORPORATION
1601 MARKET STREET
SUITE 2400
PHILADELPHIA, PA 19103-2307 (US)

Appl. No.: 11/303,060
Filed: Dec. 13, 2005

A multilayer capsule is comprised of a core-shell structure wherein the core portion comprises at least one organic peroxycarboxylic acid in solid particulate form and the shell portion comprises at least one coating layer comprising a material selected from the group consisting of at least one polyelectrolyte, at least one ionic surfactant or a combination thereof.
PEROXYCARBOXYLIC ACID-BASED POLYELECTROLYTE CAPSULE SYSTEM HAVING A LONG SHELF LIFE

CROSS-REFERENCE TO RELATED APPLICATIONS


STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

INCORPORATION-BY-REFERENCE OF MATERIAL SUBMITTED ON A COMPACT DISC

[0003] Not Applicable

BACKGROUND OF THE INVENTION

[0004] (1) Field of the Invention

[0005] The present invention relates to a process for producing a multilayer capsule system laden with at least one organic peroxycarboxylic acid, and also to the capsule system produced in this way itself. The present invention further relates to the use of this capsule system as a bleach or bleach component, especially for its use in laundry detergents and cleaning compositions, especially in liquid laundry detergents and cleaning compositions, dental care compositions, hair dyeing compositions and decolorizer and bleach compositions for industrial applications, and also to the products comprising this capsule system themselves, i.e. laundry detergents and cleaning compositions, especially liquid laundry detergents and cleaning compositions, dental care compositions, hair dyeing compositions and decolorizer or bleach compositions for industrial applications which comprise the inventive capsule system.

[0006] In the case of liquid, especially aqueous, laundry detergents and cleaning compositions, which are enjoying increasing popularity owing to their positive product properties, such as better and faster solubility and usability, the formulation or incorporation of bleaching components is problematic for numerous reasons. For instance, bleaches used frequently lose their activity even in the course of storage, for example owing to decomposition or hydrolysis reactions and incompatibilities with other constituents of the laundry detergent formulation, for example enzymes or surfactants. A disadvantageous consequence is that the laundry detergent formulation suffers a distinct loss of washing performance, especially bleaching capacity, so that bleachable stains in particular can no longer be removed satisfactorily.

[0007] The bleach components typically used for solid laundry detergent formulations, for example perborates or percarbonates, are extremely moisture-sensitive, so that, in a liquid and especially aqueous laundry detergent and cleaning composition, a distinct decline in their bleaching action is observed frequently within a few days owing to the loss of active oxygen. Therefore, such active ingredients may frequently already have lost their bleaching action at the time of their use, especially in the wash liquor, and are thus ineffective.

[0008] Compared to them, peroxycarboxylic acids, especially imidoperoxycarboxylic acids, whose most important representative is phthalimidoperoxycarboxylic acid (PAP), are more efficient and less hydrolysis-sensitive, and are known in the prior art as bleaches for laundry detergents and cleaning compositions. However, their storage stability is in no way sufficient to ensure long-term usability of the corresponding laundry detergent or cleaning composition without associated loss of activity. It is therefore particularly problematic to use peroxycarboxylic acids, especially imidoperoxycarboxylic acids, in liquid laundry detergents and cleaning compositions.

[0009] (2) Description of Related Art, Including Information Disclosed Under 37 C.F.R. §§ 1.97 and 1.98

[0010] Owing to the disadvantages which arise in relation to a change in the laundry detergent or cleaning composition formulation owing to the degradation of imidoperoxycarboxylic acids, especially PAP, attempts have been made in the prior art to effectively encapsulate the imidoperoxycarboxylic acids (e.g., PAP), so that the imidoperoxycarboxylic acid cannot come into direct contact with its environment, especially the remaining components of the laundry detergent or cleaning composition formulation, or the contact of the imidoperoxycarboxylic acids with their environment is reduced.

[0011] For instance, waxes are frequently used in the prior art as a protective coating for sensitive laundry detergent additives, for example peroxycarboxylic acids. In this context, EP 0 510 761 B1, or U.S. Pat. No. 5,230,822 belonging to the same patent family, describes a general process for encapsulating laundry detergent additives of any type, for example enzymes, bleaches, including PAP, bleach precursors and bleaching catalysts. The use described there of a wax whose melting point is between 40° C. and 50° C. leads to the active substances being released in the wash liquor only at temperatures above the melting point of the wax used, which is disadvantageous against the background of the development of high-performance laundry detergent and cleaning composition formulations and the saving of energy costs, since it should also be possible to wash at about 30° C. Furthermore, the use of a wax with a high melting point has the disadvantage that it causes residues on the laundry especially at low temperatures, since it is not fully emulsified at these temperatures.

[0012] It has also been attempted in the prior art to develop other methods of stabilizing peroxycarboxylic acids: U.S. Pat. No. 6,080,715 describes granule compositions based on phthalimidoperoxycarboxylic acid. The granules described there include phthalimidoperoxycarboxylic acid (PAP), N-oxide compounds of tertiary amines and carboxylic acids with a pKₐ value of less than 3.5. The granules described there are not in the form of capsule systems composed of a core and a coating, but rather merely in the form of a mixture of the particular components. It follows from this that the peroxy-carboxylic acid can be in direct contact with the environment, especially in the region of the surface of the granules,
which is disadvantageous with regard to their stability. Moreover, these granules are not intended for use in aqueous dispersions, especially liquid laundry detergents and cleaning compositions. Instead, this document merely envisages the use of the granules in pulverulent laundry detergents and cleaning formulations.

WO 9739097 A1 describes bleach granules which are present in the form of an intimate mixture of peroxycarboxylic acid, for example PAP, and surfactant, for example an amine oxide. The granules described there likewise do not have a capsule structure composed of a core and a capsule coating. The granules are optimized primarily in relation to a reduction of damage to the textile dyes caused by the bleach.

U.S. Pat. No. 4,126,573 describes bleach particles whose core comprises peroxycarboxylic acids and whose only one-layer coating comprises water-soluble surfactants, for example organic anionic sulfate or amine oxide compounds.

Moreover, WO 94/15010 A1 describes the coating or encapsulation of an active substance with water-soluble acidic polymers, for example polyacrylic acid, the capsule system comprising an only one-layer coating and the envisaged active substance being a bleach activator.

WO 01/51196 A1 describes the encapsulation of uncharged or hydrophobic substances with at least one polyelectrolyte layer. The substances or active ingredients listed there are, for example, vitamins, hormones, growth factors, pesticides and antibiotics. The uncharged or hydrophobic active ingredient first has to be coated with an amphiphilic substance, and the particular polyelectrolyte capsule coating is applied by means of adsorption processes from a solution. In this case, the thicknesses of the resulting layers are only in the molecular range, so that the interaction between the individual layers proceeds over their entire thickness substantially via interionic interactions which lead to the formation of complexes. Between the application of the individual layers, the unadsorbed material first has to be removed. This process is complicated and relatively impracticable on the industrial scale. Owing to the only low coating layer thicknesses, these systems are unsuitable for the efficient stabilization of peroxycarboxylic acids in aqueous formations with controlled release in the wash liquor.

Moreover, WO 02/15888 A2 describes a general teaching on the production of capsules which have a coating layer composed of oppositely charged polyelectrolytes, the capsules being produced by means of a layer-by-layer (LbL) process. The substance to be encapsulated may, for example, be fluorescein. Also described there is a general process for influencing the permeability of the capsules described there, especially via modification of the pH or by influence of light. As is the case in the above-described prior art, the coating layers here too have a thickness only in the molecular range and are applied by means of adsorption from a solution, with the associated process technology disadvantages. Owing to the only low coating layer thicknesses, these systems are likewise unsuitable for efficient stabilization of peroxycarboxylic acids in aqueous formulations with controlled release in the wash liquor.

WO 02/31092 A2 too describes a coating or encapsulation process based on the "layer-by-layer" technique, but only liquid substances, for example perfume oils, are encapsulated here.

Finally, WO 99/47252 A2 describes, in general terms, the production of nano- and microparticles by layer-by-layer polyelectrolyte self-assembly. Here too, the capsules only have a low wall thickness, the coatings being produced in such a way that the appropriate polyelectrolyte molecules are added to a dispersion of template particles to be encapsulated. Here too, complicated removal of the excess polyelectrolyte molecules is required between the application of the individual coatings. The encapsulation of peroxycarboxylic acids, including measures required specifically for this purpose, is not disclosed in this document.

BRIEF SUMMARY OF THE INVENTION

Against this background, it is thus an object of the present invention to provide incorporation or encapsulation or coating of peroxycarboxylic acids, especially imidoperoxycarboxylic acids, such as phthalimidoperoxycaproic acid (PAP), with properties improved compared to the prior art, and also a corresponding production process.

It is a further object of the present invention to provide peroxycarboxylic acids, especially imidoperoxycarboxylic acids, such as phthalimidoperoxycaproic acid (PAP), in storage-stable form. A formulation form of peroxycarboxylic acids shall be developed, which at least substantially prevents or reduces full or partial dissolution of the peroxycarboxylic acids and preferably retains their solid or crystalline state even in the presence of surfactants or in another environment which has dissolution capacity for peroxycarboxylic acids, especially in laundry detergent or cleaning composition formulations, and shall especially at least substantially prevent or at least reduce contact of the peroxycarboxylic acids with the environment.

Yet another object of the present invention is the provision of a capsule system which is laden with peroxycarboxylic acids in solid form and leads to good stabilization of the peroxycarboxylic acids and thus to improved storage stability. In particular, a capsule system shall be provided in the context of the present invention, which, especially during the washing operation, is dissolved and/or solubilized or dispersed substantially without residue, so that the release of the peroxycarboxylic acids is not hindered and residues on the laundry are simultaneously prevented. In particular, such a process should enable the production of a capsule system laden with at least one peroxycarboxylic acid as an active substance, which at least substantially avoids the above-outlined disadvantages of the prior art.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

Not Applicable

DETAILED DESCRIPTION OF THE INVENTION

Applicants have now found that, surprisingly, organic peroxycarboxylic acids such as imidoperoxycarboxylic acids (e.g., PAP) can be stabilized to a high degree by a multilayer capsule system whose layers or coating layers comprise polyelectrolytes or ionic surfactants, or consist thereof.

In a first aspect, the present invention thus provides a process for producing a multilayer capsule system laden
with at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, in which at least two different coating layers each based on a polyelectrolyte and/or ionic surfactant are applied successively to an organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, present in the form of solid particles, so as to result in a capsule system which comprises at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, in a multilayer capsule coating composed of at least two coating layers.

[0026] In the context of the present invention, the peroxycarboxylic acid to be encapsulated is incorporated into a capsule coating which comprises at least two coating layers, or enclosed by it, so that the peroxycarboxylic acid forms the core of the inventive capsule system; thus, in accordance with the invention, a capsule system with a core/shell structure is present. The inventive capsule system may also comprise a plurality of capsule cores, especially when agglomerates of peroxycarboxylic acid particles form in the production, for example in a fluidized bed apparatus. It is also possible in particular for agglomerates to form after application of the particular coating layers or of the capsule coating. In this way, so to speak, a matrix can form, into which a plurality of capsule cores are embedded or incorporated.

