(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 019 585 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
04.09.2019 Bulletin 2019/36

(21) Application number: **14739525.5**

(22) Date of filing: **08.07.2014**

(51) Int Cl.:
C11D 3/37 $^{(2006.01)}$
C11D 3/39 $^{(2006.01)}$
C11D 17/00 $^{(2006.01)}$
C11D 17/06 $^{(2006.01)}$
C11D 3/48 $^{(2006.01)}$
C11D 3/386 $^{(2006.01)}$
C11D 11/00 $^{(2006.01)}$
C11D 3/14 $^{(2006.01)}$
C11D 3/00 $^{(2006.01)}$

(86) International application number:
PCT/GB2014/052079

(87) International publication number:
WO 2015/004444 (15.01.2015 Gazette 2015/02)

(54) **NEW CLEANING FORMULATION AND METHOD**

NEUE REINIGUNGSZUSAMMENSETZUNG UND VERFAHREN

NOUVELLE FORMULATION DE NETTOYAGE ET PROCÉDÉ CORRESPONDANT

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **08.07.2013 GB 201312189**

(43) Date of publication of application:
18.05.2016 Bulletin 2016/20

(73) Proprietor: **Xeros Limited**
Rotherham, South Yorkshire S60 5BL (GB)

(72) Inventors:
- **WADDON, Alan John**
  Sheffield South
  Yorkshire S8 0UT (GB)
- **BIRD, Robert Andrew**
  Sheffield South
  Yorkshire S11 9NG (GB)
- **JENKINS, Stephen Derek**
  Middlesborough
  Cleveland TS9 5AS (GB)

(74) Representative: **Carpmaels & Ransford LLP**
One Southampton Row
London WC1B 5HA (GB)

(56) References cited:
WO-A1-2012/140442
WO-A2-2012/056252
US-A1- 2004 242 133
WO-A1-2014/006425
US-A- 5 324 649
US-A1- 2012 225 025

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] This invention is concerned with the treatment of substrates using a formulation comprising solid cleaning particles and dosing particles. Specifically, the invention discloses a method which involves the dosing of additives during the treatment of the substrate using dosing particles mixed in with the solid cleaning particles, and a formulation for use in said method. The dosing particles can comprise at least one releasable material comprising at least one post-cleaning agent and optionally at least one cleaning agent and optionallyat least one other treatment additive. The method is especially suited to providing substrates, such as laundry, which are especially clean and hygienic.

Background to the Invention

[0002] Aqueous cleaning processes are a mainstay of both domestic and industrial textile fabric washing. This washing generally comprises agitating fabrics in an aqueous solution of detergent, often at elevated temperatures. Supplemental additives, such as fabric conditioners, dye transfer inhibitors, anti-redeposition agents, perfumes or products for enhancing hygiene are customarily added as separate dosing operations, often with the detergent.

[0003] On the assumption that the desired degree of cleaning is achieved, the efficacy of textile fabric washing processes is usually characterised by the levels of consumption of energy, water and detergent associated with the processes. In general, the lower the requirements with regard to these three parameters, the more efficient the washing process is deemed. The downstream effect of reduced water and detergent consumption is also significant, as this minimises the need for disposal of aqueous effluent, which is both extremely costly and detrimental to the environment. Similarly, the lower the quantity of any supplemental additive used - whilst providing the desired effect - the more efficient is the operation.

[0004] Such washing processes, whether involving domestic washing machines or their industrial equivalents (usually referred to as washer extractors), involve aqueous submersion of fabrics followed by soil removal, aqueous soil suspension, and water rinsing. Higher levels of energy (or temperature), water and detergent usually result in better cleaning. One key issue, however, concerns water consumption, as this sets the energy requirements (in order to heat the wash water), and the level of detergent dosage (to achieve the desired detergent concentration). In addition, the water usage level strongly influences the mechanical action of the process on the fabric, which is another significant performance parameter; this is the agitation of the cloth surface during washing, which plays a key role in releasing embedded soil. In aqueous laundry processes, such mechanical action is provided by the water usage level, in combination with the drum design for any particular washing machine. In general, it is found that the higher the water level in the drum, the better the mechanical action. Hence, there is a dichotomy created by the desire to improve overall process efficiency (i.e. the reduction of energy, water and detergent consumption), and the need for efficient mechanical action in the wash.

[0005] WO-A-2007/128962 discloses a method and formulation for cleaning a soiled substrate, which greatly reduces the usage of water, energy and detergent while still providing the mechanical action necessary for cleaning. The method comprises the treatment of the moistened substrate with a formulation comprising a multiplicity of polymeric particles, wherein the formulation is free of organic solvents. Preferably, the substrate is wetted so as to achieve a substrate to water ratio of between 1:0.1 to 1:5 w/w, and optionally, the formulation additionally comprises at least one cleaning material, which typically comprises a surfactant, which most preferably has detergent properties. In preferred embodiments, the substrate comprises a textile fibre and the polymeric particles may, for example, comprise polyamide, polyester, polyalkene, polyurethane or a copolymer thereof, but are most preferably in the form of nylon beads. WO-A-2012/056252 describes a method for the most efficient use and removal of such polymeric particles in a cleaning process, and WO-A-2012/095677 extends this method to the use of non-polymeric cleaning particles, and mixtures of non-polymeric and polymeric cleaning particles.

[0006] The apparatus required to separate polymeric or non-polymeric cleaning particles from the cleaned substrate at the conclusion of the cleaning operation is addressed in WO-A-2010/094959. This provides a novel design of cleaning apparatus requiring the use of two internal drums capable of independent rotation, and which finds application in both industrial and domestic cleaning processes.

[0007] In WO-A-2011/064581, there is provided a further apparatus which facilitates efficient separation of cleaning particles from the cleaned substrate at the conclusion of the cleaning operation, and which comprises a perforated drum and a removable outer drum skin which is adapted to prevent the ingress or egress of fluids and solid particulate matter from the interior of the drum, the cleaning method requiring attachment of the outer skin to the drum during a wash cycle, after which the skin is removed prior to operating a separation cycle to remove the cleaning particles, following which the cleaned substrate is removed from the drum.

[0008] In a further development of the apparatus, there is disclosed in WO-A-2011/098815 a process and apparatus which provides for continuous circulation of the cleaning particles during the cleaning process, and thereby dispenses with the requirement for the provision of an outer skin.

[0009] The improvements to textile fabric cleaning disclosed in WO-A-2007/128962, WO-A-2012/056252, WO-A-2012/095677, WO-A-2010/094959, WO-A-2011/064581, and WO-A-2011/098815 lead to reductions in the levels of water, energy and detergent used in the cleaning operation. WO-A-2011/128680 goes on to describe a method for the dosing of said detergent into such particle cleaning systems, whereby the detergent is split into its constituent chemical parts, these being added at different times during the cleaning operation. Specifically, it is required that the cleaning parts of the formulation are added before or during the main wash cycle in order to provide the degree of stain removal required, whilst the remaining, more expensive - and hence more value adding - parts of the formulation are added as a post-treatment, usually during rinsing, following removal of the polymeric particles from the wash process. Typically, the cleaning components comprise surfactants, enzymes and oxidising agents or bleaches, whilst the post-treatment components include, for example, anti-redeposition agents, perfumes and optical brighteners. Addition of the cleaning and post-treatment components in this way allows further reduction in levels of use, and hence significant cost savings in comparison to conventional all-in-one detergent formulations.

[0010] Whilst the method of WO-A-2011/128680 allows the use of cleaning and post-treatment components in a detergent formulation at different times during the cleaning operation, it still requires transport of each component onto the fabric surface. This is typically achieved by dilution in a quantity of water, then spraying of this diluted solution onto the washload. Although the dilution in this case is much lower than in conventional wash processes, this is still essentially an inefficient means to dose the various detergent components. Furthermore, discrete time periods are required within the wash cycle for such dosing, resulting in an overall cycle time penalty.

