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(54) **CLEANING AGENT**

(57) A cleaning agent comprising a supporting substrate with a pro-oxidizing agent immobilized thereof.

EP 3 444 328 A1

Description

TECHNICAL FIELD

[0001] The present invention is in the field of cleaning. It relates to a cleaning agent, in particular, a cleaning agent comprising a supporting substrate with a pro-oxidizing agent immobilized thereon. The invention also relates to a cleaning kit comprising the cleaning agent and a method of cleaning using the kit. The invention provides better cleaning by decolourising the wash liquor, avoiding soil re-deposition and preventing and/or reducing malodour while caring for the surface cleaned.

BACKGROUND OF THE INVENTION

[0002] When cleaning a surface by immersion in a wash liquor, dirt goes from the surface to be cleaned to the liquor. Dirt encompasses stains, soils, malodours, bacteria, etc. Dirt can be redeposited onto the surface being cleaned. There can also be transfer of colour from the surface being cleaned to the liquor. Colour bleeding can occur during the cleaning of a surface with a wash liquor. During the cleaning process dyes can migrate from the surface to the wash liquor. These dyes can be deposited onto other surfaces immersed in the wash liquor impairing on the appearance of the surface, similarly colours coming from stains can also be deposited onto the surface being cleaned. This can be more apparent in the case of laundry loads containing white fabrics. The white fabrics tend to become greyish when washed in the presence of fabrics that are not completely white. Dyes in the wash liquor can also contribute to colour deterioration of coloured fabrics. Soils, stains, bacteria, malodours removed from the fabrics can also being re-deposited on the fabrics in detriment of the cleaning process.

[0003] In the case of mixed laundry loads, i.e. loads containing coloured and white fabrics, high level of bleach cannot always be used because it could alter the colours of coloured fabrics. This can also be the case when cleaning patterned hard-surfaces.

[0004] The object of the present invention is to provide improved cleaning and at the same time protect the colour of surfaces. In particular, to provide cleaning while caring for the colours of coloured fabrics and prevent the greying of white fabrics in mixed loads as well as preventing and/or reducing malodours and soil re-deposition.

SUMMARY OF THE INVENTION

[0005] According to the first aspect of the invention, there is provided a cleaning agent. The cleaning agent comprises a pro-oxidizing agent immobilized on a supporting substrate.

[0006] A "cleaning agent" within the meaning of the invention is an agent that can be used in a cleaning process

to contribute to the cleaning on its own but preferably in combination with a cleaning composition.

[0007] A "supporting substrate" within the meaning of the invention is any substrate capable of having an oxidoreductase mediator immobilized on its surface.

[0008] An "pro-oxidizing agent" is an agent that can perform oxidation after it has been activated. It can be activated chemically, photochemically, enzymatically, etc. to a form that will oxidize or react with dyes to alter the color of the dye. It can also help to reduce and or prevent soil re-deposition and malodour and additionally it can prevent bacteria growth in the wash liquor. The object of this invention is to promote dye decolourization, soil re-deposition and malodour in the wash liquor while caring for the surface being cleaned. This is achieved by immobilizing a pro-oxidizing agent on a substrate. The transfer of oxidising species would take place in the wash liquor and not on the surface to be cleaned, this would result in a cleaner wash liquor that would be translated into cleaner surfaces without exposing the surface to the chemical aggression that mediators can present.

[0009] Colour bleed can occur when fabrics, or any other surfaces, get wet and dye leaches out of the fibers. This commonly occurs in the washing machine and can result in colour transfer between items in the load.

[0010] There are two different ways to attack a dye, chemically, to remove its colour. One is by *oxidation*, in which electrons are removed, while the other is by *reduction*, in which electrons are added.

[0011] Chromophores cause colours by reflecting a certain portion of the visible spectrum of light. For example, a blue fabric contains chromophores that reflect blue light that our eyes see as the colour blue.

[0012] An oxidizing agent works by breaking the chemical bonds of a chromophore (part of a molecule that has colour). This changes the molecule so that it either has no colour or else reflects colour outside the visible spectrum.

[0013] A reducing agent works by changing the double bonds of a chromophore into single bonds. This alters the optical properties of the molecule, making it colourless.