[0027] The coating layers or layers of the capsule coating are of different nature and formed in such a way that, in particular, a first layer (coating layer) at least substantially fully encloses or coats the peroxycarboxylic acid, and the second and, where appropriate, third, fourth, etc., coating layer or coating is in direct contact with the adjacent coating or coating layer in each case. It is particularly preferred in accordance with the invention that at least the first or innermost coating layer (coating) is at least substantially inert toward the peroxycarboxylic acid, i.e. essentially does not lead to undesired chemical reactions, especially degradation, oxidation or reduction reactions and/or hydrolysis reactions with the peroxycarboxylic acid.

[0028] The further components or coating layers which are used in the process according to the invention for producing the inventive capsule system should preferably be selected in the same way such that they are at least substantially compatible in relation to the peroxycarboxylic acid to be encapsulated, i.e. no undesired chemical reactions, especially degradation, oxidation or reduction reactions and/or hydrolysis reactions, should occur between these components and the peroxycarboxylic acid, nor any reactions of the peroxycarboxylic acid induced by the further components which lead to its degradation, especially loss of activity.

[0029] The particular coating layers are configured on the basis of polyelectrolytes and/or ionic surfactants, the term “on the basis of polyelectrolytes or ionic surfactants” in the context of the present invention being understood such that further materials may also be used in addition to the polyelectrolytes or ionic surfactants, especially as listed below, to form the individual coating layers.

[0030] The polyelectrolytes and/or ionic surfactants of the coating layers directly adjacent in each case are, in accordance with the invention, preferably oppositely charged; in the case of more than two layers, for example three, four, five, etc., layers, the first, third, fifth, etc., layer each have the same charge or are of the same ionic character, i.e. anionic or cationic, and the second, fourth, sixth, etc., layer each have the same charge but the opposite charge to the first, third, fifth, etc., layer. The result in accordance with the invention is thus a capsule system with a multilayer capsule shell, the layers (coatings or coating layers) which are direct adjacent or directly successive or directly adjoining in each case are oppositely charged, i.e., so to speak, are configured “counterionically”.

[0031] In the context of the description for the present invention, the terms “polyelectrolyte” and “polyon” are to be understood essentially synonymously. In particular, this may be understood to mean a polymer having a large number of ionically dissociatable or dissociated groups which may, for example, be an integral part of the main chain of the polymer, or else may be attached to it via side chains. In the context of the present invention, the polyelectrolytes or polyon used preferably have a certain resulting electrical net charge, so that they are present in particular as polyanions, i.e. provided with a negative net charge, or as polycations, i.e. provided with a positive net charge. According to the invention, the term “net charge” is to be understood to mean that the polyelectrolyte or the polyon has predominantly positively charged or predominantly negatively charged, dissociated groups; this term thus denotes the resulting charge of the polyelectrolyte or of the polyon (i.e. without counterion). The resulting overall charge of a solution or dispersion which comprises polyelectrolytes, counternets and solvents or dispersants is, in contrast, zero.

[0032] The process according to the invention for producing a multilayer capsule system laden with at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid (e.g., PAP), is in particular carried out as follows:

[0033] (a) application of a solution and/or dispersion comprising at least one first polyelectrolyte and/or at least one first ionic surfactant I to at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, present in the form of solid particles, so that the peroxycarboxylic acid is at least substantially fully enclosed or coated by a first coating layer based on the first polyelectrolyte and/or the first ionic surfactant I; then

[0034] (b) application of at least one solution and/or dispersion comprising a second polyelectrolyte and/or at least one second ionic surfactant II to the first coating layer obtained in process step (a), the second polyelectrolyte and/or the second ionic surfactant II being different from the first polyelectrolyte and/or first ionic surfactant I, especially being oppositely charged, so that a second coating layer based on the second polyelectrolyte and/or the second ionic surfactant (II) is applied to the first coating layer obtained in process step (a), the second coating layer at least substantially fully enclosing or coating the first coating layer and the two coating layers being in direct contact with one another; then

[0035] (c) optional application of at least one further coating layer, especially of a third, fourth, etc., coating layer, the polyelectrolytes and/or ionic surfactants forming the coating layer(s) being selected such that coating layers directly adjoining one another in each case comprise different, especially oppositely charged, polyelectrolytes and/or oppositely charged ionic surfactants or consist thereof; then
[0036] (d) optional processing, especially drying and/or purification and/or classification, especially sieving, of the resulting capsule system.

[0037] In the process according to the invention, the substances used, which are incorporated into the inventive capsule system composed of a plurality of coating layers, are organic peroxycarboxylic acids. These may be selected from organic mono- and diperoxycarboxylic acids. Examples thereof are in particular dodecanedioxy acid or preferably imidoperoxyxyacidic acids, more preferably 6-phthalimidoperoxyxyacidic acid (6-phthalimidoperoxyhexanoic acid, PAP). Advantageously, the peroxyxyacidic acid should have a melting point at atmospheric pressure of above 25°C, especially above 35°C, preferably above 45°C, preferentially above 50°C, more preferably above 100°C. This ensures that the peroxyxyacidic acid used is present at least substantially in the form of solid particles, so that degradation of the peroxyxyacidic acids during the production of the capsule system in the process according to the invention is at least substantially prevented or reduced, and controlled release is achieved when the inventive capsule system is employed.

[0038] It is possible in accordance with the invention to carry out an adjustment of the particle size of the peroxyxyacidic acids, for example before the application of the first coating layer, by processes known as such to those skilled in the art, for example by means of shearing, vibration and/or ultrasound input, comminuting, grinding, etc., so that controlled adjustment of the particle size in accordance with their particular later use is possible in accordance with the invention.

[0039] Preferably in accordance with the invention, the one or more polyelectrolytes and/or the one or more ionic surfactants of a solution have the same electrical net charge. The solution of the at least one polyelectrolyte and/or of the at least one ionic surfactant may be applied in process steps (a), (b) and/or (c) in each case, for example, by means of spray application, for which a spray drier may be used for the first layer and, for example, a Wurster coater for the further layers. However, it is also possible to apply all layers in a fluidized bed unit. The term “the same electrical net charge” may be understood as a qualitative statement such that, although the above-listed components of the solution have the same charge sign (positive or negative), certain deviations from the stoichiometry are possible or may even be desired in order, for example, to obtain a certain solubility of the components.

[0040] The individual coating layers are contacted and adhere to one another in the region of the interface layers formed by adjoining coating layers, as will be detailed below, especially via electrostatic interactions such as ion-ion or ion-dipole interactions. In particular, complexes (i.e. polyelectrolyte/polyanion complexes, cationic surfactant/polyanion complexes, polyelectrolyte/anionic surfactant complexes, anionic surfactant/cationic surfactant complexes, depending on the particular composition of the coating layers) may form at the boundary or interface between two coating layers owing to the opposite net charge of the particular coating layer materials, and ensure good contact or good adhesion between the individual coating layers. In addition, there are, on the other hand, owing to the relatively large thicknesses of the individual coating layers, also certain subregions in the particular coating layers in relation to which there are no interactions with the adjacent coatings.

[0041] In the process according to the invention, the polyelectrolyte or the ionic surfactant of the first coating layer obtained in process step (a) and the third, fifth, etc., coating layer which may be obtained in process step (c) preferably have a positive net charge; in this case, the first coating layer should be formed by a cationic surfactant or a cationic polyelectrolyte (polycation), preferably by a cationic surfactant, and the polyelectrolyte of the third, fifth, etc., coating layer which may be present shall be a cationic polyelectrolyte (polycation). The polyelectrolyte or the ionic surfactant of the second coating layer obtained in process step (b) and the fourth, sixth, etc., coating layer which may be obtained in process (c) should, in contrast, preferably have a negative net charge and in particular be an anionic polyelectrolyte (polynion). The outermost coating layer which forms the boundary to a medium, i.e. to the outside environment, in which the capsule system may be present, should preferably have at least one anionic polyelectrolyte or consist thereof.

[0042] Preferably in accordance with the invention, the first coating layer has a positive net charge, so that, especially owing to electrostatic interactions, especially to ion-ion or ion-dipole interactions, good contact or good adhesion of the first coating layer in relation to the peroxyxyacidic acid is ensured. This measure is carried out against the background that the peroxyxyacidic acid has, in the region of the pH values preferred in accordance with the invention, a negative (partial) surface charge, in particular a negative partial charge, on the surface, which is caused principally by the oxygen atoms of the peroxyxyacidyl group.

[0043] If required, or desired for the application, the first coating layer may also have a negative net charge, i.e. an anionic polyelectrolyte or an anionic surfactant. The second coating layer should then preferably have a positive net charge, and the coating layers which may follow should each have an opposite charge to the directly adjacent coating layer.

[0044] In the capsule system produced by the process according to the invention, the first coating layer comprises, in a particularly preferred embodiment, at least one ionic surfactant, more preferably at least one cationic surfactant. The second coating layer and any third, fourth, etc., coating layer comprise preferably, or consist preferably of, at least one polyelectrolyte or a mixture of at least one polyelectrolyte with at least one ionic surfactant, the at least one polyelectrolyte and the at least one surfactant in such a mixture each having the same kind of net charge. According to the invention, the second coating layer and any third, fourth, etc., coating layer more preferably comprises at least one polyelectrolyte.

[0045] The cationic surfactant used especially for the first coating layer in the context of the present invention may be selected from quaternary ammonium salts whose ammonium radical corresponds to the general formula R⁺R⁺R⁺R⁺ where the R⁺, R⁻ and R⁺ radicals, identically or differently, are a hydrogen atom or a linear or branched alkyl, alkylenether or alkylenitril radical having from 1 to 40 carbon atoms, in particular from 1 to 25 carbon atoms, the counterion preferably being halide-free (e.g., phosphate, sulfate, methylsulfate, tosylate, cumenesulfonate, etc.).
factant may be selected from the group of alkyldimethylammonium surfactants, N-alkylpyridinium salts and ester quats. According to the invention, the cationic surfactant should contain no halide ions, in particular no chloride ions, or be at least substantially halide-free, in particular chloride-free. The cationic surfactants may be selected from methylsulfate, sulfate, phosphate, tosylate or cuneenesulfonate compounds.

[0046] The cationic polyelectrolyte used especially for the first coating layer in accordance with the invention should include at least one functional group selected from quaternary amine, imine and imidazole groups. Moreover, the cationic poly electrolyte used especially for the first coating layer may be selected from amine oxides or pyridine N-oxides, preferably polyvinylpyridine N-oxide, which are present in protonated form at acidic pH values and are therefore cationic. The cationic polyelectrolyte should preferably contain no halide ions, in particular no chloride ions, or be at least substantially halide-free, in particular chloride-free.