[0011] A cartridge dosing system as described in WO-A-2011/128676 may also be used for this purpose. In this system, each detergent component is typically concentrated such that a number of dosages are contained within the cartridge, these being used up gradually over a number of wash cycles. Hence, there is a convenience benefit for the user in not having to individually dose each wash. The cartridge itself and the docking system for insertion into the cleaning apparatus can, however, be complex in construction, and hence costly.

[0012] In one aspect of the present invention, therefore, the inventors provide a method which addresses the difficulties of dilution and transport of detergent components as hereinbefore described. Thus, there are provided dosing particles which release additives over a wash cycle for use in conjunction with the solid cleaning particles. Release of the additives occurs through dissolution of the outer layer of the dosing particles, which are in the form of core-shell particles. The dosing particles can contain the detergent components preferred for effective cleaning and post treatment and, as they are intimately mixed with the solid cleaning particles, they are carried directly to the fabric surface, thereby delivering the detergent components to the washload in the most targeted way possible. Hence, there is neither a requirement for separate dilution in water and spraying in order to deliver the detergent components, nor for a complex cartridge dosing system.

[0013] The present invention also envisages the dosing of other beneficial additives via the dosing particles. Examples include the addition of antimicrobial agents in order to sterilise the fabric, or of boosted levels of optical brightening agents, anti-redeposition agents, fragrances or dye transfer inhibitors. In each case, the benefit of the dosing particle is its direct and targeted delivery of the specific additive to the fabric surface by a particularly elegant and effective means, i.e. in admixture with the solid cleaning particles.

[0014] The use of core-shell particles for the delivery of cleaning and post-treatment materials in substrate treatment processes is known from the prior art. Thus, WO-A-2011/150138 discloses encapsulated, solid, water soluble benefit agents and products comprising such encapsulates, as well as processes for making and using the encapsulates and products. In a preferred embodiment, a melamine formaldehyde and/or urea formaldehyde encapsulation process is described.

[0015] US-A-2004/242133 teaches an abrasive cleaning article comprising spread abrasive particles and microencapsulated particles of a perfumed substance contained in urea-formaldehyde walls bonded to a three-dimensional nonwoven fibre web by a resin adhesive and also refers to a process for the production process of the abrasive cleaning article.

[0016] US-A-2011/245136 is concerned with encapsulated, solid, water soluble benefit agents and products comprising such encapsulates, in addition to processes for making and using the encapsulates and products. The disclosed invention seeks, by employing a protective suspension agent, to overcome emulsification problems and to minimise negative interactions between the benefit agents and shell materials that occur during particle production and processing.

[0017] WO-A-2010/079466 relates to encapsulated benefit agents, compositions comprising such encapsulated benefit agents, and processes for making and using the compositions. Disadvantages associated with prior art encapsulated benefit agents are eliminated or minimised so as to provide, for example, enhanced perfume delivery.

[0018] GB-A-2432844 describes polymer particles which comprise a perfume, a polymer and a cationic deposition aid which are delivered to fabric during laundering and provide long lasting adherence of the perfume to the fabric. A method of depositing perfume onto a substrate via such a composition is also disclosed. The particle optionally has a core/shell morphology and is prepared using miniemulsion polymerisation. The polymer of the particle is preferably butyl methacrylate, and a shell layer of vinyl acetate is optionally present; the cationic deposition aid may be a cationically modified cellulose or guar gum.

[0019] In WO-A-98/42818, there is disclosed a laundry additive particle having multiple coatings, together with compositions comprising such particles. The particle comprises a central core comprising a porous carrier core material and a glassy encapsulating material intermixed with the carrier material. The encapsulating material is derived from at least partially water-soluble hydroxylic compounds and an external coating material is coated on the core particle to provide a substantially non-tacky surface. The external coating material is derived from at least partially wash soluble or dispersible compounds selected from waxes, water-soluble polymers, fatty compounds, carbohydrates, cellulose and cellulose derivatives, natural and synthetic gums, silicates, borates, phosphates, chitin and chitosan, and mixtures thereof. A laundry or cleaning agent such as a perfume is preferably supported on or contained in the porous carrier. US 2004/242133 A1 discloses an abrasive cleaning article, made of spread abrasive particles and microencapsulated particles of an aromatizing substance contained in urea-formaldehyde walls, through a three-dimensional non-woven web of fiber that are bonded to the web by a resin adhesive. The item, of any geometric shape, offers the user a sensation of cleanliness due to the constant presence of a "fresh" scent associated to the fiber; the scent remains during the whole life of the abrasive item since the microcapsules break partially during the normal use of the item. It also refers to the production process of such abrasive item. WO 2014/006425 A1 discloses a formulation and method for the treatment of a substrate, the method comprising the treatment of the substrate with the formulation, the formulation comprising a multiplicity of solid cleaning particles and a multiplicity of dosing particles, wherein the dosing particles comprise at least one host material and at least one releasable material, wherein the host material comprises at least one partially or completely water soluble polymeric material and the at least one releasable material comprises at least one cleaning or post-cleaning agent or other treatment additive for the treatment of the substrate. The method and formulation are advantageously applied to the cleaning of textile fabrics.

[0020] None of these prior art documents, however, teaches a formulation for treatment of a substrate which includes a multiplicity of solid cleaning particles and a multiplicity of core-shell dosing particles which comprise a host material and a releasable material, wherein the shell is formed of a host material comprising a partially or completely water soluble polymeric material and the core comprises a releasable material which is a cleaning or post-cleaning agent or other additive for the treatment of the substrate.

[0021] The present invention thereby addresses, at least in part, one or more of the following technical problems:

(1) Improved cleaning performance;

(2) Reduced dye transfer;

(3) Reduced redeposition of soil onto the substrate; and

(4) Improved substrate hygiene, especially in relation to bacteria on laundry items such as textiles and fabrics.

Summary of the Invention

[0022] The present invention derives from an appreciation on the part of the inventors that the above mentioned technical problems can be solved, at least in part, by the release of at least one post-cleaning agent, and optionally at least one cleaning agent and optionally at least one other treatment additive, from dosing particles intimately mixed with the solid cleaning particles.

[0023] Thus, according to a first aspect of the present invention, there is provided aformulation comprising a multiplicity of solid cleaning particles and a multiplicity of dosing particles, wherein said dosing particles comprise core-shell particles comprising at least one host material and at least one releasable material, wherein said host material comprises, as the shell of the dosing particles, at least one partially or completely water soluble polymeric material and said at least one releasable material comprises the core material of the dosing particles, comprising:

at least one post-cleaning agent; and

optionally at least one cleaning agent; and

optionally at least one other treatment additive;

for the treatment of a substrate,

wherein said solid cleaning particles are polymeric and/or non-polymeric cleaning particles,
wherein said polymeric solid cleaning particles have an average density in the range of 0.5-2.5 g/cm^3 and an average

volume in the range of 5-275 mm^3, and wherein said post-cleaning agent comprises at least one dye transfer inhibiting agent:

wherein said host material is selected from at least one of polyvinyl alcohol, copolymers of poly(vinyl alcohol) and poly(vinyl acetate), poly(ethyl vinyl alcohol), hydroxypropylmethylcellulose, cellulose, starch, hydroxypropylcellulose, hydroxyethylcellulose, carboxymethyl cellulose, poly(vinyl pyrrolidinone), poly(ethylene glycol) and gelatin, or salts thereof; and,

said dye transfer inhibiting agent is selected from chitosan, and crosslinked polyvinylpyrrolidone polymers; and

wherein said non-polymeric cleaning particles comprise glass, silica, stone, wood, metals or ceramic materials and wherein said non-polymeric solid cleaning particles have an average density in the range of 3.5-12.0 g/cm^3 and an average volume in the range of 5-275 mm^3.