[0014] The pro-oxidizing agent is immobilised onto a supporting substrate. The immobilization of the pro-oxidizing agent makes the oxidation to take place where the agent is located rather than on the fabrics. As discussed before this results in better cleaning while caring for the cleaned surfaces. This differs from a traditional cleaning process where the oxidation/reduction takes place on the surface to be cleaned.

[0015] Preferably the pro-oxidizing agent is selected from the group consisting of bleach catalyst, photobleach and a mixture thereof. A bleach catalyst is the preferred pro-oxidizing agent.

[0016] The pro-oxidizing agent can be immobilized on the substrate but any means, physical or chemical means. It is preferably immobilised on the substrate by means of chemical bond. The substrate can be selected

from the group consisting of fabrics, non-woven materials, plastics and inorganic particles. In particular, substrates in the form of a tri-dimensional hollow body that favours the flow of wash liquor through it are preferred herein. Plastic substrates in the form of a tri-dimensional hollow body are preferred for use herein. Preferably, the pro-oxidizing agent is immobilized on the inside of the hollow body, this further prevents the interaction of the oxidizing agent with the surface to be cleaned. Also preferred are inorganic particles having a large surface area such as zeolites.

[0017] According to a second aspect of the invention, there is provided a cleaning kit comprising a cleaning composition and the cleaning agent of the invention. According to a third aspect of the invention, there is provided a method for cleaning a surface comprising contacting the surface with a wash liquor, the wash liquor comprising a cleaning composition comprising a pro-oxidizing agent and the cleaning agent of the invention. The method of the invention is applicable to any type of surfaces, including hard surfaces and soft surfaces. The method of the invention is especially suitable for the cleaning of fabrics, in particular for the cleaning of fabrics of mixed colours. According to a fourth aspect of the invention, there is provided the use of the cleaning agent of the invention for cleaning a surface comprising immersing the surface in a wash liquor to reduce dye transfer in the wash liquor. A preferred use of the cleaning agent of the invention is a laundry process. In particular when a load comprising white fabrics are subjected to a laundry process, more in particular when the load comprises fabrics of more than one colour, or fabrics of different colours. The cleaning agent contributes to better cleaning and avoids greying of white fabrics and protects the colour of coloured fabrics.

[0018] The elements of the cleaning agent of the invention described in connection with the first aspect of the invention apply *mutatis mutandis* to the other aspects of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The present invention envisages a cleaning agent comprising a supporting substrate with a pro-oxidizing agent immobilized on the substrate, a cleaning kit comprising the cleaning agent, a method of cleaning using a cleaning composition and the cleaning agent and the use of the cleaning agent in a cleaning process for cleaning surfaces by immersing the surfaces in a wash liquor, preferably the use of the cleaning agent of the invention in the laundry of fabrics, in particular when the laundry load comprises white fabrics, more in particular when the load further comprises other colours on the fabrics, either in the same piece of fabric or in different pieces of fabric. The cleaning agent of the invention prevents dye transfer, thereby keeping the white fabrics whiter than if there were cleaned in the absence of the cleaning agent. The cleaning agent can also contribute to re-

duction and/or prevention of soil re-deposition and mal-odour. It might additionally prevent bacterial growth. All this would be translated in better cleaning and care for the cleaned surface.

[0020] As used herein, articles, for example, "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

Immobilisation

[0021] Immobilisation of the pro-oxidizing agent on the substrate can be achieved by any means. Immobilisation can be achieved via chemical means including covalent, ionic, hydrogen, polar bonds; or non-chemical means such as absorption and entrapment.

[0022] Immobilisation of the pro-oxidizing agent on the substrate may be achieved by direct treatment of the substrate with the pro-oxidizing agent. Alternatively the substrate can be initially treated with at least one activating agent in order to modify the chemical properties at the surfaces of the substrate in order that the modified substrate may subsequently be treated with at least one pro-oxidizing agent in order to facilitate immobilisation of the agent.

[0023] The activated substrate can then be further treated with a linking agent which facilitates attachment of the pro-oxidizing agent by means of a covalent bond.

[0024] Activation of the surface may also be achieved by the use of physical agents, such as heat or electromagnetic radiation, e.g. ultra-violet radiation or microwave radiation prior to reaction with a linking agent.

[0025] Suitable linking agents may include glutaraldehyde, or may be selected from, for example, typical crosslinking agents such as dimethyl adipimide, dimethyl suberimide, pentafluorophenyl ester, hydroxymethyl phosphine, imidoesters and N-hydroxysuccinimide esters.