[0047] According to the invention, for example, a cationic surfactant or a cationic poly electrolyte may be used for the first coating layer, as is known, for example, from cosmetic applications, for example with the general name “Polyquaternium-8”, for example Polyquaternium-11, obtainable under the trade name Luvisquat® PQ 11 (quaternized vinylpyrrolidone/dimethylaminomethyl methacrylate copolymer), and also Polyquaternium-16, obtainable under the trade name Luvisquat® FC 370 (vinylpyrrolidone/quaternized vinylimidazolide copolymer).

[0048] In the process according to the invention, the anionic poly electrolyte, especially of the second, fourth, etc., coating layer, may be a synthetic anionic poly electrolyte which may be selected from the group of polymeric sulfonic acids, especially poly styrenesulfonic acids and (partial) salts thereof; preferably poly carboxylic acids and (partial) salts thereof, especially polycarboxylic acid, polymaleic acid and their copolymers. The anionic poly electrolyte may, for example, be a polymer sulfonated in a polymer-like manner and/or a natural anionic polymer which may be selected from the group of alginic acid, xanthan or derivatized natural polymers such as carboxymethylcellulose.

[0049] The anionic polyelectrolyte used in accordance with the invention, especially of the second, fourth, etc., coating layer may, though, for example, also be a natural anionic polymer which may be selected, for example, from the group of alginate, carboxymethylamyllose, carboxymethylcellulose, carboxymethylcellulose, carboxymethyl dextran, cageenan, cellulose sulfate, chondroitin sulfate, chitosan sulfate, dextran sulfate, gum arabic, guar gum, gellan gum, heparin, hyaluronic acid, pectin, xanthan and anionic proteins. The anionic poly electrolyte may, in accordance with the invention, also be a synthetic anionic poly electrolyte and especially be selected from the group of polyacrylates, anionic polyamido acids and copolymers thereof, poly malate, poly acrylactate, poly styrene sulfate, poly styrenesulfonate, polyvinyl sulfate, polyvinylphosphonate, polyvinyl sulfate, polyacrylamide methylpropanesulfonate, poly lactate, poly (butadiene/maleate), poly (ethylene/maleate), poly (ethacrylate/acrylate) and polyglycerol (methacrylate).

[0050] The cationic poly electrolyte used in the process according to the invention, especially of the third, fifth, etc., coating layer, may, for example, be a natural cationic poly electrolyte or modified, natural cationic poly electrolyte which may be selected from the group of chitosan, modified dextrans such as diethylaminoethyl-modified dextrans, hydroxymethylcellulose trimethylamine, lysosome, polylysine, protamine sulfate, hydroxyethylcellulose trimethylamine and cationic proteins. The cationic poly electrolyte may be a synthetic cationic poly electrolyte and may in particular be selected from the group of polyallylamine, polyallylamine hydrosols, poly amme, poly vinylbenzyldimethylammonium salts, polybren, polyallyldimethylammonium salts, polyethylenimine, polyimida zolone, polyvinylamine, polyvinylpyridine, poly (acrylamide/methacryloyloxypropyltrimethylammonium salts), poly(diallyldimethylammonium salts/N-isoproyl acrylamide), poly (dimethylaminoethyl acrylate/acrylamide), polydimethylaminoethyl methacrylate, polydimethylaminoethyl methacrylate, poly (dimethylaminopropyl) methacrylamide, poly (dimethylaminoethyl methacrylate) and poly (vinylpyrrolidone/dimethylaminoethyl methacrylate) and polyvinylpyridinum salts. The cationic poly electrolyte should contain substantially no halide ions, especially no chloride ions, or be at least substantially halide-free, in particular chloride-free.

[0051] The poly electrolyte used in accordance with the invention may also be an amphiphilic poly electrolyte which may be selected from the group of amphiphilic block and random copolymers with partial poly electrolyte character. In general, it is possible to use linear or branched poly electrolytes, preference being given in accordance with the invention to linear poly electrolytes. The use of linear poly electrolytes leads to relatively incompact poly electrolyte layers or coatings having a relatively high degree of layer porosity. To increase the capsule stability, it is possible to crosslink poly electrolyte molecules within or between the individual layers, for example by crosslinking amino groups with aldehydes.

[0052] In an embodiment preferred in accordance with the invention, it is possible in the process according to the invention for the cationic surfactant or the cationic poly electrolyte, especially of the first, third, fifth, etc., coating layer, to be a cationic surfactant or poly electrolyte dependent upon the pH, especially upon the pH of the dispersant. The cationic surfactant or poly electrolyte dependent upon the pH should at least substantially be in protonated or cationic form at an acidic pH, preferably at a pH less than 7, especially at a pH less than 6.5, preferably less than 6. The cationic surfactant or poly electrolyte dependent upon the pH may be present at least substantially in deprotonated or electrically neutral form at a neutral or alkaline pH. The cationic surfactant or poly electrolyte dependent upon the pH may, in the context of the present invention, have at least one functional group which may be selected from amino, imino, amine oxide, phosphine oxide and pyridine N-oxide groups, preferably amine oxide, phosphine oxide, pyridine N-oxide and pyridine groups.

[0053] As explained above, polycation/polyanion complexes, cationic surfactant/poly anion complexes, polycation/anionic surfactant complexes or anionic surfactant/cationic surfactant complexes may be formed in the process
according to the invention in boundary layers formed between the particular coating layers (depending on the particular composition of the coating layers). These boundary layer complexes may be in water-soluble, moderately water-soluble or preferably water-insoluble form, the solubility being dependent especially on the stoichiometry. In this context, the term “stoichiometry” is understood to mean the ratio of the dissociable or dissociated, optionally electrically charged groups or functions of the cationic polyelectrolytes or cationic surfactants to the corresponding groups or functions of the anionic polyelectrolytes or anionic surfactants used. Water-insoluble formation of the boundary layer may be achieved especially in the event of charge neutralization. In an embodiment preferred in accordance with the invention, the water solubility of the boundary layer complexes, as detailed above, may be controlled via the pH, especially via the pH of the dispersant. In the context of the present invention, this may be either the concentrated laundry detergent or cleaning composition formulation or else the dilute wash liquor present in the washing or cleaning operation, i.e. especially the dilute laundry detergent or cleaning composition formulation.

Without wishing to commit to a specific theory, the formation of the interface layer between coating layers, as illustrated above, proceeds, for example, on the basis of chemical and/or physical, especially physical, interactions, especially electrostatic interactions, for example interionic interactions, such as ion/ion interactions or ion/dipole interactions. This can form a preferably water-insoluble complex which can increase the stability of the peroxycarboxylic acid to be encapsulated, especially in the concentrated laundry detergent formulation. In particular, the capsule coatings, as a result of the thickness of the coating layers, equally have regions in which the ionic polyelectrolyte or the ionic surfactant is present preferably in uncomplexed form, i.e. does not interact with oppositely charged groups, especially of the adjacent coating layer. In contrast, the polyelectrolytes or polyanions and/or polycations used in accordance with the invention are as such water-soluble, so that it is possible in accordance with the invention for a capsule coating to be present which comprises, in an alternating manner, preferably water-insoluble layers or layers whose water solubility depends, for example, upon the pH, which are formed by the aforementioned complexes.

The use, preferred in accordance with the invention, of cationic surfactants or cationic polyelectrolytes whose electrical charge depends upon the pH allows the water solubility, especially of the boundary layer, to be effectively influenced. For example, at an acidic pH, for example at a pH of from about 3.5 to about 5 (as may be the case for the inventive laundry detergent or cleaning formulation), the cationic surfactant dependent upon the pH or the polyelectrolyte dependent upon the pH is present preferably in protonated or positively charged, i.e. cationic, form, so that the water solubility of the complexed interface layer is low under these conditions. In the event of an increase in the pH, as is the case, for example, for the use of an inventive laundry detergent or cleaning formulation which comprises the inventive capsule system in a wash liquor (for example increase to a pH of 7 or more), the cationic surfactant dependent upon the pH or the polyelectrolyte dependent upon the pH used is present preferably in neutral or deprotonated form, which can increase the water solubility of the particular boundary layer, so that the release of the encapsulated peroxycarboxylic acid can be facilitated as a result within the wash liquor and the formation of residues can be prevented.

According to the invention, the cationic surfactant dependent upon the pH or the cationic polyelectrolyte dependent up on the pH thus, so to speak, has the function of a pH switch (i.e. dependent upon the pH) in relation to the partial dissolution, full dissolution, solubilization or release of a coating layer comprising such a polyelectrolyte and/or such a surfactant. For example, in a weakly acidic liquid laundry detergent formulation, such substances give rise to a stable capsule coating which has good protective action for the peroxycarboxylic acid. When the pH in the wash liquor increases, these substances dissolve better.

According to the invention, a multitude of coating layers may be applied to the at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, organic peroxyacarboxylic acid, especially imidoperoxycarboxylic acid. The number of coating layers may in particular be at least two and up to ten or more coating layers. In this context, Applicants have found that, to achieve effective encapsulation or protective action in relation to the peroxycarboxylic acid on the one hand and good release of the peroxycarboxylic acid to be encapsulated in the wash liquor on the other, especially at least two and preferably up to ten or more coating layers lead to an optimal result. Applicants have found that, especially in the case of capsule systems with eight or more coating layers, good results can be achieved with regard to effective encapsulation and good release of the peroxycarboxylic acid to be encapsulated.

In the process according to the invention, the solutions or dispersions which comprise at least one polyelectrolyte and/or at least one ionic surfactant and are provided in process step (a), (b) and/or, where appropriate, (c) should have a pH of at most 6, especially a pH of from 1 to 6, preferably from 2 to 5, preferentially from 3 to 4, more preferably of 3.5, in order to at least substantially prevent or to reduce degradation of the peroxycarboxylic acid, which can be stabilized relatively effectively at a pH of ≤3.5 but is decomposable relatively rapidly at neutral or alkaline pH, in the production of the inventive capsule systems.

In the process according to the invention, in process step (a), (b) and, where appropriate, (c), the solution and/or dispersion is applied to the peroxycarboxylic acid to be stabilized and/or to the preceding coating layer in a fluidized bed unit and/or by coating pans, drum coaters, mixers, especially spray dryers, Wurster coaters, preferably by spraying the solution and/or dispersion in a fluidized bed unit.

In industrial production, it is possible in a preferred process to work with two spray nozzles in alternation in a fluidized bed unit, with which the particular solutions and/or dispersions of the particular coating layer material are applied to the peroxycarboxylic acid to be stabilized or to the preceding coating layer, so that in principle as many coating layers as desired may be applied. The process time required is determined by the amount of water to be evaporated.

In a preferred embodiment, for example, the first layer may be applied by means of a spray drier, and the second, third, fourth, etc., layer, for example, by means of a
The process according to the invention thus allows the individual layers to be applied in a simple manner; complicated removal of unadsorbed substances between the application of the coating layers is not required.