[0024] Merely for the purposes of clarification, it is emphasised that the present invention and the claims cover the possibility that the dosing particles comprise two or more releasable materials selected in accordance with the first aspect of the present invention.

[0025] Said shell material provides, *inter alia,* mechanical integrity to the particles and facilitates efficient handling and delivery of the particles.

[0026] The solid cleaning particles comprise polymeric and/or non-polymeric cleaning particles.

[0027] Solid polymeric cleaning particles are typically substantially ellipsoidal, cylindrical or spherical in shape.

[0028] In certain embodiments, said formulation is used for the cleaning of soiled substrates and said at least one releasable material comprises at least one cleaning agent.

[0029] Most particularly, said at least one releasable material comprises at least one cleaning agent, most particularly at least one detergent, which typically comprises at least one surfactant. Said at least one releasable material additionally or solely comprises at least one post-cleaning agent as defined in the first aspect of the present invention.

[0030] Said cleaning agents are especially cleaning chemicals which are typically components of the detergent formulation used in a wash process. Cleaning agents are, therefore, typically surfactants, enzymes, oxidising agents or bleaches, whilst post-cleaning agents are transfer inhibition agents as defined in the first aspect of the present invention.

[0031] Said host material comprises a non-active material which serves to transport the releasable material to the washload surface in a controlled manner but plays no active part in the cleaning process. The materials employed for this purpose include, poly(vinyl alcohol) (PVOH), copolymers of poly(vinyl alcohol) and poly(vinyl acetate), poly(ethyl vinyl alcohol) (EVOH), hydroxypropylmethylcellulose (HPMC), cellulose, starch, hydroxypropylcellulose (HPC), hydroxyethylcellulose (HEC), carboxymethyl cellulose (CMC), poly(vinyl pyrrolidinone) (PVP), poly(ethylene glycol) (PEG) and gelatin, or salts thereof. Typical poly(vinyl alcohols) for use in the present invention have a degree of hydrolysis of from 50 to 99%, more typically from 70 to 98%, and even more typically from 80 to 97%. The percentage is typically expressed as a molar percentage. Poly(vinyl alcohol) having a degree of hydrolysis of 94% is typically suitable for the purposes of the invention. The degree of hydrolysis has an effect on the release rate of the releasable material. The typical degrees of hydrolysis correspond to the best release profile. Poly(ethylene glycol) (PEG) has also been found to be an especially suitable host material.

[0032] Said dosing particles are used and consumed in a single substrate treatment operation.

[0033] Said dosing particles may be obtained by means of any of the standard preparative methods for core-shell particles which are available and well known in the art, and which typically involve the coating of the core (releasable) material with the shell (host) material using any of a number of standard coating methods.

[0034] Typically the core is formed from powders or mixtures of powders comprising at least one post-cleaning agent and optionally at least one cleaning agent and optionally at least one other treatment additive and these materials are compressed under pressure to form a solid tablet by means of procedures which are well known in, for example, the pharmaceutical industry. The shell is conveniently formed on the core by coating the core with a solution of the host material by spray coating the solution onto the core or, alternatively, by dipping the core into the solution and then drying the particles; again, such techniques are well known in, for example, the pharmaceutical industry. In embodiments where the core material is soluble in water, the shell is applied as a solution of shell material in an organic liquid, optionally at ambient or elevated temperatures. One suitable organic liquid is ethanol, especially when the shell material is poly(ethylene glycol).

[0035] Solid polymeric cleaning particles may comprise either foamed or unfoamed polymeric materials. Furthermore, the polymeric particles may comprise polymers which are either linear or crosslinked.

[0036] Solid polymeric cleaning particles preferably comprise polyalkenes such as polyethylene and polypropylene, polyamides, polyesters or polyurethanes. Typically, however, said polymeric particles comprise polyamide or polyester, most particularly nylon, polyethylene terephthalate or polybutylene terephthalate, often in the form of beads. Said polyamides and polyesters are found to be particularly effective for aqueous stain/soil removal, whilst polyalkenes are especially useful for the removal of oil-based stains.

[0037] Optionally, copolymers of the above polymeric materials may be included in said polymeric cleaning particles. Specifically, the properties of the polymeric materials may be tailored to specific requirements by the inclusion of monomeric units which confer particular properties on the copolymer. Thus, the copolymers may be adapted to attract particular staining materials by comprising monomers which, *inter alia*, are ionically charged, or include polar moieties or unsaturated organic groups.

[0038] The solid non-polymeric cleaning particles comprise particles of glass, silica, stone, wood, or any of a variety of metals or ceramic materials. Suitable metals include, but are not limited to, zinc, titanium, chromium, manganese, iron, cobalt, nickel, copper, tungsten, aluminium, tin and lead, and alloys thereof. Suitable ceramics include, but are not limited to, alumina, zirconia, tungsten carbide, silicon carbide and silicon nitride. Each of said solid non-polymeric cleaning particles is typically substantially ellipsoidal, cylindrical or spherical in shape.

[0039] In certain embodiments of the invention, a mixture of polymeric and non-polymeric solid cleaning particles can be used.

[0040] According to a second aspect of the invention, there is provided a method for the treatment of a substrate, said method comprising the treatment of the substrate with a formulation according to the first aspect of the invention.

[0041] The method of the invention is typically carried out in an aqueous environment and, more typically, in the presence of limited quantities of water. In other words, the amount of water present during the performance of the method of the invention is far less than in the case of the methods of the prior art, thereby providing one of the principal benefits associated with said method. Thus, water is generally added so as to achieve a water to substrate ratio which is typically between 2.5:1 and 0.1:1 w/w.

[0042] In embodiments of the invention, said treatment method comprises a method for the cleaning of a soiled substrate.

[0043] According to the method of the present invention, said releasable materials are typically delivered directly to the substrate surface by means of controlled localised release from dosing particles containing these agents. In this way the at least one post-cleaning agent, and optionally at least one cleaning agent and optionally at least one other treatment additive, are delivered in the most targeted manner possible, thereby reducing the amount of releasable material required to achieve the desired cleaning, post-cleaning or treatment effect. Furthermore, there is no requirement for the use of complex cartridge or other dosage devices, and no need to use additional water to transport the agent to the fabric surface. The release of said releasable material from the dosing particle may be controlled by selection of a suitable host material as previously indicated, such that it completely releases in one wash cycle.

[0044] Polymeric or non-polymeric solid cleaning particles, or mixtures thereof, are typically added at a particle to substrate addition level of 0.1:1-30:1 by dry mass of substrate (washload).

[0045] The substrate treated by the claimed method may comprise any of a wide range of substrates, including, for example, plastics materials, leather, paper, cardboard, metal, glass or wood. In practice, however, said substrate most preferably comprises a textile fibre, which may be either a natural fibre, such as cotton, or a synthetic textile fibre, for example nylon 6,6 or a polyester, or a blend of natural and synthetic fibres.

[0046] The dosing particles are typically added at a ratio from 0.1-50.0% w/w of the total mass of the cleaning particle formulation. Each of said dosing particles is typically substantially cylindrical or spherical in shape and typically has an average density in the range of 0.5-2.5 g/cm^3 and typically has an average volume in the range of 5-500 mm^3.

[0047] Further embodiments of the invention envisage a method for the treatment of a substrate wherein the surface of a substrate is treated with a post-cleaning agent in accordance with the first aspect of the present invention, the method comprising treating the substrate with a multiplicity of solid cleaning particles and a multiplicity of dosing particles, wherein said dosing particles comprise additives which are free from cleaning agents. Said embodiments are again carried out in the presence of wash water, and involve the use of dosing particles containing post-cleaning agents in accordance with the first aspect of the present invention.