[0026] Other suitable linking agents include, for example:

N-Hydroxysuccinimide (NHS) and N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC);

Acylimidazoles (e.g. Carbonyl Diimidazole (CDI) and N,N'-carbonylbis(3-methylimidazolium) triflate (CBMIT);

Phosphonium salts (e.g. benzotriazol-1-yl-oxytris-(dimethylamino)-phosphonium hexafluorophosphate (BOP);

Uronium salts (e.g. 0-((ethoxycarbonyl)cyanomethylene amino)-N,N,N',N'-tetramethyl-uronium tetrafluoroborate (TOTU); and

Mukaiyama's reagent (2-chloro-1-methylpyridinium iodide).

[0027] Alternatively, embodiments utilising activating agents may include the treatment of polymeric particles incorporating polar groups, including for example Nylon 6,6 or poly(ethylene terephthalate), initially with a polar group-containing material - such as, for example, gelatin, starch, cellulose, chitosan, chitan, carboxymethylcellulose, poly(vinylimidazoles), poly(acrylic acid), poly(methacrylic acid), poly(lactic acid), poly(maleic acid), poly(glycolic acid), poly(acrylonitrile), poly(vinylpyrrolidone), poly(dimethylaminoethyl methacrylate), poly(ethylene imine), poly(allylamine), poly(allylamine) hydrochloride, poly(ethylene glycol), poly(propylene glycol), poly(acrylamide), polyvinyl alcohol, polyvinyl acetate, polyvinyl formamide, poly(vinylamine), amine-containing molecules (including biomolecules such as proteins), carboxylic acids such as maleic acid and itaconic acid, and carboxylic acid-containing polymers, as well as derivatives and copolymers of all the foregoing - wherein ionic interactions are formed between the polymer particles and a layer of the polar group-containing material, and subsequently with the mediator wherein further ionic interactions are established between the layer of polar group-containing material and the layer of mediator.

[0028] Optionally, embodiments utilising at least one activating agent may comprise multiple treatments with the at least one activating agent and/or multiple subsequent treatments or reactions with the at least one mediator. Said embodiments, which rely on ionic interactions, do not require the use of a linker.

Substrates

[0029] Porous substrates are preferred for use herein.

[0030] A variety of materials that can be used as substrate for immobilization of the pro-oxidizing agent include cellulose, polystyrene, alkylamine glass beads through covalent coupling, cation exchange resin, photographic gelatin, plastic supports, agar gel, acrylonitrile/acrylamide membranes, poly(2-hydroxyethyl methacrylate) microspheres, poly(methyl methacrylate-acrylic acid) microspheres, polyacrylamide gel, glass beads, sodium alginate beads, superporous celbeads, polyester surface free and affixed alkyl and arylamine glass beads, alginate gel beads, cyclic carbonate bearing hybrid materials, cellulose fibre materials and cellulose-coated magnetite (CCM) nanoparticles.

[0031] Other materials suitable as substrate for immobilization of the pro-oxidizing agent include polyurethane foam, tri(4-formyl phenoxy) cyanurate, polyacrylamide-acrylic gel, acrylamide grafted acrylonitrile copolymer (PAN), chemically modified pumic particles, nanofibrous poly(vinyl alcohol) PVA, passive epoxy acrylate films modified by magnetic filtered plasma stream, silicate clay mineral, modified polyvinyl alcohol coated chitosan beads, loofa sponge, liposomes, brick dust via glutaraldehyde and silicon wafers of amino terminated surface.

[0032] Other suitable substrates for immobilization of the pro-oxidizing agents are particles, preferably select-

ed from inorganic particles, however, some organic particles can also be used. A suitable supporting substrate herein is selected from the group consisting of a silica particle, a zeolite, an aluminum oxide, an organic polymer having either a carboxyl or an amino group, and a mixture thereof. These organic polymers are, preferably, selected from the group consisting of a polyacrylic acid, a polymaleic acid, a poly peptide, chitosan and a mixture thereof. Preferably, the supporting substrate has a median particle size (as measured as the diameter of the particle) of from about 1 nanometer to about 10 micrometers, more preferably, from about 1 nanometer to about 1 micrometer and even more preferably, the supporting substrate is selected from a silica having a particle size of from about 5 nanometers to about 1 micrometer. The median particle size is measured by SEM (Scanning Electron Microscope). A highly preferred silica is SiO_x (MN1P, which is provided by Zhou Shan Ming Ri Nano Material Company (Zhejiang Province, China). Other preferred supporting substrates are described in PCT patent publication No. WO 90/04181 which is assigned to Nilsson, published on Apr. 19, 1990.