In the course of the application, especially of the first coating layer, agglomerates of the solid peroxycarboxylic acid particles may form, so that it is possible in this way to establish the desired particle size. In this context, it is thus also possible to produce a capsule system which comprises a plurality of capsule cores.

With the aid of the inventive production process, it is possible to form layer thicknesses within a wide range which are significantly thicker than a molecular layer, so that a successive or alternating sequence of boundary layers which comprise the above-described complexes and layers of uncomplexed polyelectrolytes or ionic surfactants may be formed. This results in particularly positive properties of the inventive capsule system with regard to the storage and release of the peroxycarboxylic acid.

If required, or desired for the application, further additives or assistants (for example substances which serve to increase the handling safety such as boric acid, stabilizers, modifiers, inorganic salts, dyes, etc.) may be added to the core material (peroxycarboxylic acid) and/or to the capsule coating.

In the context of the present invention, at least one complexing agent can thus be added to at least one coating layer and can especially be selected from the group of quinoline and/or its salts, phosphates, alkali metal polyphosphates, picolinic acid and dipicolinic acid, mono- or polyphosphonic acids, especially 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), azacycloheptane diphosphonate (AHP) and/or nitritotriacetic acid (NTA), especially for complexing heavy metal ions, so that heavy metal ions which catalyze especially degradation, oxidation or reduction reactions and/or hydrolysis reactions in relation to the peroxycarboxylic acid, for example PAP, can be bound effectively.

In addition, at least one plasticizer, especially at least one plasticizer for water-soluble polymers, preferably polyethylene glycol (PEG), glycerol, glycol or triacetin, may be added to at least one coating layer, as a result of which the mechanical properties of the capsule coating or of the coating layers and thus the mechanical properties of the capsule system may be influenced.

In addition, at least one powdering agent may be added to at least one coating layer, as a result of which the tack of the material is reduced and its processibility can thus be improved. The powdering agent should preferably not have an䛿alkine reaction. Powdering agents preferred in accordance with the invention are, for example, sulfate salts and silica, for example Sipemat® from Degussa.

In general, in the process according to the invention, in process step (a), (b) and/or, where appropriate, (c), a processing operation, in particular a drying operation and/or a purifying operation and/or a classifying operation of the capsule system, for example after application of the particular coating layer(s), is effected by customary methods, especially by freeze-drying (lyophilization), evaporation of the dispersant, preferably at a temperature of from 40°C to 60°C in a fluidized bed unit, ultrafiltration, dialysis or spray-drying under gentle conditions, or sieving.

The processing step which may be carried out in process step (d), for example drying step and/or purifying step or classifying step, may likewise be effected by customary methods as described above. In this context, shaping may also be effected in relation to the capsule system, for example by rounding or the like.

In the process according to the invention, capsule systems laden with at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, may be obtained with a mean size (sphere diameter) of from 20 μm to 4000 μm, preferably from 50 μm to 3000 μm, preferentially from 100 μm to 2000 μm, so that controlled adjustment of the size of the capsule system in accordance with its particular later use is possible.

If appropriate, should this be desired or required for the application, it is possible to separate the inventive capsule system in accordance with its size or granulometry, for example by means of sieving.

In the process according to the invention, the proportion of the particular coating layer in the capsule coating may be from 1 to 15% by weight, preferably from 5 to 10% by weight, preferentially from 2 to 10% by weight, based on the capsule system. The proportion of the entire capsule coating comprising the particular coating layers may be up to 70% by weight based on the capsule system. The molecular weight of the polyelectrolyte in the particular coating layer may be ≥1000, preferably ≥10 000, preferentially ≥15 000. The content of organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, preferably PAP, may be ≥30% by weight, preferably ≥40% by weight, preferentially ≥50% by weight, based on the capsule system. Depending on the application, an adjustment of the content of peroxycarboxylic acid may be undertaken, for example against the background of increasing the handling safety of the inventive capsule system. For instance, an excessively high content of peroxycarboxylic acids may not be desirable or practicable for reasons of product safety. For these cases, the content of peroxycarboxylic acid should not exceed, for example, 50% by weight based on the capsule system.

In an embodiment particularly preferred in accordance with the invention, in which the capsule coating of the capsule system comprises four coating layers, the proportion of the first coating layer preferably comprising at least one cationic surfactant or polymer and also the third coating layer preferably comprising at least one cationic polymer or cationic surfactant in each case from 2 to 5% by weight, and the proportion of the second and also fourth coating layers each comprising at least one anionic polyelectrolyte or at least one anionic surfactant is in each case from 5 to 10% by weight based in each case on the capsule system.

The fractions, preferred in accordance with the invention, of the particular coating layers are selected against the background of enabling effective protective action and also good release with regard to the peroxycarboxylic acid to be encapsulated in the wash liquor.
already stated, particular preference is given in accordance with the invention to applying coating systems whose coating layer thicknesses are distinctly greater than that of a layer with molecular thickness, so that a complexed boundary layer can be formed between the individual coating layers and also layers with uncomplexed polyelectrolytes and/or ionic surfactants, especially those which are water-soluble in the washing and cleaning liquors.

[0076] The capsule system produced by the process according to the invention has a controlled-release effect. A controlled-release effect is in particular a slight delay, preferably of between 1 and 15 minutes, to dissolution of the capsules when they are used, for example in a wash liquor, or a delay to the release of the peroxycarboxylic acid from the inventive capsule system.

[0077] In the process according to the invention, it is finally additionally possible to apply a further coating or coating layer to the inventive capsule system, as a result of which an additional stabilizing effect in relation to the organic peroxycarboxylic acid to be stabilized or to be encapsulated is brought about. For example, a complexing agent which can complex heavy metal ions may be incorporated in this additional coating, so that heavy metal catalyzed decomposition of the peroxycarboxylic acid can be at least substantially prevented. The application of an additional coating may also serve to modify the dissolution rate further and to adjust it in a desired manner; this allows an additional controlled-release effect with regard to the peroxycarboxylic acid present in the inventive capsule system to be achieved. The application of the additional coating may be carried out in a manner known to those skilled in the art, for example by means of fluidized bed processes or by adsorption of the additional coating material onto the capsule system from a solution, spraying of a solution or melt of the coating material onto the capsule system and subsequent evaporation of the solvent, preferably water, or by means of coating in a mixer, tank, etc. It is possible in accordance with the invention to use materials known per se to those skilled in the art as additional coating substances, for example inorganic compounds, e.g., salts and inorganic oxides, especially sulfates or phosphates, or else high molecular weight compounds such as organic polymers, e.g., cellulose ethers, polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), etc.

[0078] It is also possible in the process according to the invention, for example, for a substance which can enter into endothermic reactions especially with itself, for example water of crystallization elimination reactions or decomposition reactions, at a temperature below 80° C., in particular below 70° C., to be applied to the organic peroxycarboxylic acid, preferably before application of the coating layers or capsule coating. According to the invention, this substance may also be blended with the peroxycarboxylic acid, especially mixed. Such a substance is, for example, boric acid. In the context of the present invention, this substance, preferably before application of the coating layers or capsule coating, may be applied directly to the peroxycarboxylic acid, for which, for example, the same process steps as for the formation of the further coating may be used. The substance added leads to an increase in the handling safety of the inventive capsule system since it can capture or compensate for any exothermicity which occurs. Exothermicity may be understood to mean a temperature increase occurring locally in the capsule system, which can be caused by an exothermic decomposition of the peroxycarboxylic acid which takes place or begins locally, but also a temperature increase occurring in a container or in the dispersal itself, for example in the course of storage. The added substance, for example boric acid, may also be introduced into the coating layers or capsule coating. However, preference is given in accordance with the invention to an application to the peroxycarboxylic acid or a blending or mixing with the peroxycarboxylic acid, since this leads to a higher effectiveness with regard to the handling safety.

[0079] The capsule system obtained in process step (b), (c) and/or, where appropriate, (d) in the process according to the invention may be formulated, for example, together with further ingredients, to a laundry detergent or cleaning composition, especially a liquid laundry detergent or cleaning composition. The laundry detergent or cleaning composition should have at least substantially no halide ions, especially no chloride ions, or the amount of halide ions, especially chloride ions, should be at most 500 ppm, preferably at most 100 ppm, more preferably at most 30 ppm. The pH should be at most 7, in particular between 3.5 and 7, preferably between 4.0 and 6.5, more preferably between 4.5 and 6. Moreover, the laundry detergent or cleaning composition may comprise at least one complexing agent; this may, for example, be selected from the group of quinoline and/or its salts, alkali metal polyphosphates, picolinic acid and dipicolinic acid, mono- or polyphosphonic acids, especially 1-hydroxyethylene-1,1-diphosphonic acid (HEDP), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), azacycloheptane diphosphonate (AHP), nitritriacetic acid (NTA), citrate and/or short-chain dicarboxylic acids; these complexing agents are used in the process according to the invention especially for complexing heavy metal ions. Moreover, the laundry detergent or cleaning composition may optionally comprise at least one water-miscible solvent with a low dissolution capacity for the organic peroxycarboxylic acid, especially amidoperoxycarboxylic acid (for example in amounts of preferably more than 20% by weight, more preferably more than 30% by weight, based on the laundry detergent or cleaning composition), or else the water-miscible solvent is the dispersant of the dispersion. For example, the solvent may be glycerol. However, the solvent preferred in accordance with the invention is water. In addition, at least one catalase may optionally be added to the laundry detergent or cleaning composition. For further details in relation to the laundry detergent or cleaning composition, reference may be made to remarks below.

[0080] The process according to the invention is equally a process for stabilizing peroxycarboxylic acids, especially amidoperoxycarboxylic acids, preferably PAP, or a process for increasing the storability of peroxycarboxylic acids, especially amidoperoxycarboxylic acids, preferably PAP.