Examples of such embodiments, involve dosing with a dye transfer inhibition agent as defined in the first aspect of the present invention.

[0048] The invention, however, is not limited to procedures for cleaning, post-cleaning and other treatments of fabrics, and is applicable to dish washing or carpet cleaning.

[0049] It should be mentioned that the use of dosing particles in the absence of solid cleaning particles is significantly less effective and, whilst not wishing to be limited by theory, it is considered that this is because the physical action of the solid cleaning particles enhances the disintegration of the dosing particles, the release of the releasable material, the dispersal of the releasable material throughout the washload, and the penetration of the releasable material into the fibres of fabrics and textiles.

Brief Description of the Drawings

[0050] Embodiments of the invention are further described hereinafter with reference to the accompanying drawings, in which:

Figure 1 is a graph illustrating the effect of the quantity of Dosing Beads according to the invention on measured values of a* using a 1.4 kg washload ;

Figure 2 is a graphical representation of the effect of the quantity of Dosing Beads according to the invention on measured values of L* for a 1.4 kg washload;

Figure 3 shows a graph which illustrates the effect of the quantity of Dosing Beads according to the invention on measured values of b* for a 1.4 kg washload;

Figure 4 is a graph which shows DE Values observed after washing according to the invention for a 1.4 kg washload;

Figure 5 provides a photographic illustration of cloths washed according to various procedures;

Figure 6 is a graphical representation of the effect on Dye Transfer Inhibition performance of variations in the weight of Dye Eluting Material and of Chitosan Core-Shell Beads in the wash;

Detailed Description of the Invention

[0051] The first aspect of the invention envisages a formulation comprising a multiplicity of solid cleaning particles and a multiplicity of dosing particles, wherein said dosing particles comprise at least one host material and at least one releasable material, as hereinbefore defined.

[0052] Typically, the cleaning agents dosed by the dosing particles comprise surfactants, enzymes, oxidising agents and bleach, whilst the post-cleaning agents are dye transfer inhibition agents in accordance with the first aspect of the present invention.

[0053] The cleaning agents may optionally also include, for example, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzyme stabilizers, catalytic materials, bleach activators, polymeric dispersing agents, clay soil removal agents and suds suppressors.

[0054] Examples of suitable surfactants may be selected from non-ionic and/or anionic and/or cationic surfactants and/or ampholytic and/or zwitterionic and/or semi-polar nonionic surfactants. The surfactant is typically present at a level of from about 0.1%, from about 1%, or even from about 5% w/w of the dosing particle mass up to about 99.9%, to about 80%, to about 35%, or even to about 30% w/w of the dosing particle mass, or any of the ranges defined thereby.

[0055] Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, other cellulases, other xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, [beta]-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, mannanase and amylases, or mixtures thereof. A typical combination may comprise a mixture of enzymes such as protease, lipase, cutinase and/or cellulase in conjunction with amylase.

[0056] Optionally, enzyme stabilisers may also be included amongst the cleaning agents. In this regard, enzymes for use in detergents may be stabilised by various techniques, for example by the incorporation of water-soluble sources of calcium and/or magnesium ions in the compositions.

[0057] Examples of suitable bleach compounds include, but are not limited to, peroxygen compounds, including hydrogen peroxide, inorganic peroxy salts, such as perborate, percarbonate, perphosphate, persilicate, and mono persulphate salts (e.g. sodium perborate tetrahydrate and sodium percarbonate), and organic peroxy acids such as peracetic acid, monoperoxyphthalic acid, diperoxydodecanedioic acid, N,N'-terephthaloyl-di(6-aminoperoxycaproic acid), N,N'-phthaloylaminoperoxycaproic acid, phthalimido peroxy hexanoic acid and amidoperoxyacid. Percarbonates, and especially sodium percarbonate, are particularly preferred bleach compounds. Bleach activators include, but are not limited to, carboxylic acid esters such as sodium nonanoyloxybenzene sulfonate. Other bleach activators include tetraacetylethylenediamine (TAED). Of these, TAED is especially preferred as a bleach activator. Most particularly, percarbonate/TAED combinations are especially preferred as they can provide substrates (such as textiles and fabrics) which are more hygienic. By hygienic it is preferably meant that the treated substrate has less bacteria, for example at least 1000x, at least 10,000x, at least 100,000x or even at least 1,000,000x less bacteria when compared to the untreated substrate. In the art this is often referred to by Log kills, which equate to Log 3, 4, 5 and 6 kills of bacteria. Log 5 and Log 6 kills are especially difficult to achieve without using high (>60°C) temperatures and/or high loadings of hypochlorite. In some embodiments this can be achieved by a treatment according to the method of the invention at a temperature of less than 50°C, at a temperature of less than 45°C, at a temperature of less than 40°C or even at a temperature of less than 35°C. Typically, the temperature of the treatment is more than 0°C, more typically more than 10°C. Such a treatment offers substantial energy savings and provides for good fabric/textile fibre care as compared to chlorine-based bleach chemicals which tend to slowly damage the fabric/textile fibres and which are more harmful to the environment.

[0058] In certain embodiments, the dosing particles comprise at least one releasable material comprising at least one bleach compound, which is preferably a percarbonate, more preferably sodium percarbonate. In some embodiments, the dosing particles comprise a bleach activator, which is preferably tetraacetylethylenediamine (TAED). In some embodiments the dosing particles comprise both a bleach compound (as preferred above) and a bleach activator (as preferred above).

[0059] In certain embodiments, two or more types of dosing particles are present in the formulation. In certain specific embodiments, one dosing particle comprises a bleach compound (as preferred above) and another dosing particle comprises a bleach activator (as preferred above).

[0060] When the dosing particles comprise both a bleach compound and a bleach activator, the typical weight ratio of bleach compound to bleach activator is from 10:1 to 1:10; more typically from 5:1 to 1:5; even more typically from 3:1 to 1:3; yet more typically from 2:1 to 1:2. When one dosing particle comprises a bleach compound and another dosing particle comprises a bleach activator, the amounts of bleach compound and bleach activator used in the method according to the present invention typically provide the abovementioned preferred weight ratios.

[0061] Suitable builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates, alkali metal silicates, alkaline earth and alkali metal carbonates, aluminosilicates, polycarboxylate compounds, ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxybenzene-2,4,6-trisulphonic acid, and carboxymethyl-oxysuccinic acid, various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

[0062] One or more copper, iron and/or manganese chelating agents and one or more dye transfer inhibiting agents in accordance with the first aspect of the present invention may also be included. The dye transfer inhibiting agents used in the formulation of the first aspect of the invention are selected from chitosan and crosslinked polyvinylpyrrolidone polymers.

[0063] The cleaning agents can also optionally contain dispersants. Suitable water-soluble organic dispersants are homo- or co-polymeric polycarboxylic acids, or their salts, in which the polycarboxylic acid may comprise at least two carboxyl radicals separated from each other by not more than two carbon atoms.

[0064] Examples of post-cleaning anti-redeposition agents include, but are not limited to, carboxymethylcellulose (CMC), polyacrylates and polyethylene glycol (PEG), or salts thereof. Of these, carboxymethylcellulose and salts thereof, e.g. the sodium salt thereof, are especially suitable.

[0065] Suitable post-cleaning fragrances include, but are not limited to, multi-component organic chemical formulations which can contain alcohols, ketones, aldehydes, esters, ethers and nitrile alkenes, and mixtures thereof. Commercially available compounds offering sufficient substantivity to provide residual fragrance include *Galaxolide* (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran), *Lyral* (3- and 4-(4-hydroxy-4-methyl-pentyl) cyclohexene-1-carboxaldehyde and *Ambroxan* ((3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyl-2,4,5,5a,7,8,9,9b-octahydro-1H-benzo[e][1]benzofuran). One example of a commercially available fully formulated perfume is Amour Japonais supplied by Symrise® AG.