[0033] When an inorganic particle is selected as the substrate, it must be modified by a linking molecule before being activated. Any compounds which can provide the substrate with either carboxyl and/or amino groups can be used as a linking molecule herein. A suitable linking molecule is a silane linking molecule, preferably the structure of the silane molecule is $R_1-(CH_2)_{n1}-Si(O(CH_2)_{n2}CH_3)_3$, wherein R_1 is selected from -COOH or -NH₂; $n1$ is from about 1 to about 16, preferably from about 3 to about 8; $n2$ is from about 0 to about 10, preferably from about 0 to about 4. A preferred linking molecule for use herein is 3-aminopropyltriethoxysilane (APS). The weight ratio of the linking molecule to the substrate is preferably from about 0.001:1 to about 10:1, and more preferably from about 0.1:1 to about 5:1. Other linking molecules useful herein are described in U.S. Pat. No. 6,004,786 to Yamashita, et al., issued Dec. 21, 1999.

[0034] The linking molecule modifies the substrate to connect the substrate and the pro-oxidizing agent. In some instances, it is preferred to add a functional group introducer together with the linking molecule to the substrate. A preferred functional group introducer is a carboxylic group introducer or an amino group introducer, more preferably a carboxylic group introducer such as a carboxylic acid anhydride. It is conceivable that the linking molecule itself may sometimes work as the functional group introducer. For example, when selecting carboxylic silane as the linking molecule, an additional functional group introducer is not necessary.

[0035] The modification of the substrate by the linking molecule or functional group introducer can be accomplished by mixing the substrate with the linking molecule with functional group introducer into a common organic solvent such as toluene, and re-fluxing for from about 4 hours to about 7 hours, preferably about 6 hours. The

refluxed mixture is extracted by filtration, washed with ethanol and dried at about 30° C to about 70° C, preferably from about 45° C to about 55° C, for 20 minutes. The mixture is preferably kept in the vacuum dry container until being applied to next step.

[0036] Preferred carboxylic acid anhydrides are selected from the group consisting of a succinic anhydride, a maleic anhydrides, or a mixture thereof. In order to link a carboxyl group onto the substrate, the substrate is usually dissolved in organic solvents, preferably, a mixture of pyridine and anhydrous diethylether, and is mixed with a carboxylic acid anhydride at 25° C, for 17 hours. After mixing, the mixture is extracted by filtration and washed with organic solvents, preferably, anhydrous diethylether is used.

[0037] After the substrate has been modified, an activating molecule activates the substrate to connect or entrap a mediator onto the substrate. The activation can be performed by adding an activating molecule to the activated substrate and stirring together for from about 30 minutes to about 60 minutes, at 4° C. A preferable activating molecule for use herein is a water soluble carbon diimide. More preferably, the water soluble carbon diimide is selected from the group consisting of ethyl-3-(3-dimethylaminopropyl)-carbon diimide hydrochloride (EDC), a succinimide, and a mixture thereof. The weight ratio of the activating molecule to the substrate is preferably from about 0.01:1 to about 1:1, more preferably, from about 0.05:1 to about 0.5:1. After the substrate is activated, the supporting substrate is isolated by centrifuging the sample and decanting the supernatant.

[0038] A suitable way to immobilize the pro-oxidizing agent can be coating the substrate with polyphenol. The coating can be formed on diverse material surfaces under mild aqueous conditions. Examples of polyphenols include tannic acid, pyrogallol, pyrogallol 2-aminoethane, dopamine, etc, tannic acid is preferred for use herein.

Substrate configuration

[0039] The substrate can have any configuration but it would preferably have a configuration that promotes the contact between the pro-oxidizing agent and the wash liquor and avoid the contact with the surface to be cleaned. Preferably, the substrate will be a tri-dimensional hollow body and the pro-oxidizing agent would be placed on the inside of the hollow body. Other preferred substrates for use herein are insoluble particles in which the mediator has been immobilized on the internal surface of the particle. Zeolites are preferred for use herein. Non-woven substrates are also preferred for use herein.