[0081] In a typical embodiment, the process according to the invention may be carried out as follows: to encapsulate or to protect the peroxycarboxylic acid, especially amidoperoxycarboxylic acid (e.g., PAP), which is in the form of solid particles, especially in crystalline form, a capsule coating is applied to the peroxycarboxylic acid in a multi-layer process. To this end, the first layer applied to PAP is a polyelectrolyte or a surfactant having a positive or negative net charge. Since PAP crystals have a small negative surface
charge even at weakly acidic pH values, it is advantageous to use a cationic material for this first layer. The cationic surfactants used may be customary cationic surfactants, for example quaternary ammonium salts whose ammonium radical corresponds to the general formula $R^1R^2R^3N^+$ where the $R^1$, $R^2$ and $R^3$ radicals, identically or differently, are each a hydrogen atom or a linear or branched alkyl, alkenyl or alkynyl radical having from 1 to 40 carbon atoms, especially from 1 to 25 carbon atoms, such as alkyltrimethylammonium surfactants, ester quats and also N-alkylpyridinium salts. It has been found to be advantageous when the counterions of the surfactants are not halide ions. Suitable counterions are, for example, methylsulfate, sulfate, phosphate, tosylate or cuminesulfonate anions. Alternatively, the material used for the first layer may be a cationic polymer. Suitable cationic polymers are quaternized polymers bearing amine, imine or imidazole groups, for example polydiallyldimethylammonium polymers. Also suitable are all polymers of the general designation “Polyquaternium/□” known, for example, from cosmetic applications. Particularly suitable polymers being those whose counterions are not halide ions, especially chloride ions. As a second layer, a polymer of opposite charge is applied. When the first layer used is a cationic material, an anionic material now follows. Particular preference is given here to synthetic polymers such as polycarboxylic acids and their partial salts. Suitable polymers are, for example, polyacrylic acid, polymaleic acid and their copolymers. Also suitable are polyelectrolytes such as, for example, polyacrylic acid and their partial salts. Polymers sulfonated in a polymer-like manner are also possible. Moreover, it is also possible to use natural anionic polymers, for example algic acid, xanthan, etc. Furthermore, derivatized natural polymers such as carboxymethylcellulose are also possible. Optionally, a third, fourth, etc., layer may be applied, each of which consists of material of opposite charge to the preceding layer. For the second, third, fourth, etc., layer, preference is given to polymers over the surfactants, but surfactants and mixtures of polymers with surfactants having the same kind of charge may also be used without difficulty. In the context of the present invention, the materials of the coating layers are sprayed on, for example, in an alternating manner in a fluidized bed unit as an acidic aqueous solution preferably having a pH of about 3.5. It is appropriate to work in a fluidized bed unit in which the coating material can be sprayed in or on via at least two nozzles which are fed from different reservoir tanks. Alternating spraying from the two nozzles or spatial transport of the material being coated (peroxycarboxylic acid particles, unfinished capsule system) from one region which is sprayed with one solution or dispersion to another region which is sprayed with another solution or dispersion thus allows the application of the coating layers or of the multilayer capsule coating to be produced without a high level of complexity associated with cleaning or alteration of the apparatus. Also suitable, especially for applying the first layer, are spray dryers, and, for the further layers, Wurster coaters, but also other apparatus for coating macroscopic particles, for example coating pans, drum coaters, mixers, etc. In the spray application of the first layer, it is optionally possible to form agglomerates of a desired particle size. The particle size is in the range from 50 to 3000 μm, preferably from 100 to 200 μm. In the spray application of each further layer, an interface layer complex (for example a polyanion/polycation complex, etc.) forms on the boundary layer to the preceding layer. Depending on the stoichiometry, this is water-soluble, moderately water-soluble, or, especially in the case of charge neutralization, insoluble; in this regard, reference may be made to the above remarks.

[0082] In this process, it has been found that, surprisingly, these layers produced in a multistep process offer particularly good protection for PAP in a water-based liquid laundry detergent or cleaning composition formulation, especially in a water-based liquid laundry detergent or cleaning composition formulation. Particularly advantageous capsule systems according to the present invention may be obtained by a class of coating layers, preferably the cationic coating layers, consisting not of permanently cationic substances, but rather of cationic substances dependent upon the pH, or comprising them. Suitable pH-dependent cationic surfactants which are present in protonated form at acidic pH values but in neutral form at neutral pH values are amine oxide- or phosphine oxide-based surfactants, and also pyridinium-based surfactants. Suitable cationic polymers dependent upon the pH are those which have amino groups, imino groups, amine oxide groups, phosphine oxide groups or pyridine N-oxide groups. One example is polyvinylpyridine N-oxide. In a weakly acidic liquid laundry detergent formulation, these substances give rise to a stable capsule coating which has good protective action for the bleach (e.g., PAP). When the pH in the wash liquor is neutralized, they dissolve better. The inventive coatings may comprise further substances. These may serve to make heavy metal ions which promote the degradation of the bleach harmless. Particularly suitable examples of complexing agents are nitrate, EDTA, phosphates and, more preferably, phosphonates such as HDEP. Further additives may serve, for example, to positively influence the mechanical properties of the layers. For example, plasticizers may be used for this purpose. Suitable plasticizers are customary plasticizers for water-soluble polymers, for example polyethylene glycol (PEG), glycerol, glycols or triacetin, etc. In this typical embodiment of the present invention, a multilayer capsule system which comprises a bleach, preferably PAP, as a core material with a multilayer, at least two-layer capsule coating composed of in each case oppositely charged ionic surfactants and/or ionic polymers is thus.

[0083] In a second aspect, the present invention further provides the multilayer capsule system which is laden with at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid (e.g., PAP), and is preparable by the process according to the invention. The capsule system thus comprises at least one organic peroxycarboxylic acid, especially imidoperoxycarboxylic acid, preferably PAP, which is at least substantially enclosed or coated with a multilayer capsule coating. The capsule coating comprises at least two different coating layers, especially at least one first coating layer which at least substantially fully encloses or coats the peroxycarboxylic acid, and a second coating layer which at least substantially fully encloses or coats the first coating layer. The coating layers are each based on at least one polyelectrolyte and/or ionic surfactant.

[0084] According to the invention, the inventive capsule system comprises a multilayer capsule coating which has, for example, a third, fourth, fifth, etc., coating layer.

[0085] According to the invention, the first and second coating layers of the inventive capsule system should have
different, especially opposite, net charges. According to the invention, any further coating layers immediately adjoining one another should each also have different, especially opposite, net charges.

[0086] The organic peroxy-carboxylic acid to be encapsulated is especially selected from mono- and diperoxycarboxylic acids, in particular dodecanedioxyacid and preferably imidoperoxycarboxylic acids, more preferably 6-phthalimidoperoxycaproic acid (6-phthalimidoperoxycaproic acid, PAP). The peroxy-carboxylic acid should have a melting point at atmospheric pressure above 25°C, in particular above 35°C, preferably above 45°C, preferably above 50°C, more preferably above 100°C.

[0087] According to the invention, the multilayer capsule coating which comprises at least two coating layers and surrounds the peroxy-carboxylic acid to be encapsulated is such that the peroxy-carboxylic acid to be encapsulated is at least substantially fully surrounded by the capsule coating, so that the peroxy-carboxylic acid is at least substantially not in direct contact in relation to the surrounding medium, especially dispersant, i.e. the peroxy-carboxylic acid to be encapsulated is present in the inventive capsule system preferably as a core material which is surrounded by the multilayer capsule coating comprising at least two coating layers.

[0088] For further details in relation to the inventive capsule system, reference may be made to the above remarks on the process according to the invention which apply correspondingly to the inventive capsule system.

[0089] In the inventive capsule system, the proportion of the particular coating layer in the capsule coating is from 1 to 15% by weight, preferably from 1.5 to 10% by weight, preferably from 2 to 10% by weight, based on the capsule system. The proportion of the total capsule coating comprising the particular coating layers may be up to 70% by weight, based on the capsule system. The molecular weight of the polymeric surfactant in the particular coating layers should be ≥1,000, preferably ≥10,000, preferably ≥15,000. The content of an organic peroxy-carboxylic acid, especially imidoperoxycarboxylic acid, preferably PAP, is ≥30% by weight, preferably ≥40% by weight, preferably ≥50% by weight, based on the capsule system.

[0090] In the context of the present invention, the peroxy-carboxylic acid to be encapsulated, especially imidoperoxycarboxylic acid, preferably PAP, can be released from the capsule system on use, especially in a wash liquor. The release may especially be effected by partially or fully dissolving, dispersing or solubilizing the coating layers, for example by increasing the pH or surfactant reactivation, especially surfactant action, and action of the washing mechanics in the wash liquor. When, for example, a laundry detergent or cleaning composition concentrate comprises the inventive capsule system and also surfactants in inactivated form (for example by salting out, for example with sodium sulfate, or in the form of liquid crystals), dilution of this concentrate in the course of use in the wash liquor converts the surfactants from their inactivated or salted-out form to their active form, so that the surfactants activated in this way can partly or fully dissolve, disperse or solubilize the coating layers or capsule coating. In the case of dilution in the wash liquor, there is a simultaneous pH jump, so that the solubility of the peroxy-carboxylic acid increases distinctly. The peroxy-carboxylic acid, especially imidoperoxycarboxylic acid (PAP), may also be released from the capsule system in the wash liquor by osmotic processes and/or diffusion operations. For example, water molecules may diffuse along the concentration gradient through the semipermeable capsule coating, i.e. permeable to water and impermeable to peroxy-carboxylic acid, into the core region of the capsule system and lead there to partial or full dissolution of the peroxy-carboxylic acid at an appropriate pH of the wash liquor, especially at a pH ≥7. Without wishing to commit to a theory, this allows a high osmotic pressure to be generated in the capsule, which, so to speak, can lead to the capsule coating bursting open with associated release of the peroxy-carboxylic acid in the wash liquor. Without wishing to commit to a theory, the capsule coating or the coating layers can be partly or fully dissolved by an increase in the pH in the wash liquor by, as already stated, cationic polyelectrolytes or cationic surfactants whose electrical charge depends upon the pH being neutralized and thus the capsule coating being more readily partly or fully dissolved. Finally, mechanical operations are also significant, for example, mechanical destruction of the capsule system by the laundry items present in the wash liquor or by contact with the laundry drum. In particular, a combination of the individual aforementioned processes in relation to the release of the peroxy-carboxylic acid from the inventive capsule system is also possible.

[0091] The inventive capsule system has numerous possible uses. Thus, the inventive capsule system, in a further aspect of the present invention, may be used in laundry detergents and cleaning compositions, especially liquid laundry detergents and cleaning compositions, dental care compositions, hair dyeing compositions and for decolorizer or bleach compositions for industrial applications.

[0092] In this context, the inventive capsule system may also be used as a delivery system for the controlled release of peroxy-carboxylic acids, in which case the release of the peroxy-carboxylic acid can be controlled especially by the composition or by the number of the coating layers which at least substantially surround the peroxy-carboxylic acid. According to the invention, composition is understood to mean especially the type and/or amount of the appropriate polyelectrolyte or of the appropriate ionic surfactant in the particular coating layer. The release of the peroxy-carboxylic acid can be controlled especially by means of the water solubility as such or the water solubility as a function of the pH of the dispersant in relation to the particular coating layer. A further means of modification is that of applying an additional coating to the inventive capsule system.

[0093] The inventive capsule system may be used especially as a delivery system in which the peroxy-carboxylic acids are dispensed by prolonged or delayed release or over a long period (sustained-release effect).

[0094] The present invention further provides, in a further aspect of the present invention, laundry detergents and cleaning compositions, especially liquid laundry detergents and cleaning compositions, dental care compositions, hair-care compositions, dyeing and bleaching compositions for industrial applications, which comprise the inventive multilayer capsule system laden with at least one organic peroxy-carboxylic acid, especially imidoperoxycarboxylic acid.
The inventive laundry detergents and cleaning compositions which comprise the inventive capsule system are usable both in the domestic and in the industrial sector. In particular, the inventive laundry detergents and cleaning compositions are liquid laundry detergents and cleaning compositions which comprise the inventive capsule system.