[0066] Suitable post-cleaning optical brightening agents include, but are not limited to, several organic chemical classes, of which the most popular are stilbene derivatives, whilst other suitable classes include benzoxazoles, benzimidazoles, 1,3-diphenyl-2-pyrazolines, coumarins, 1,3,5-triazin-2-yls and naphthalimides. Examples of such compounds include, but are not limited to, 4,4'-bis[[6-anilino-4(methylamino)-1,3,5-triazin-2-yl]amino]stilbene-2,2'-disulfonic acid, 4,4'-bis[[6-anilino-4-[(2-hydroxyethyl)methylamino]-1,3,5-triazin-2-yl]amino]stilbene-2,2'- disulphonic acid, disodium salt, 4,4'-bis[[2-anilino-4-[bis(2-hydroxyethyl)amino]-1,3,5-triazin-6-yl]amino]stilbene-2,2'-disulfonic acid, disodium salt, 4,4'-bis[(4,6-dianilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid, disodium salt, 7-diethylamino-4-methylcoumarin, 4,4'-bis[(2-anilino-4-morpholino-1,3,5-triazin-6-yl)amino]-2,2'-stilbene-disulfonic acid, disodium salt, and 2,5-bis(benzoxazol-2-yl)thiophene.

[0067] Other treatment additives which may be dosed according to the invention include antimicrobial agents, suitable examples of which include, but are not limited to, hexadecyltrimethylammonium bromide (CTAB), ionic silver containing zeolites, benzalkonium choride, Triclosan® and silver nitrate. The antimicrobial agent may also be generated *in situ.* In certain embodiments, at least one of the antimicrobial precursors is in the dosing particles as the releasable material. In some embodiments, all of the components needed to generate the antimicrobial compounds are present in the dosing particles as the releasable materials. Typically, combinations of TAED and percarbonate (as mentioned herein) can be used to generate the active antimicrobial compounds.

[0068] In typical embodiments of the invention, the dosing particles comprise a host material comprising a shell comprising poly(vinyl alcohol) (PVOH), copolymers of poly(vinyl alcohol) and poly(vinyl acetate), hydroxypropylmethylcellulose (HPMC), cellulose, starch, hydroxypropylcellulose (HPC), hydroxyethylcellulose (HEC), poly(vinyl pyrrolidinone) (PVP), poly(ethylene glycol) (PEG) and gelatin.

[0069] Typically, at least 50 wt%, more typically at least 75 wt%, and most typically all of the host material comprising the shell is comprised of one or more partially or completely water soluble polymeric materials. Typically, the host material comprising the shell comprises no water-insoluble polymeric materials.

[0070] The solid cleaning and dosing particles are of such a shape and size as to allow for good flowability and intimate contact with a soiled substrate, which typically comprises a textile fabric. In the context of the present invention, therefore, said particles typically comprise cylindrical or spherical beads; other shapes are possible, such as ellipsoidal, cuboid, etc. It is found that the combination of particle size, shape and density is such that the mechanical interaction of the particle with the fabric is optimised, it being sufficiently vigorous to provide effective cleaning but, at the same time, uniform and gentle enough to reduce fabric damage when compared with conventional aqueous processes. It is, in particular, the uniformity of the mechanical action generated by the chosen particles across the entire fabric surface that is the key factor in this regard. Such uniform mechanical action is also the key to localised and controlled application of the at least one post-cleaning agent and optionally at least one cleaning agent, and optionally at least one other treatment additive from the dosing particles across the entire substrate surface.

[0071] The particle parameters are also controlled so as to allow for easy separation of the particles from the washload at the end of the wash process. Thus, particle size and shape may be controlled in order to minimise entanglement with the substrate, and the combination of suitable particle density and high free volume (ullage) in the washing machine tumbling process together promote particle removal. This is especially relevant in the case of fabric treatment processes.

[0072] The solid cleaning particles typically have an average particle size of from 1 to 100 mm, more typically from 1 to 50 mm; even more typically from 1 to 15 mm, yet more typically from 2 to 10 mm and most typically from 3 to 6 mm. The size is typically the longest linear size measurable.

[0073] The dosing particles typically have a particle size of from 1 to 100 mm; more typically from 5 to 50 mm. The dosing particles typically have a weight of from 1 to 50 g, more typically from 1 to 30 g and most typically from 5 to 30 g.

[0074] Typically, the dosing particles contain less than 5 wt%, more typically less than 1 wt% of liquid components, and most typically are substantially free of such liquid components.

[0075] Typically the weight ratio of solid cleaning particles to dosing particles is from 100,000:1 to 1:1, more typically from 10,000:1 to 10:1 and most typically from 10,000:1 to 100:1

[0076] In the method according to the second aspect of the invention, the ratio of solid cleaning particles to substrate is generally in the range of from 30:1 to 0.1:1 w/w (dry mass of substrate (washload)), preferably in the region of from 10:1 to 1:1 w/w, with particularly favourable results being achieved with a ratio of between 5:1 and 1:1 w/w, and most particularly at around 2:1 w/w. Thus, for example, for the cleaning of 5 g of fabric, 10 g of solid cleaning particles would be employed, and therefore up to a further 5 g of dosing particles would be used in addition to dose at least one post-cleaning agent, and optionally at least one cleaning agent and optionally at least one other treatment additive.

[0077] In order to provide additional lubrication to the system, and thereby improve the transport properties within the system, water is added to the system. Optionally, a soiled substrate may be moistened by wetting with mains or tap water prior to loading into a cleaning apparatus. In any event, water is added to the process such that the washing treatment is carried out so as to achieve a water to substrate ratio which is typically between 2.5:1 and 0.1:1 w/w; more frequently, the ratio is between 2.0:1 and 0.8:1, with particularly favourable results having been achieved at ratios such as 1.5:1, 1.2:1 and 1.1:1.

[0078] As previously noted, the method of the invention finds particular application in the cleaning of textile fibres and fabrics. The conditions employed in such a cleaning system are very much in line with those which apply to the conventional wet cleaning of textile fibres and, as a consequence, are generally determined by the nature of the fabric and the degree of soiling. Thus, typical procedures and conditions are in accordance with those which are well known to those skilled in the art, with fabrics generally being treated according to the method of the invention at, for example, temperatures of between 5 and 95°C, typically for a duration of between 10 minutes and 1 hour, then optionally being rinsed in water and dried. Typically, the release of additives from the dosing particles is controlled such that these release completely in one wash. This can provide increased convenience for the user.

[0079] The localised delivery of at least one post-cleaning agent, and optionally at least one cleaning agent and optionally at least one other treatment additive, to the fabric surface by the dosing particles is the predominant feature that ensures excellent cleaning and post-cleaning performance. No problems are observed with solid cleaning or dosing particles adhering to the fibres at the conclusion of the cleaning operation, and all particles may subsequently be removed from the substrate of the washload. The method of the invention may particularly advantageously be carried out by using, for example, cleaning apparatus as disclosed in WO-A-2010/094959, WO-A-2011/064581 and especially WO-A-2011/098815.

[0080] Additionally, as previously noted, it has been demonstrated that re-utilisation of the solid cleaning particles is possible. Preferably, the solid cleaning particles are re-used in further procedures according to the method of the present invention. However, the dosing particles are typically consumed in a single wash and are not usually available for re-use.