Pro-oxidizing agent

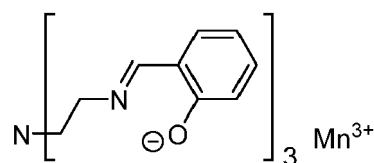
[0040] Preferred pro-oxidizing agents are selected from bleach catalyst, photobleach and a mixture thereof. Bleach catalyst being specially preferred for use herein.

[0041] One type of bleach catalyst is a metal-contain-

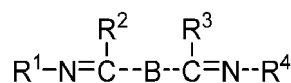
ing bleach catalyst comprising a transition metal cation of defined bleach catalytic activity, such as: copper, iron, nickel, chromium, titanium, ruthenium, tungsten, molybdenum, or manganese cations. Suitable bleach catalysts include the manganese-based complexes. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ (often referred to simply as MnTACN), $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, and mixtures thereof.

[0042] Still another type of bleach catalyst is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a noncarboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

[0043] Tinocat® TRS KB2 (BASF) is another bleach catalyst suitable for use herein. Tinocat® TRS KB2 is composed of a manganese ion complexed to three Schiff base ligands as shown in one possible rendering below:



[0044] Other suitable bleach catalysts comprise a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R^1 , R^2 , R^3 , and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $\text{R}^1\text{-N}=\text{C}(\text{R}^2)$ and $\text{R}^3\text{-C}=\text{N-R}^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR^5R^6 , NR^7 and $\text{C}(\text{O})$, wherein R^5 , R^6 , and R^7 can be independently selected from H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, -bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include $\text{Co}(2,2'\text{-bispyridylamine})\text{Cl}_2$,

Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyrildylamine-cobalt(II) perchlorate, $\text{Co}(2,2\text{-bispyridylamine})_2\text{O}_2\text{ClO}_4$, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

[0045] Other examples include Mn gluconate, $\text{Mn}(\text{CF}_3\text{SO}_3)_2$, $\text{Co}(\text{NH}_3)_5\text{Cl}$, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

[0046] The bleach catalysts may also be prepared by combining a water-soluble ligand with a water-soluble manganese salt in aqueous media and concentrating the resulting mixture by evaporation. Any convenient water-soluble salt of manganese can be used herein. Manganese (II), (III), (IV) and/or (V) is readily available on a commercial scale.

[0047] Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. Pat. No. 4,728,455 (manganese/multidentate ligand catalyst), U.S. Pat. No. 4,711,748 and European patent application publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. Pat. No. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. Pat. No. 4,626,373 (manganese/ligand catalyst), U.S. Pat. No. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. Pat. No. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. Pat. No. 4,728,455 (manganese gluconate catalysts).

[0048] Another example of a metal catalyst suitable for the present invention is described in U.S. Pat. No. 6,528,469. U.S. Pat. No. 6,528,469 describes certain other manganese compounds that are also excellent bleach catalysts for peroxy compounds and, relative to known bleach catalysts, provide enhanced bleach effects at low wash temperatures (e.g. at 15 to 40° C.) and/or using shorter washing times. The peroxy compounds may be produced by known methods, e.g. by the methods analogous to those disclosed in U.S. Pat. No. 4,655,785 relating to similar copper compounds.

[0049] Other catalysts, such as Fe, Ni, Cr, Cu, etc. could be employed. In addition, U.S. Pat. No. 6,093,343 describes various cobalt catalysts that could be used in the present invention.

[0050] Photobleaches are suitable pro-oxidizing agents for use herein, for example sulfonated zinc phthalocyanine sulfonated aluminium phthalocyanines, xanthene dyes, thioxanthenes, and mixtures thereof. The photo bleaches are activated by light.

[0051] A cleaning agent comprising a bleach catalyst is preferably used in combination with a cleaning composition comprising a peroxygen source. The peroxygen source is generally present in the composition in an

amount of from about 0.01 to about 5%, more preferably from about 0.5 to about 2% by weight of the composition.

[0052] The amounts of peroxygen source and bleach catalyst may be selected such that the molar ratio of available oxygen (from the peroxide source) to bleach catalyst is from 1:1 to 35:1, or even 2:1 to 10:1.

[0053] Sources of peroxygen include inorganic perhydrate salts, including alkali metal salts such as sodium salts of perborate (usually mono- or tetra-hydrate), percarbonate, persulphate, perphosphate, persilicate salts and mixtures thereof.