The inventive laundry detergents and cleaning compositions may be used to clean hard surfaces and/or soft, especially textile, surfaces. The inventive laundry detergents and cleaning compositions may be used especially as dishwasher detergents, all-purpose cleaners, bath cleaners, floor cleaners, car cleaners, glass cleaners, furniture care compositions or cleaners, facade cleaners, laundry detergents or the like, more preferably as laundry detergents. The inventive laundry detergents and cleaning compositions are preferably also suitable for cleaning fibers, textiles, carpets and the like.

In addition to the inventive capsule system, the inventive laundry detergents and cleaning compositions comprise ingredients or constituents customary per se (for example surfactants, fragrances, dyes, enzymes, enzyme stabilizers, odorants or builders, pH modifiers, other bleaches, bleach activators, silver protectants, soil repellents, optical brighteners, staining inhibitors, disintegration assistants, thickeners, defoamers or foam inhibitors, complexing agents for heavy metals, soil repellents, dye transfer inhibitors, solvents, optical brighteners and/or further customary ingredients, etc.), and should be taken in the context of the present invention that the individual ingredients or constituents are compatible both with one another and with regard to the inventive capsule system or the peroxyacrylaidic acids encapsulated therein, which is realized by specific selection of the ingredients or constituents and/or their particular quantitative ratios. In this way, undesired interaction of these ingredients or constituents with the inventive capsule system or the peroxyacrylaidic acids incorporated therein can be prevented. As will be explained in detail below, the specific selection of certain ingredients or constituents and/or their quantitative ratios can bring about a stabilizing effect in relation to the inventive capsule system or to the peroxyacrylaidic acids encapsulated therein.

An inventive laundry detergent or cleaning composition, especially liquid laundry detergent or cleaning composition, comprises, for example, the following ingredients:

(i) capsule system laden with at least one organic peroxyacrylaidic acid, especially imidoperoxyacrylaidic acid, according to the present invention, preferably in amounts of from 0.1 to 20% by weight; and/or

(ii) surfactants, especially cationic and/or anionic surfactants, preferably in amounts of from 5 to 30% by weight, and/or nonionic surfactants, preferably in amounts of from 0% to 30% by weight; and/or

(iii) optionally electrolytes, especially inorganic and/or organic salts, preferably sodium sulfate, preferably in amounts of from 0% to 30% by weight; and/or

(iv) optionally complexing agents, especially selected from the group of galacturonic acid and/or its salts, alkali metal polyphosphates, picolinic acid and dipicolinic acid, mono- or polyphosphonic acids, especially 1-hydroxyethylene-1,1-diphosphonic acid (HEDP), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), azacycloheptane diphosphonate (AHP), nitritoltriacetic acid (NTA), citrate and/or short-chain dicarboxylic acids, preferably in amounts of from 0 to 5% by weight; and/or

 optionally enzymes such as proteases, amylases, cellulases and/or lipases, optionally together with enzyme stabilizers, preferably in amounts of from 0 to 10% by weight; and/or

 optionally builders, especially fatty acids, preferably saturated and/or branched fatty acids, especially having a melting point below 30°C, and/or citric acid and/or citrate, preferably in amounts of from 0 to 15% by weight; and/or

 optionally fragrances, preferably in amounts of from 0 to 5% by weight; and/or

 optionally assistants such as defoamers, pH regulators, rheology modifiers (thickeners), solvents, dyes; and/or

 optionally further customary ingredients such as brighteners, etc.; and/or

 (x) water;

all weight data being based on the laundry detergent or cleaning composition.

In the inventive laundry detergents or cleaning compositions, especially liquid laundry detergents or cleaning compositions, the surfactants in the laundry detergent or cleaning composition formulation may be inactivated, especially by salting-out, i.e. inducing a phase separation into a low-surfactant continuous phase and a preferably lamellar, generally highly viscous, crystalline or liquid-crystalline, surfactant-rich phase, preferably by introducing a sulfate compound, more preferably sodium sulfate, into the laundry detergent or cleaning composition formulation. In the laundry detergent or cleaning composition formulation, this especially at least substantially prevents or eliminates full and/or partial dissolution of the capsule system or of the organic peroxyacrylaidic acid, especially imidoperoxyacrylaidic acid. According to the invention, the term “continuous phase” is understood to mean the dispersant with the constituents or ingredients (for example salts, surfactants, etc.) dissolved therein. Preferably in accordance with the invention, the dispersant is water.

In this context, Applicants have been able to show that organic peroxyacrylaidic acids, especially PAP, are decomposed rapidly in the presence of active surfactants (i.e. surfactants present in free and/or micellar form in the laundry detergent or cleaning composition formulation), since the peroxyacrylaidic acids are dissolved to an enhanced extent by the surfactants and are extremely unstable in this dissolved state. Especially nonionic surfactants, for example based on alkyl polyglycol ethers, lead to accelerated decomposition of the peroxyacrylaidic acids. The addition of sulfate at least partly inactivates the surfactants, which is done especially by salting-out, which converts the surfactants from the especially micellar, active form into a preferably lamellar, crystalline or liquid-crystalline form (crystal or liquid-crystal formation). These liquid crystals themselves, which may be removed, for example, by centrifugation, should have a high viscosity. In
addition, the content of free surfactants in the inventive laundry detergent and cleaning composition formulations or in the continuous phase of the inventive laundry detergent and cleaning composition formulations should be at most 1%.

[0111] The sulfate concentration in the inventive laundry detergent or cleaning composition should be selected such that, when the laundry detergent or cleaning composition is used in the wash liquor, the surfactants are again present in active form, which can be achieved, for example, by a dilution effect when the laundry detergent or cleaning composition is introduced into the wash liquor. In particular, the concentration should be selected such that, as mentioned above, less than 1% dissolved surfactant is present in the continuous phase of the undiluted laundry detergent or cleaning composition, and, when the temperature is lowered, especially when the temperature is lowered down to 0°C, no crystallization of the sulfate takes place.

[0112] Since nonionic surfactants in particular are problematic with regard to the stability of peroxycarboxylic acids, the inventive laundry detergents and cleaning compositions have an appropriately adjusted or optimized nonionic surfactant/charged surfactant ratio. The content of alkyl polyglycol ethers should be at a minimum.

[0113] In the context of the present invention, the inventive laundry detergents and cleaning compositions, especially liquid laundry detergents and cleaning compositions, should comprise at least substantially no halide ions, especially chloride ions. The amount of halide ions, especially chloride ions, is at most 500 ppm, preferably at most 100 ppm, more preferably at most 30 ppm. This is because Applicants have found that, surprisingly, a high halide, especially chloride, ion concentration, as is customary, for example, in conventional laundry detergents and cleaning compositions owing to contaminations of some raw materials or ingredients, leads to increased degradation of peroxycarboxylic acids. Thus, a decrease in the halide, especially chloride, ion concentration can lead to reduced degradation of the peroxycarboxylic acid. A low chloride ion concentration can be achieved in accordance with the invention especially by the use of sulfate, methylsulfate, phosphate, tosylate or cumenesulfonate compounds, especially in relation to the surfactants of the laundry detergent or cleaning composition formulation. Moreover, raw materials or ingredients should be selected which have a particularly low chloride content (for example use of substantially halide-free components, for example halide-free surfactants, halide-free phosphonates, etc.).

[0114] Moreover, the inventive laundry detergents and cleaning compositions should have a pH of at most 7; in particular a pH of from 3.5 to 7, preferably from 4.0 to 6.5, more preferably from 4.5 to 6.0, most preferably of about 5. This is because bleaches based on peroxycarboxylic acids such as PAP can surprisingly be stabilized relatively effectively in an acidic environment, especially at a pH of ≥3.5, whereas relatively rapid decomposition of peroxycarboxylic acids such as PAP takes place at neutral or alkaline pH values. The pH in the inventive laundry detergents and cleaning compositions can be lowered, for example, by adding acidic salts. Preference is given to bisulfates and/or bicarbonates or organic polycarboxylic acids, which may, for example, simultaneously also be used as builder substances. Moreover, the phosphonates used as complexing agents may be incorporated as phosphonic acids, and the desired pH subsequently established by addition of alkalis.

[0115] The inventive laundry detergents or cleaning compositions may comprise at least one fatty acid. Preference is given in accordance with the invention to saturated and/or branched fatty acids, especially having a melting point below 30°C. In the context of the present invention, it is possible, for example, to use Isocarb-16% from Suisol in the inventive laundry detergent or cleaning compositions.

[0116] The inventive laundry detergents or cleaning compositions have an optimized citric acid or citrate content. As has been found by Applicants, citric acid or citrates can lead to a degradation of peroxycarboxylic acids, especially PAP. Nevertheless, it may be required in some cases to use citric acid or citrates in the laundry detergent or cleaning composition or in the dispersant for the inventive capsules (for example as builders and/or as complexing agents). However, the amounts used should not be too high and be adjusted in relation to the peroxycarboxylic acids, especially PAP.

[0117] In addition, the inventive laundry detergent or cleaning composition may comprise at least one complexing agent which may especially be selected from the group of quinoline and/or its salts, mono- or polyphosphonic acids, especially 1-hydroxyethylidene-1,2-diphosphonic acid (HEDP), ethylenediaminetetraacetic acid (EDTA), diethylentriaminepenta(methylene phosphonic acid) (DTPMP), azacycloheptane diphosphonate (AHP), nitriotriacetic acid (NTA), citrate and/or short-chain dicarboxylic acids. Further examples of complexing agents, usable in accordance with the invention, for heavy metals are, for example, aminopolyacrylic acids, aminohydroxypropylocarboxylic acids, polyphosphonic acids and aminopolyphosphonic acids. These complexing agents are used in accordance with the invention to effectively inactivate or to bind heavy metal ions which function especially as catalysts of oxidation processes and can thus lead a degradation of peroxycarboxylic acids such as PAP, and which may be introduced in traces into the inventive laundry detergent or cleaning composition, for example, via water pipes or metallic components of the production plants or else via raw materials or ingredients.

[0118] Furthermore, the inventive laundry detergents and cleaning compositions may optionally comprise at least one water-miscible solvent with a low dissolution capacity for the organic peroxycarboxylic acids, preferably glycerol.

[0119] Furthermore, the inventive laundry detergents and cleaning compositions may optionally comprise at least one catalase in order to effectively remove any hydrogen peroxide formed by reaction of the peroxycarboxylic acid with water from the continuous phase of the product, especially of the laundry detergent and cleaning composition formulation, so that, especially there, any enzymes present are protected effectively from oxidation processes which may lead in some cases to a loss of activity of the enzymes. For this purpose, it is equally possible for at least one peroxidase and/or at least one antioxidant, optionally in addition to the at least one catalase, to be added to the inventive laundry detergents or cleaning compositions. Antioxidants preferred in accordance with the invention are, for example, ascorbic acid, tocopherol, gallic acid or derivatives thereof.