[0081] Release of the at least one post-cleaning agent and optionally at least one cleaning agent, and optionally at least one other treatment additive onto the soiled substrate from the dosing particle occurs through physical dissolution of the shell material during the wash or other treatment procedure. The solid, typically polymeric, cleaning particles are also active in this regard, in that they assist in promoting the disintegration of the core-shell particles, so as to aid in the release of the core material. Accordingly, the use of core-shell dosing particles in the absence of solid cleaning particles is sub-optimal because, in those circumstances, the dosing particles do not fully disintegrate and leave residues on the substrate (as illustrated in Example 1).

[0082] The method according to the second aspect of the invention typically involves the cleaning of a soiled substrate and comprises, in sequence, the steps of:

i. washing the soiled substrate with a multiplicity of solid cleaning particles and a multiplicity of dosing particles;

ii. performing a first extraction of excess water;

iii. performing a first separation of said solid cleaning particles;

iv. rinsing;

v. performing a second extraction of excess water;

vi. optionally repeating steps (iv) and (v) at least once; and

vii. performing a second separation of said solid cleaning particles.

[0083] The method of the second aspect of the present invention may be used for either small or large scale batchwise processes. It also finds application in both domestic and industrial cleaning processes.

[0084] The method of the invention may be applied to the cleaning of any of a wide range of substrates including, for example, plastics materials, leather, paper, cardboard, metal, glass or wood. In practice, however, said method is principally applied to the cleaning of substrates comprising textile fibres and fabrics, and has been shown to be particularly successful in achieving efficient cleaning of textile fabrics which may, for example, comprise either natural fibres, such as cotton, or man-made and synthetic textile fibres, for example nylon 6,6, polyester, cellulose acetate, or fibre blends thereof.

[0085] The conditions employed in such cleaning systems when applied to textile fabrics do, however, allow the use of surprisingly lower wash temperatures from those which typically apply to the conventional wet cleaning of textile fabrics and, as a consequence, offer significant environmental and economic benefits.

[0086] In other embodiments, the treatment in the method according to the second aspect of the present invention can comprise a rinse cycle. Accordingly, the treatment typically comprises rinsing the substrate in the presence of the dosing particles and cleaning particles. The rinsing typically comprises the addition of water which is subsequently or simultaneously removed.

[0087] The invention will now be further illustrated, though without in any way limiting the scope thereof, by reference to the following examples.

Examples

Example 1 Dye Transfer Inhibition by "Core-Shell" Beads of ***Chitosan,*** *Cross-linked Polyvinyl Pyrrolidone (PVP) and the Comparative Example Calcium Bentonite*

[0088] This Example shows how the use of single-use core-shell dosing beads in combination with cleaning beads reduces the amount of red dye transferred to a white cloth from a dye eluting material in a laundry "bead cleaning" process.

[0089] In this example, core-shell dosing beads are used in conjunction with polymeric cleaning beads; specifically, the cleaning beads consisted of nylon 6,6 filled with 40% barium sulphate (Technyl XA 1493). These were cut to an ellipsoid shape (-4.5 x 3.5 x 3.2 mm) by under-water die face cutting. The material was supplied by Solvay Chemicals, Lyon France.

Preparation of Dosing Beads

[0090] Powders of a) chitosan (ChitoClear 40400, from Primex EHF, Siglufjord, Iceland), b) chitosan (from Sigma-Aldrich, Gillingham, UK, product number 448869) and c) cross-linked polyvinyl pyrrolidone (PVP) (Disintex 2000, Ashlands Speciality Ingredients, Wayne, NJ 07470, USA) were compressed in a Casburt tableting machine. The diameter of the tableting die was 10 mm. Tablet thickness values were measured with a Copley TBF100 device. The physical properties of the pellets are listed in Table 1; these tablets form the "core" of the core-shell pellets with cores of chitosan or PVP.

TABLE 1 PROPERTIES OF COMPRESSED TABLETS

	Chitosan (ChitoClear 40400)	Chitosan (Sigma Aldrich 448869)	PVP
Compression force used to form tablet, kN	21	21.5	19
Thickness, mm	2.9 ± 0.1	2.88 ± 0.05	2.97 ± 0.05
Weight per tablet, g	0.13 ± 0.03	0.17 ± 0.01	0.159 ± 0.004
N.B. Errors are standard deviations			

[0091] Calcium bentonite in pelletised form ("Mikolit B") (obtained from Marton Geotechnical Services Ltd., Geotechnical Centre, Rougham, Bury St Edmunds, Suffolk, UK) was also used. This material formed the "core" of the calcium bentonite particle.

Formation of Shell

[0092] Tablets were coated with a shell of polyvinyl alcohol (Elvanol 85-82, Du Pont, Wilmington, DE, USA) by pouring an 11% solution of Elvanol 85-82 through a sieve containing the tablets. Tablets were then dried in an oven at 65°C.

Reduction of Transfer of Red Dye onto White Cotton by Core-Shell Dosing Particles

[0093] A 1.4 kg washload was used and the temperature of wash treatment was 40°C.

[0094] The source of red dye was two new, unwashed red tee shirts (Fruit of the Loom, size XXL). The ballast consisted of used polyester clean-room suits. The weight of the washload is defined as the weight of the tee shirts plus the weight of the ballast, and this was kept at 1.4 kg. In all cases the weight ratio of Technyl cleaning beads to washload was 2:1.

[0095] One and a half sebum sheets (one sheet measuring 23 x 61cm) (Product code SBL 2004, WFK Testgewebe GmbH, D-41379, Germany) and four cotton cloths (17 x 28 cm) were also added to the washload.

[0096] The materials making up the wash are listed in Table 2

TABLE 2 CONTENTS OF WASH FOR 1.4 KG WASHLOAD EXCLUDING CORE-SHELL PARTICLES

Technyl XA1493 beads	2.8 kg
Polyester clean room suits	0.95 kg
New, unwashed red cotton tee shirts (Fruit of the Loom)	0.45 kg
Sebum cloths	One and a half
White cotton cloths (17 x 28 cm)	4 cloths

[0097] In addition to the items in Table 2, which were used in every wash cycle, the following quantities of core-shell dosing particles shown in Table 3 were also included.

TABLE 3 TYPE AND QUANTITY OF CORE-SHELL PARTICLES (1.4 kg WASHLOADS)

Run	Core material of "core-shell" particles	Weight of "core-shell" particles
1		0 g
2	Chitosan	1.1 g
3	Chitosan	2.5 g
4	Chitosan	5 g
5	Chitosan	10 g
6	PVP	2.5 g
7	PVP	5 g

(continued)

Run	Core material of "core-shell" particles	Weight of "core-shell" particles
8	PVP	10 g
9	Calcium bentonite	10 g
10	Calcium bentonite	25 g
11	Calcium bentonite	50 g

[0098] The items for each wash load were placed in a net mesh bag; beads and/or dosing paricles were mixed thoroughly with the fabric materials. The fabric materials were inserted into the mesh bag in layers to disperse items evenly throughout the mesh bag, which was sealed by tying.

[0099] The mesh bag was washed in a Beko domestic washing machine using a 40°C cotton cycle with 11.2 g of Pack I detergent available from Xeros Ltd. (a proprietary formulation comprising surfactants and enzymes). The spin speed set was 1200 rpm. The ratio (by weight) of wash load to Xeros Pack I detergent was therefore approximately 8 g/kg.

[0100] For comparison, a similar experiment was carried out using a commercial dye catching sheet (Dr Beckmann's "Colour Catcher") used in conjunction with the Technyl XA1493 beads (using the same conditions but without core-shell dosing particles). The weight of the dye catching sheet was 1.59 g.

[0101] At the end of each wash cycle, white cotton cloths were recovered, dried by hanging at room temperature and then analysed for colour character using a Konica Minolta CM-3600A photospectometer to obtain values of L*, a* and b*. The size of aperture on the photospectrometer was 25.4 mm using 100% UV component and excluding the specular component. Values of L*, a* and b* were also recorded for virgin, unwashed cloth. Measurements on 16 areas of the cloths (four areas per cloth) were averaged.