Cleaning composition

[0054] The cleaning composition of the present invention is suitable for the cleaning of any type of surfaces when the cleaning involves the immersion of the surface in a wash liquor. The cleaning composition is suitable for use in hard surfaces and soft surfaces. It is particularly useful for use in laundry.

[0055] The cleaning composition of the present invention would comprise the customary ingredients for the cleaning process, such as surfactants and builders. The cleaning composition would preferably comprise components which can be combined under the term cleaning aids and which comprise different active ingredient groups such as foam regulators and enzymes. The composition can comprise a low level of a source of peroxygen, in particular when the cleaning agent comprises a bleach catalyst. The composition, especially when the composition is for use in laundry, can comprise cleaning auxiliaries including substances which are intended to prevent dyed textiles from causing a change in colour impression after the wash (dye transfer inhibitors). This colour change of washed, i.e. clean, textiles can be due to the fact that dye components are removed from the fabric ("fading") by the washing process, and on the other hand, dyestuffs released from differently coloured fabrics can be deposited on the textile ("discolouring"). Other cleaning auxiliaries include electrolytes, pH regulators and in the case of compositions for use in laundry, optical brightener, dye transfer inhibitors, fragrances, etc.

[0056] The composition preferably contains a surfactant or a plurality of surfactants, particularly anionic surfactants, nonionic surfactants and mixtures thereof, but it can also comprise cationic, zwitterionic and amphoteric surfactants.

[0057] Preferably the composition of the invention is a laundry cleaning composition. A laundry cleaning composition is any composition suitable to be used in a fabric laundering operation. The laundry cleaning composition may be in the form of a powder, a liquid or a mixture thereof.

[0058] The cleaning composition may comprise between 10% and 60%, preferably between 15% and 55%, more preferably between 20% and 50%, most preferably between 25% and 45% by weight of the composition of a surfactant system. Preferably, the surfactant system

comprises a non-soap surfactant. Preferably, the surfactant system comprises an anionic surfactant and optionally a non-ionic surfactant. More preferably, the weight ratio of anionic surfactant to non-ionic surfactant is from 1:2 to 20:1, preferably from 1:1 to 15:1, more preferably from 1.5:1 to 10:1, most preferably from 5:1 to 10:1.

[0059] The non-soap anionic surfactant is preferably selected from sulphate or sulphonate anionic surfactants or mixtures thereof, preferably linear alkylbenzene sulphonate, alkyl sulphate, alkoxylated alkyl sulphate or a mixture thereof. Preferably, the alkoxylated alkyl sulphate is an ethoxylated alkyl sulphate preferably with an average degree of ethoxylation of between 0.5 and 4, preferably between 1 and 4, more preferably between 2 and 4, most preferably about 3.

[0060] Preferably, the weight ratio of linear alkylbenzene sulphonate to alkoxylated alkyl sulphate is between 15:1 and 1:3, preferably 10:1 and 1:2, more preferably 5:1 and 1:1, even more preferably 3:1 and 1:1, most preferably 2:1 and 1:1.

[0061] The non-ionic surfactant may be selected from a fatty alcohol alkoxylate, an oxosynthesised fatty alcohol alkoxylate, Guerbet alcohol alkoxylates, alkyl phenol alcohol alkoxylates, alkyl polyglucoside or a mixture thereof. Preferably, the non-ionic surfactant comprises a fatty alcohol ethoxylate non-ionic surfactant. Even more preferably the nonionic surfactant consists of a fatty alcohol ethoxylate surfactant.

[0062] Suitable fatty alcohol ethoxylate nonionic surfactants include the condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, guerbet, primary or secondary, and generally contains from 8 to 22 carbon atoms. The starting alcohol can be naturally derived, e.g. starting from natural oils, or synthetically derived, e.g. alcohols obtained from for example oxo-, modified oxo- or Fischer-Tropsch processes. Examples of oxo-process derived fatty alcohols include the Lial and Isalchem 5 fatty alcohols ex Sasol company and Lutensol fatty alcohols ex BASF company.