[0120] Moreover, the inventive laundry detergent or cleaning composition formulation should be configured such that
it especially substantially does not partly or fully dissolve the inventive capsule system. In general, the components which are used in the inventive laundry detergent or cleaning composition should be selected such that they are at least substantially compatible in relation to the inventive capsule system, i.e., especially in the laundry detergent or cleaning composition itself, especially within the period before its use (storage time), no undesired chemical reactions, especially degradation, oxidation or reduction reactions and/or hydrolysis reactions, which lead to a premature degradation and a loss of activity of the peroxycarboxylic acid, should take place between these components and the capsule system.

[0121] At the same time, it should be ensured, that in the laundry detergent or cleaning composition itself, there is no release of the peroxycarboxylic acid, and especially no removal and no partial or full dissolution of the capsule coating or of the coating layers takes place, and peroxycarboxylic acid does not dissolve or diffuse out of the capsule system owing to the osmotic conditions. This can be achieved in accordance with the invention in the laundry detergent or cleaning composition formulation, for example, by addition of sulfate in combination with water as a solvent, as the result of which an increase in the osmotic pressure in the laundry detergent or cleaning formulation is achieved. Moreover, the pH of the laundry detergent or cleaning formulation should be within the acidic region, especially as defined above, so that the peroxycarboxylic acid, for example PAP, has low solubility and, on the other hand, any coating layers present of the capsule system with cationic surfactants or cationic polyelectrolytes dependent upon the pH, especially as defined above, are present in protonated form and therefore have only low water solubility.

[0122] Compared to the prior art, the present invention has a series of advantages:

[0123] In the process according to the invention, the capsule coating and the coating layers are formed on the basis of physicochemical or physical interactions, so that no polymerization steps, especially free-radical polymerization steps, are needed for the formation of the capsule structure, as is the case in some prior art processes. Such polymerizations frequently lead to the decomposition of the active substance, especially of the sensitive peroxycarboxylic acid. The present invention thus provides an encapsulation process directed to the chemically sensitive peroxycarboxylic acids.

[0124] In addition, the process according to the invention has the advantage that it provides a multilayer capsule system laden with peroxycarboxylic acids, especially amidoperoxycarboxylic acids, which can be varied or tailored widely with regard to its size and its active substance content, so that individual adjustment to the particular requirements, especially in relation to the laundry detergents and cleaning compositions, is possible.

[0125] In this context, it is especially advantageous that both the number of capsule coatings and the composition of the corresponding coatings can be varied within a wide range, so that it becomes possible in the context of the present invention firstly to provide the peroxycarboxylic acid to be encapsulated with a high storage stability, especially in relation to the period before its use in the wash liquor, and secondly to achieve good release of the peroxy-carboxylic acid during the washing operation in the wash liquor. The adjustability of the active substance/coating ratio makes possible the effective metering of the active substance, i.e. of the peroxycarboxylic acid, with regard to the appropriate use; in this context, the inventive capsule system is notable for a high content of peroxycarboxylic acid.

[0126] The inventive production process and the capsule system obtainable in this way ensure firstly that the inventive capsule system can be applied from aqueous solutions or dispersions and secondly that the capsule system is not partly or fully dissolved in an aqueous liquid formulation, for example a liquid laundry detergent or cleaning composition. The process according to the invention for producing such a capsule system is practicable and realizable on the industrial scale.

[0127] Moreover, the controlled modification of the capsule coating, especially the addition of complexing agents for heavy metal ions, can achieve a further improvement in the protection of the peroxycarboxylic acid and, associated therewith, a further increase in its storage stability. Further modifications of the capsule coating, for example the addition of softeners, leads to outstanding adaptability of the inventive capsule system with regard to the particular use.

[0128] In contrast to encapsulation systems which are based on waxes for example, the inventive capsule system does not comprise any troublesome capsule coatings which lead within the washing process to undesired residues on the laundry. This is because, even though the boundary layers between the particular coating layers are in substantially water-insoluble form, Applicants have been able to show that, under wash conditions, no significant residues are formed on the laundry.

[0129] The inventive capsule system has the crucial advantage that, compared to prior art systems, it possesses a distinct increase in the storage stability and thus, even after a prolonged period, a high bleaching activity.

[0130] In particular, the inventive capsule system is suitable for incorporation and use in systems comprising surfactants, for example surfactive (surfactant-containing) dispersions for liquid laundry detergents and cleaning compositions. This is a particular advantage since the unencapsulated or unprotected peroxycarboxylic acids, especially PAP, are not stable and are decomposed rapidly in the presence of surfactants, so that their use in surfactant-containing liquid, especially aqueous, media has to date not been possible or at best have been possible to a very restricted degree. The stabilizing effect of the capsule system, which is associated additionally with a desired controlled release of the encapsulated peroxycarboxylic acid, can be enhanced in a synergistic manner by the medium in which the inventive gel capsules are disposed being adjusted such that it affords additional stabilization in relation to the peroxycarboxylic acids, especially by inactivation of the surfactants, optimization or lowering of the pH, reduction of the halide content, use of a solvent with low dissolution capacity in relation to peroxycarboxylic acids and the like.

[0131] The inventive capsule system can be incorporated stably especially into liquid laundry detergents and cleaning compositions. Additional prevention or reduction of sedimentation processes can be achieved, for example, by suitable thickener systems known to those skilled in the art. It possesses a high storage stability there and can, even after prolonged periods, release the peroxycarboxylic acid effectively.
The inventive capsule system can be produced in the inventive formulation form with customary process technology means on the industrial scale. In particular, the inventive coating layers may be applied directly onto one another without unabsorbed material having to be removed beforehand in a complicated operation.

With the aid of the inventive production process, it is possible to form layer thicknesses within a wide range which are significantly thicker than a molecular layer, so as to result in a successive or alternating sequence of complexed and uncomplexed boundary layers. This results in particularly positive properties of the inventive capsule system with regard to the storage and release of the peroxycarboxylic acid.

Owing to their above-detailed synergistically active modifications adjusted to one another, i.e. adaptation of the formulation, especially low halide ion content, optimization of the pH, addition of complexing agents, specific solvents (e.g., glycerol) and/or enzymes (e.g., catalase), inactivation of the surfactants, the inventive laundry detergent and cleaning composition formulations which comprise the inventive capsule system have considerable advantages over the prior art, since the degradation of the sensitive bleaches based on peroxycarboxylic acid is distinctly reduced in conjunction with the inventive capsule system.

Further embodiments, modifications and variations and also advantages of the present invention are immediately recognizable and realizable by the person skilled in the art on reading the description without leaving the scope of the present invention.

The present invention is illustrated with reference to the following WORKING EXAMPLES, which in no way restrict the invention:

WORKING EXAMPLES

Example 1

A laboratory fluidized bed unit (Aromatic®) was initially charged with 300 g of Eureco® W (72% PAP content). At an air supply temperature of 50°C, 150 ml of Luviquat Care® (polyacrylate) which had been admixed with 1% Sequion® 10H60 were sprayed on. After drying, 100 ml of Sokalan® CP 45 (polyanion), again admixed with 1% Sequion® 10H60, were sprayed on. A third and a fourth layer were sprayed on in the same manner. The resulting capsule system (compound) was removed and sieved to a particle size of from 200 to 2000 μm. It had an active substance content (PAP) of 61%.

Example 2

In the EXAMPLE which follows, it is shown how the inventive formulation increases the PAP stability in a surfactant-containing liquid formulation:

The capsule system from EXAMPLE 1 was introduced into a liquid formulation of the following composition (the percentages are active substance data):

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthan gum</td>
<td>1%</td>
</tr>
<tr>
<td>Capsule system from EXAMPLE 1</td>
<td>4%</td>
</tr>
<tr>
<td>Water</td>
<td>ad 100%</td>
</tr>
</tbody>
</table>

Example 3

Owing to the phosphonate (Sequion® 10H60), the pH of this formulation is strongly acidic. It was adjusted to 5.0 with sodium hydroxide solution. The product was incorporated at a temperature of 40°C. The COMPARATIVE EXAMPLE used was the same liquid formulation in which unformulated Eureco® W was incorporated. After one week, the active oxygen loss of the inventive formulation was only 1%. In the COMPARATIVE EXAMPLE, 15% of the PAP had degraded. After two weeks, the inventive formulation had a loss of only 5%. In the COMPARATIVE EXAMPLE, the content fell by 25%.

Example 4

The capsule systems were produced in accordance with EXAMPLE 1, except that the composition of the particular solutions or dispersion used to produce the coating layers varied in the EXAMPLES 4a to 4d which follow, the materials used for the particular solution or dispersion of the coating layer material and also their concentrations, based on the solution or dispersion (unless stated otherwise), are specified. The particular solutions or dispersions were sprayed in alternation onto the Eureco® W to be encapsulated, so as to form a capsule system with alternating coating layers.

The capsule systems were introduced into a liquid formulation according to EXAMPLE 3 and incorporated at a storage temperature of 40°C. The active oxygen retentions for various incorporation times are specified, based on the active oxygen retention before incorporation. In comparison to EXAMPLE 2, the active oxygen retentions are somewhat lower, but the formulation used possesses significantly better washing performance.

Example 4a: Example of a Capsule System with 8 Coating Layers:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Luviquat Care®</td>
<td>1%</td>
</tr>
<tr>
<td>4</td>
<td>Sokalan® CP 45</td>
<td>3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Week 1</th>
<th>Week 2</th>
<th>Week 4</th>
<th>Week 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.5%</td>
<td>90.8%</td>
<td>81.3%</td>
<td>64.0%</td>
</tr>
</tbody>
</table>
4b: Example of a Capsule System with Powdering Agent:

- 4 coating layers: 2% Luviduat Care (R) (with 10% Sipemat (R) S22, based on Luviduat Care (R))
- Week 1: 95.1%
- Week 2: 89.4%

4c:

- 4 coating layers: 3% Luvidquat (R) PQ 11 (R) N
- Week 1: 95.4%
- Week 2: 89.7%
- Week 4: 82.4%
- Week 8: 64.0%

4d: (Comparative Example):

- 4 coating layers: 3% polyvinylpyrrolidone (PVP)
- 4 coating layers: 5% Sokalan (R) CP 45
- The pH of the polyvinylpyrrolidone solution was 4.0 (adjustment with sulfuric acid).
- Week 1: 95.3%
- Week 2: 89.7%

4e: (Comparative Example):

- Unformulated Eureco® W ("uncoated PAP") in the same formulation:

<table>
<thead>
<tr>
<th>Week 1</th>
<th>Week 2</th>
<th>Week 4</th>
<th>Week 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>85.7%</td>
<td>76.9%</td>
<td>63.5%</td>
<td>41.5%</td>
</tr>
</tbody>
</table>

1. A process for producing a multilayer capsule system comprised of at least one organic peroxycarboxylic acid, comprising contacting an organic peroxycarboxylic acid in solid particulate form with at least one coating layer comprised of at least one polyelectrolyte, at least one ionic surfactant or a combination thereof, wherein the layers are applied successively to the organic peroxycarboxylic acid to form a multilayer capsule coating comprised of at least two coating layers.