Results

[0102] The values of L*, a* and b* for unwashed cloth are shown in Table 4. The values are the means of 16 measurements and errors are standard deviations.

TABLE 4 VALUES OF L*, a*, b* FOR UNWASHED VIRGIN WHITE CLOTH

L^*_v	97.57 ± 0.20
a^*_v	-0.19 ± 0.02
b^*_v	1.45 ± 0.05

[0103] The values of a* for the cotton cloths after the wash tests described above are shown in Figure 1. The a* parameter is indicative of the red-green balance of the colour; a change to a more positive a* means an increasingly redder colour while a change to more negative a* means an increasingly green colour. Figure 1 shows that the value of a* with Technyl cleaning beads and no dosing particles was 8.17 ± 0.38. In all cases the use of dosing particles with Technyl cleaning beads reduced a* and brought it closer to the value for virgin, unwashed white cloth of -0.19 ± 0.02, thereby showing that the dosing particles suppressed transfer of red dye. The suppression of change in a* is particularly noteworthy in the case of core-shell particles with chitosan cores where 10 g of dosing particles reduced a* by ~ 6 units compared to the experiment without dosing particles.

[0104] Figure 1 also shows that the core-shell dosing particles compare very well with the commercial dye catching sheet, where the reduction of a* (compared to the experiment without dosing particles) was approximately 2.3.

[0105] Figure 2 provides an illustration of the use of core-shell dosing particles on a white-grey scale. It is apparent that particles with cores of PVP and chitosan both have the effect of brightening the fabric, which is a desirable effect.

[0106] In Figure 3, the effect of dosing particles on b* is illustrated. The b* parameter is indicative of the blue-yellow balance of the colour; a change to a more positive b* means an increasingly more yellow colour, while a change to more negative b* means an increasingly blue colour. Figure 3 shows that dosing particles with a calcium bentonite core impart a yellow colour to the white fabric compared to Technyl cleaning beads alone; however, dosing particles with cores of PVP and chitosan do not cause a significant yellowing effect. In fact, the use of PVP and chitosan particles bring the value of b* closer to that of virgin cloth (1.45 ± 0.05) than does the use of cleaning beads alone.

[0107] Values of DE for washes with dosing particles were calculated with respect to unwashed virgin white cloth where:

$$DE = ((L^*-L^*_v)^2+(a^*-a^*_v)^2+(b^*-b^*_v)^2)^{1/2} .$$

[0108] Values of DE are presented in Figure 4. Values of DE provide a measure of the overall change in appearance of cloth compared to unwashed, virgin cloth. The lower the value of DE, the closer the appearance of the material is to a reference material (in this case, virgin cloth). Figure 4 shows that the use of chitosan or PVP particles in conjunction with Technyl cleaning beads significantly reduces DE values when compared to the case of washing with Technyl cleaning beads alone.

[0109] It should be noted that a value of DE is simply an overall indication of the changes in the three parameters, L*, a* and b*, compared to the virgin cloth; it does not take into account whether a change in any of these individual parameters in desirable or not. In the cases of dosing particles of chitosan and PVP, the increase in L* is desirable (brighter cloth); nevertheless, this desirable change in L* leads to an increase in the value of DE. Consequently, the appearance of the final cloths washed in the presence of chitosan and PVP dosing particles is actually found to be better than would be suggested by the values of DE in Figure 4.

Role of Cleaning Beads

[0110] This assessment showed that the role of the polymeric cleaning beads (Technyl XA1493) is to prevent deposition of powder residue on fabric, and demonstrated that the use of dosing particles without the cleaning beads resulted in unacceptable powder residue on the fabrics.

[0111] The same wash protocol as described above was used with the modifications as shown in Table 5:

TABLE 5 REVISED TEST CONDITIONS

Run A	As above with 2.5 g chitosan core-shell particles; Technyl cleaning beads were omitted
Run B	As above with 2.5 g chitosan in powder form; Technyl cleaning beads were omitted
Run C	As above with 2.5 g chitosan core-shell particles; Technyl cleaning beads present

[0112] Runs A and B therefore simulated conventional washes (without cleaning beads) whilst Run C was a bead cleaning wash.

Results

[0113] The results of the tests are illustrated in the photographs of cloths from Runs A, B and C which are presented in Figure 5 which show, from left to right, A to B to C.

[0114] Thus, it is observed that, in the absence of the polymeric cleaning beads, an unacceptable powder deposit was left on the cloth (highlighted by the arrows). Moreover, creasing was also very noticeable. In the presence of the cleaning beads, however, no such deposit remained and creasing was reduced. Hence, it is seen that the role of the cleaning beads is to assist the disintegration and eventual removal of the chitosan powder from the wash and also to reduce creasing.

Example 2 Dye Transfer Inhibition by Chitosan and cross-linked PVP Used in Powder Form

[0115] Similar experiments were carried out to assess the dye transfer performance of chitosan (ChitoClear 40500) (10 g) and crosslinked PVP (Disintex 200) (2.5 g) when added in powder form compared with core-shell bead form. The experimental protocol was as described in Example 1, with the cleaning beads, using a 1.4 kg washload. The data when the dosing material was in particle form is taken from Example 1. Calcium bentonite was not available in powder form, therefore precluding a similar comparison between bead and powder.

[0116] The observed values of L*, a*, b* and DE are shown in Table 6.

TABLE 6 VALUES OF L*, a*, b* AND DE FOR DYE TRANSFER MATERIAL IN CORE-SHELL DOSING BEAD FORM AND POWDER FORM

	L*		a*		b*		DE	
	bead	powder	bead	powder	bead	powder	bead	powder
2.5 g PVP	94.28 ± 0.27	93.52 ± 0.32	5.68 ± 0.43	7.08 ± 0.66	0.87 ± 0.11	1.60 ± 0.16	6.75 ± 0.51	8.33 ± 0.64
10 g chitosan	95.99 ± 0.14	94.74 ± 0.32	2.30 ± 0.21	4.54 ± 0.29	1.52 ± 0.06	2.60 ± 0.15	2.95 ± 0.25	5.64 ± 0.32

[0117] Surprisingly, Table 6 shows that the a* value for PVP particles is 1.4 units below that for PVP powder, i.e. there is less red dye transfer with the particle than with the powder. Equally surprisingly, for 10 g of chitosan, the value of a* is 2.24 lower for chitosan in particle form than when in powder form, again showing there is less red dye transfer with the particle than with the powder. An additional benefit of dosing particles of precise weight is that they facilitate the introduction of precise levels of dosing materials to the wash (thereby reducing wastage) in a form which is highly convenient to the end-user.

Example 3 Effect of Quantity of Dye; Reduction of Transfer of Red Dye onto White Cotton by Chitosan Core-Shell Dosing Beads

[0118] This Example shows how the original quantity of source of vagrant dye affects degree of dye transfer in the presence of dye transfer inhibiting core-shell beads. Specifically, the amount of dye transferred to a cloth is lowered when there is less vagrant dye in the was

[0119] The wash protocol was exactly as described in Example 1, with the cleaning beads, except that the weight of dye eluting red tee shirt material was varied; additional ballast was added to keep the weight of the washload constant at 1.4k g. 2.5 g and 10 g of core-shell particles with Chitosan cores were used in this example. A 1.4 kg washload was used and the temperature of treatment was 40°C.

[0120] A control was carried out in which chitosan and the dye eluting tee shirts were omitted, the washload consisting entirely of 1.4 kg of polyester ballast.

[0121] The results, showing variations in dye transfer inhibition performance, are presented in Table 7 and in Figure 6.