[0063] Examples of modified-oxo process derived fatty alcohols include the Neodol fatty alcohols ex Shell company. Fischer-Tropsch derived fatty alcohols include Salfol fatty alcohols ex Sasol company. The alkoxylate chain of fatty alcohol ethoxylates is made up solely of ethoxylate groups. Preferably, the fatty alcohol ethoxylate non-ionic surfactant comprises on average 10 between 8 and 18, more preferably between 10 and 16 even more preferably between 12 and 15 carbon atoms in the alcohol carbon chain, and on average between 5 and 12, preferably between 6 and 10, more preferably between 7 and 8 ethoxy units in the ethoxylation chain. Preferably, the weight ratio of linear alkylbenzene sulphonate to non-ionic surfactant is between 2:1 to 20:1 preferably 2:1 and 10:1; more preferably 5:1 and 10:1.

[0064] Preferably, the weight ratio of alkoxylated alkyl sulphate to non-ionic surfactant is between 2:1 and 20:1

preferably between 2:1 and 10:1 more preferably between 2:1 and 5:1. Preferably, the weight ratio of linear alkylbenzene sulphonate to fatty alcohol ethoxylate non-ionic surfactant is between 2:1 to 20:1 preferably 2:1 and 10:1; more preferably 5:1 and 10:1. Preferably, the weight ratio of alkoxylated alkyl sulphate to fatty alcohol ethoxylate nonionic surfactant is between 2:1 and 20:1 preferably between 2:1 and 10:1 more preferably between 2:1 and 5:1.

[0065] The cleaning composition may comprise polymers, preferably selected from alkoxylated, preferably ethoxylated polyethyleneimine, alkoxylated polyalkyl phenol, a polyester terephthalate, hydroxyethylcellulose, preferably quaternized hydroxyethylcellulose, a carboxymethylcellulose or a mixture thereof.

[0066] The cleaning composition may comprise an adjunct material, wherein the adjunct material is preferably selected from cleaning polymers, soil suspension polymers, surface modifying polymers, builders, chelants, dispersants, enzymes, enzyme stabilizers, catalytic materials, bleach, bleach activators, polymeric dispersing agents, anti-redeposition agents, suds suppressors, aesthetic dyes, opacifiers, perfumes, perfume delivery systems, structurants, hydrotropes, rheology modifiers, processing aids, pigments and mixtures thereof. Having an adjunct material in the composition provides good overall cleaning, soil suspension and whiteness or colour brightness profile of the fabric to be treated.

[0067] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

Claims

1. A cleaning agent comprising a supporting substrate with a pro-oxidizing agent immobilized thereof.
2. A cleaning agent according to claim 1 wherein the pro-oxidizing agent is selected from the group consisting of bleach catalyst, photobleach and a mixture thereof.
3. A cleaning agent according to any of claims 1 or 2 wherein the pro-oxidizing agent is immobilised on the substrate by means of chemical bond.
4. A cleaning agent according to any preceding claims wherein the substrate is selected from the group consisting of fabrics, non-woven materials, plastics and inorganic particles.
5. A cleaning agent according to any of the preceding claims wherein the substrate is a tri-dimensional hol-

low body wherein the mediator is immobilised on the surface of the hollow body.

6. A cleaning agent according to any of claims 1 to 4 wherein the substrate is a non-woven substrate. 5
7. A cleaning kit comprising:
 - i) a cleaning composition; and
 - ii) a cleaning agent according to any of the preceding claims. 10
8. A cleaning kit according to the preceding claim wherein the cleaning composition comprises from 0.01% to 5% by weight of the composition of a peroxygen source and the cleaning agent comprises a bleach catalyst. 15
9. A cleaning kit according to the preceding claim wherein the peroxygen source is selected from the group consisting of hydrogen peroxide, a hydrogen peroxide precursor, a hydrogen peroxide generating enzyme system, or a peroxy-carboxylic acid or a salt thereof and a mixture thereof. 20
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10. A cleaning kit according to any of claims 7 to 9 wherein the cleaning composition comprises a surfactant system comprising an anionic surfactant and preferably a non-ionic surfactant. 30
11. A method for cleaning a surface comprising immersing the surface into a wash liquor, the wash liquor comprising a cleaning kit according to any of claims 7 to 10. 35
12. A method for doing laundry in a washing machine according to the preceding claim.
13. Use of a cleaning agent according to any of claims 1 to 6 for the cleaning of a surface comprising immersing the surface into a wash liquor to reduce dye transfer in the wash liquor. 40
14. Use according to the preceding claim wherein the cleaning process is the laundry of fabrics. 45
15. Use according to the preceding claim wherein the fabrics comprise mixed colour fabrics. 50