2. The process of claim 1, wherein the organic peroxycarboxylic acid is contacted with a solution and/or dispersion comprising at least one polyelectrolyte, at least one ionic surfactant and/or a combination thereof.

3. The process of claim 1, further comprising the step of at least partially removing the solvent or dispersant after each contacting step.

4. The process of claim 1, wherein the organic peroxycarboxylic acid is an organic mono- and diperoxycarboxylic acid.

5. The process of claim 4, wherein the organic diperoxycarboxylic acid is dodecanediperoxycarboxylic acid.

6. The process of claim 1, wherein the organic peroxycarboxylic acid is dodecanediperoxycarboxylic acid.

7. The process of claim 1, wherein the organic peroxycarboxylic acid has a melting point at atmospheric pressure above 25°C.

8. The process of claim 1, wherein the organic peroxycarboxylic acid is an imidoperoxycarboxylic acid.

9. The process of claim 9, wherein the imidoperoxycarboxylic acid is 6-phthalimidoperoxycarboxylic acid.

10. The process of claim 1, wherein the process is comprised of five or more steps, wherein each of the first, third, fifth and subsequent odd numbered coating layers formed is comprised of a cationic surfactant or a cationic polyelectrolyte.

11. The process of claim 10, wherein each of the second, fourth, sixth and subsequent even numbered coating layers formed has a negative net charge.

12. The process of claim 10, wherein the first coating layer is comprised of cationic surfactant selected from quaternary ammonium salts whose ammonium radical corresponds to the general formula R1'R2'R3'R4'N+ where the R1', R2', and R3' radicals, ideally or differently, are a hydrogen atom or a linear or branched alkyl, alkyne or alkynyl radical having from 1 to 40 carbon atoms.

13. The process of claim 12, wherein the counterion of the cationic surfactant is selected from methylsulfate, sulfate, phosphate, tosylate or cumenesulfonate.

14. The process of claim 10, wherein the first coating layer is comprised of cationic surfactant that includes at least one functional group selected from the group consisting of quaternary amine, imine and imidazole groups and is free of halide counterions.

15. The process of claim 10, wherein the cationic polyelectrolyte is an amine oxide or an amine oxide and is free of halide counterions.

16. The process of claim 10, wherein each of the second, fourth, sixth and subsequent even numbered coating layers is comprised of a synthetic anionic polyelectrolyte selected from the group consisting of polymeric sulfonic acids, polycarboxylic acids and their salts.

17. The process of claim 10, wherein each of the second, fourth, sixth and subsequent even numbered coating layers is comprised of a natural anionic polymer selected from the group consisting of alginate acid, xanthan and/or derivatized natural polymers.

18. The process of claim 16, wherein the polycarboxylic acid is polyacrylic acid, polymealactic acid, and copolymers thereof.

19. The process of claim 16, wherein the polymeric sulfonic acid is selected from the group consisting of polystyrene sulfonic acids and their salts.

20. The process of claim 17, wherein the natural anionic polymer is selected from the group consisting of alginate, carboxymethylamyllose, carboxymethylcellulose, carboxymethylxanthan, chitosan sulfate, chondroitin sulfate, chitin sulfate, dextran sulfate, gum arabic, guar gum, gellan gum, heparin, hyaluronic acid, pectin, xanthan and anionic proteins.

21. The process of claim 16, wherein the synthetic anionic polymer is selected from the group consisting of polycarboxylates, anionic polypeptides and copolymers thereof, polymealactic, polymethylacrylate, polysulfonic acid, polysty-
renesulfonate, polyvinyl phosphate, polyvinylphosphonate, polyvinyl sulfate, polyacrylamidomethylpropanesulfonate, polyacrylate, poly(butadiene/maleate), poly(ethylene/maleate), poly(ethacrylate/acrylate), and poly(glycerol/methacrylate).

22. The process of claim 10, wherein at least one of the third, fifth or subsequent odd numbered coating layers is comprised of a natural cationic polyelectrolyte selected from the group consisting of chitosan, modified dextrans, hydroxyethylcellulosetrimethylammonium, lysozyme, protamine sulfate, hydroxyethylcellulosetrimethylammonium and cationic proteins.

23. The process of claim 10, wherein at least one of the third, fifth or subsequent odd numbered coating layers is comprised of a synthetic cationic polyelectrolyte selected from the group consisting of polyallylamine, polyallylamine hydroxysalts, polyacrylamides, polyvinylbenzyltrimethylammonium salts, polybren, polydiallyldimethylammonium salts, polyethyleneimine, polyimidazolines, polyacrylamides, polyvinylpyridine, poly(acrylamide/methacryloyloxypropyltrimethylammonium salts), poly(diallyldimethylammonium salts/N-isopropylacrylamide), poly(dimethylaminomethyl acrylate/acrylamide), polydimethylaminomethyl methacrylate, polydimethylaminoepichlorohydrin, polyethyleneiminoepichlorohydrin, polyethyleneiminoepichlorohydrin, polyethyleneiminoepichlorohydrin, polyethyleneiminoepichlorohydrin, polyethyleneiminoepichlorohydrin, polyethyleneiminoepichlorohydrin, and polyethyleneiminoepichlorohydrin where the cationic polyelectrolyte is at least substantially halide-free.

24. The process of claim 1, wherein the polyelectrolyte is an amphiphilic polyelectrolyte selected from the group of amphiphilic block and random copolymers with partial polyelectrolyte character.

25. The process of claim 10, wherein at least one of the third, fifth or subsequent odd numbered coating layers is comprised of a cationic surfactant which is at least substantially in protonated and/or cationic form at an acidic pH.

26. The process of claim 25, wherein the cationic surfactant is a compound having a functional group selected from the group consisting of phosphine oxide, pyridine N-oxide groups, phosphine oxide, pyridine N-oxide and pyridinium groups.

27. The process of claim 1, wherein the boundary between coating layers is a boundary layer complex comprising a polycation/polyanion, cationic surfactant/polyanion, polycation/anionic surfactant and/or anionic surfactant/cationic surfactant complex.

28. The process of claim 27, wherein the boundary layer complex is in water-soluble, moderately water-soluble or water-insoluble form.

29. The process of claim 28, wherein the water-solubility of the boundary layer complex is pH-dependent.

30. The process of claim 1, wherein the multilayer capsule is comprised of at least 2 layers.

31. The process of claim 2, wherein the pH of the solution and/or dispersion is from 1 to 6.

32. The process of claim 2, wherein the peroxycarboxylic acid is contacted by coating pans, drum coaters, mixers, spray dryers, Wurster coaters.

33. The process of claim 2, wherein the peroxycarboxylic acid is contacted by spraying the solution and/or dispersion in a fluidized bed unit.

34. The process of claim 1, wherein the coating layer is further comprised of at least one complexing agent selected from the group consisting of quinoline and/or its salts, phosphates, alkali metal polyphosphonates, picolinate acid and dipicolinic acid, mono- or polyphosphonic acids, EDTA, diethylenetriaminopenta(methyleneephosphonic acid), azacycloheptane diphosphonate and nitrilotriacetic acid.

35. The process of claim 1, wherein the coating layer is further comprised of at least one plasticizer selected from the group consisting of polyethylene glycol, glycerol, glycol and triacetin.

36. The process of claim 1, wherein the particle size of the peroxycarboxylic acid solid particles is from 20 μm to 4000 μm.

37. The process of claim 1, wherein the proportion of a coating layer in the capsule coating is from 1 to 15% by weight.

38. The process of claim 1, wherein the molecular weight of the polyelectrolyte in a coating layer is ≥1000.

39. A laundry detergent comprising a multilayer capsule system made by the process of claim 1, wherein the laundry detergent is comprised of up to 500 ppm halide ions; at least one complexing agent selected from the group of quinoline and/or its salts, alkali metal polyphosphonates, picolinate acid and dipicolinic acid, mono- or polyphosphonic acids, EDTA, diethylenetriaminopenta(methyleneephosphonic acid), azacycloheptane diphosphonate, nitrilotriacetic acid, citrate and/or short-chain dicarboxylic acids; optionally at least one water-miscible solvent with a low dissolution capacity for the organic peroxycarboxylic acid; optionally at least one catalase and/or one peroxidase enzyme; at least one antioxidant and wherein the laundry detergent has a pH of at most 7.

40. The laundry detergent of claim 39, wherein the peroxycarboxylic acid is 6-phthalimidoperoxycaproic acid.

41. A multilayer capsule comprising a core-shell structure, wherein the core portion comprises at least one organic peroxycarboxylic acid in solid particulate form and the shell portion comprises at least one coating layer comprising a material selected from the group consisting of at least one polyelectrolyte, at least one ionic surfactant or a combination thereof.

42. The multilayer capsule of claim 41, wherein the shell portion comprises multiple coating layers comprising a material selected from the group consisting of at least one polyelectrolyte, at least one ionic surfactant or a combination thereof.

43. The multilayer capsule of claim 42, wherein the shell portion comprises at least three coating layers.

44. The multilayer capsule of claim 43, wherein the first layer of the shell portion comprises a material having a net charge opposite to that of the second layer.

45. The multilayer capsule of claim 42, wherein the organic peroxycarboxylic acid is an organic mono- and diperoxycarboxylic acid.

46. The multilayer capsule of claim 42, wherein the organic peroxycarboxylic acid is a diperoxycarboxylic acid.
47. The multilayer capsule of claim 42, wherein the organic peroxycarboxylic acid is dodecanediperoxy acid.

48. The multilayer capsule of claim 42, wherein the organic peroxycarboxylic acid has a melting point at atmospheric pressure above 25°C.

49. The multilayer capsule of claim 42, wherein the organic peroxycarboxylic acid is an imidoperoxycarboxylic acid.

50. The multilayer capsule of claim 49, wherein the imidoperoxycarboxylic acid 6-phthalimidoperoxycaproic acid.

51. The multilayer capsule of claim 42, wherein the particle size of the peroxycarboxylic acid solid particles is from 20 μm to 4000 μm.

52. The process of claim 1, wherein the proportion of a coating layer in the capsule coating is from 1 to 15% by weight.

53. The process of claim 1, wherein the molecular weight of the polyelectrolyte in a coating layer is ≥1000.

54. An aqueous dispersion comprising the multilayer capsule of claim 41.

55. A composition comprising the multilayer capsule of claim 41 and a cleaning composition selected from the group consisting of a liquid laundry detergent, a dental care composition, a hair dyeing composition, a decolorizing composition and a bleach composition.

* * * * *