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EUROPEAN SEARCH REPORT

Application Number
EP 17 18 6891

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2004/266641 A1 (GENTSCHEV PAVEL [DE] ET AL) 30 December 2004 (2004-12-30) * paragraphs [0006], [0008], [0077]; claims 1, 9, 16-18, 24; examples 6-10; tables 1-4 *	1-4,7-15	INV. C11D17/04 C11D11/00 C11D3/39 C11D3/00
X	WO 2008/132456 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; BALDAN SILVI) 6 November 2008 (2008-11-06) * page 2, paragraphs 3, 4; claims 1, 3, 6-13, 16; examples 1, 5, 8, 10, 11, 17, 19 *	1,2,4-15	
X	EP 1 889 900 A1 (BOLTON MANITOBA SPA [IT]) 20 February 2008 (2008-02-20) * paragraphs [0005], [0015], [0029], [0055]; claims 1-3, 9, 10-12, 16-21, 26-30 *	1,2,4-15	
X	WO 2010/010334 A1 (RECKITT BENCKISER NV [NL]; ZAMUNER DORA [IT]; RECKITT BENCKISER UK LTD) 28 January 2010 (2010-01-28) * page 12, lines 23-28; claims 1.9, 12, 13; examples 1, 3, 6 * * page 7, line 29 - page 8, line 6 * * page 10, lines 18-26 *	1,2,4-15	TECHNICAL FIELDS SEARCHED (IPC) C11D
X	WO 2004/046301 A1 (PROCTER & GAMBLE [US]) 3 June 2004 (2004-06-03) * claim 1; examples *	1,4,6	
X	WO 2010/139689 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; ZAMUNER DORA) 9 December 2010 (2010-12-09) * claims 1-12 *	1,2,4-7, 9,11,12	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22 January 2018	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

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

EP 17 18 6891

5

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

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004266641 A1	30-12-2004	AT 352606 T	15-02-2007
		AU 2002360982 A1	09-07-2003
		DE 10163331 A1	10-07-2003
		EP 1456337 A1	15-09-2004
		ES 2280610 T3	16-09-2007
		US 2004266641 A1	30-12-2004
		WO 03054128 A1	03-07-2003

WO 2008132456 A1	06-11-2008	AU 2008243977 A1	06-11-2008
		BR PI0810557 A2	19-07-2016
		CA 2685102 A1	06-11-2008
		EP 2148919 A1	03-02-2010
		US 2010298195 A1	25-11-2010
		WO 2008132456 A1	06-11-2008
		ZA 200907382 B	29-12-2010

EP 1889900 A1	20-02-2008	AT 553174 T	15-04-2012
		EP 1889900 A1	20-02-2008
		ES 2385604 T3	27-07-2012

WO 2010010334 A1	28-01-2010	AU 2009275368 A1	28-01-2010
		BR PI0916454 A2	16-08-2016
		CA 2730523 A1	28-01-2010
		CN 102099457 A	15-06-2011
		EP 2318503 A1	11-05-2011
		ES 2424791 T3	08-10-2013
		RU 2011105658 A	27-08-2012
		US 2011174660 A1	21-07-2011
		WO 2010010334 A1	28-01-2010
		ZA 201100284 B	28-09-2011

WO 2004046301 A1	03-06-2004	AT 340248 T	15-10-2006
		AU 2003295550 A1	15-06-2004
		CA 2505671 A1	03-06-2004
		DE 60308546 T2	13-09-2007
		EP 1560911 A1	10-08-2005
		ES 2273065 T3	01-05-2007
		JP 2006505683 A	16-02-2006
		MX PA05005149 A	22-07-2005
		US 2005107282 A1	19-05-2005
		WO 2004046301 A1	03-06-2004

WO 2010139689 A1	09-12-2010	NONE	

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- WO 9004181 A [0032]
- US 6004786 A, Yamashita [0033]
- EP 408131 A [0047]
- EP 384503 A [0047]
- EP 306089 A [0047]
- US 4728455 A [0047]
- US 4711748 A [0047]
- EP 224952 A [0047]
- US 4601845 A [0047]
- US 4626373 A [0047]
- US 4119557 A [0047]
- DE 2054019 [0047]
- CA 866191 [0047]
- US 4430243 A [0047]
- US 6528469 B [0048]
- US 4655785 A [0048]
- US 6093343 A [0049]