TABLE 7 EFFECT ON DTI OF VARIATION IN WEIGHT OF DYE ELUTING MATERIAL AND WEIGHT OF CHITOSAN CORE-SHELL PARTICLES

Value of a*			
	Weight of particle		
Weight of red shirt/kg	0 g chitosan	2.5 g chitosan	10 g chitosan
0	0.65 ± 0.13		
0.13	2.89 ± 0.17		1.01 ± 0.33**
0.24	5.13 ± 0.52	2.25 ± 0.47*	
0.48	8.17 ± 0.38	4.08 ± 0.29*	2.3 ± 0.21*
*ChitoClear 40400; **Chitosan Sigma-Aldrich 448869			

[0122] It can be seen from the data presented in Table 7 and Figure 6 that the value of a* on the cloths (i.e. the amount of dye transfer) decreases linearly as the quantity of dye source in the wash decreases. Importantly, increasing the weight of chitosan core-shell particles also progressively lowers a* for a constant shirt weight.

[0123] Cloth washed without red shirts or chitosan particles had a value of a* of 0.65 ± 0.13; this is higher than that of virgin cloth (a* = -0.19 ± 0.02), showing there is some colour change on washing with detergent and ballast, even if no dye eluting material is present. In particular, for 0.13 kg of red shirt, a* reduced from 2.89 ± 0.17 (with no dosing particles) to 1.01 ± 0.33 (with 10 g of chitosan dosing particles). This is a difference of less than 1 unit from the value of a* for cloth washed without any dye eluting material of 0.65 ± 0.13. The significance of this is that the human eye can only detect differences larger than 1 unit, which means that the chitosan dosing particles have reduced dye transfer to the extent that the human eye cannot detect the difference between the cloth washed with a dye source and a cloth washed in detergent alone.

Claims

1. A formulation comprising a multiplicity of solid cleaning particles and a multiplicity of dosing particles, wherein said dosing particles comprise core-shell particles comprising at least one host material and at least one releasable material, wherein said host material comprises, as the shell of the dosing particles, at least one partially or completely water soluble polymeric material and said at least one releasable material comprises the core material of the dosing particles, comprising:

   at least one post-cleaning agent; and
   optionally at least one cleaning agent; and
   optionally at least one other treatment additive;
   for the treatment of a substrate,
   wherein said solid cleaning particles are polymeric and/or non-polymeric cleaning particles, wherein said polymeric solid cleaning particles have an average density in the range of 0.5-2.5 g/cm^3 and an average volume in the range of 5-275 mm^3, and wherein said post-cleaning agent comprises at least one dye transfer inhibiting agent:

      wherein said host material is selected from at least one of polyvinyl alcohol, copolymers of poly(vinyl alcohol) and poly(vinyl acetate), poly(ethyl vinyl alcohol), hydroxypropylmethylcellulose, cellulose, starch, hydroxypropylcellulose, hydroxyethylcellulose, carboxymethyl cellulose, poly(vinyl pyrrolidinone), poly(ethylene glycol) and gelatin, or salts thereof; and,
      said dye transfer inhibiting agent is selected from chitosan, and crosslinked polyvinylpyrrolidone polymers; and
      wherein said non-polymeric cleaning particles comprise glass, silica, stone, wood, metals or ceramic materials and wherein said non-polymeric solid cleaning particles have an average density in the range of 3.5-12.0 g/cm^3 and an average volume in the range of 5-275 mm^3.

2. A formulation as claimed in claim 1 wherein said polymeric cleaning particles comprise a polymer selected from polyalkenes, polyamides, polyesters or polyurethanes, preferably nylon, polyethylene terephthalate or polybutylene terephthalate.

3. A formulation as claimed in any preceding claim wherein said dosing particles are added at a ratio of from 0.1-50.0% w/w of the total mass of said formulation.

4. A formulation as claimed in any preceding claim wherein said dosing particles have an average density in the range of 0.5-2.5 g/cm^3 and an average volume in the range of 5-500 mm^3.

5. A formulation as claimed in any preceding claim which comprises two or more types of dosing particles.

6. A formulation as claimed in any preceding claim for the cleaning of a soiled substrate, wherein said at least one releasable material comprises at least one cleaning agent.

7. A formulation as claimed in any preceding claim wherein said dye transfer inhibiting agent is selected from chitosan.

8. A formulation as claimed in any preceding claim wherein said at least one other treatment additive comprises at least one anti-microbial agent, optionally selected from ionic silver containing zeolites, benzalkonium choride, Triclosan®, silver nitrate and hexadecyltrimethylammonium bromide (CTAB).

9. A formulation as claimed in any preceding claim wherein said cleaning agent comprises at least one detergent and/or at least one enzyme, oxidising agent or bleach, optionally wherein said detergent comprises at least one surfactant which is selected from non-ionic and/or anionic and/or cationic surfactants and/or ampholytic and/or zwitterionic and/or semi-polar non-ionic surfactants, optionally wherein said surfactant is present at a level of from 5% to 30% of the dosing particle mass.

10. A formulation as claimed in any one of claims 1 to 5 wherein said dosing particles comprise additives which are free

from cleaning agents.

11. A method for the treatment of a substrate, said method comprising the treatment of the substrate with a formulation as claimed in any one of claims 1 to 10.

12. A method as claimed in claim 11 for the cleaning of textile fibres and fabrics, wherein said treatment is performed at temperatures of between 5 and 95°C for a duration of between 10 minutes and 1 hour.

13. A method as claimed in claim 11 or 12 wherein said method is performed in an aqueous environment wherein water is added to the system so as to provide a water to substrate ratio which is between 2.5:1 and 0.1:1 w/w, or between 2.0:1 and 0.8:1.

14. A method as claimed in any one of claims 11 to 13 wherein said solid cleaning particles are added at a particle to substrate addition level of from 30:1 to 0.1:1 by dry mass of substrate, optionally wherein the ratio of solid cleaning particles to substrate is in the range of from 10:1 to 0.1:1 w/w or between 5:1 and 1:1 by dry mass of substrate.

15. A method as claims in any one of claims 11 to 14 wherein said substrate comprises a textile fibre, optionally wherein said textile fibre comprises a natural fibre or a synthetic fibre or a blend thereof.

16. A method as claimed in any one of claims 11 to 15 wherein said solid cleaning particles are re-used in further procedures according to the claimed method.

17. A method as claimed in any one of claims 11 to 16 for the cleaning of a soiled substrate, said method comprising, in sequence, the steps of:

    i. washing the soiled substrate with a multiplicity of solid cleaning particles and a multiplicity of dosing particles;
    ii. performing a first extraction of excess water;
    iii. performing a first separation of said solid cleaning particles;
    iv. rinsing;
    v. performing a second extraction of excess water;
    vi. optionally repeating steps (iv.) and (v.) at least once; and
    vii. performing a second separation of said solid cleaning particles.

Patentansprüche

1. Formulierung, die eine Vielzahl von festen Reinigungspartikeln und eine Vielzahl von festen Dosierpartikeln umfasst, wobei die Dosierpartikel Kern-Mantel-Partikel umfassen, die mindestens ein Wirtmaterial und mindestens ein freisetzbares Material umfassen, wobei das Wirtmaterial als Mantel der Dosierpartikel mindestens ein teilweise oder vollständig wasserlösliches polymeres Material umfasst und das mindestens eine freisetzbare Material das Kernmaterial der Dosierpartikel umfasst, umfassend:

    mindestens ein Nachreinigungsmittel; und
    gegebenenfalls mindestens ein Reinigungsmittel; und
    gegebenenfalls mindestens einen weiteren Behandlungszusatz;
    zur Behandlung eines Substrats,
    wobei die festen Reinigungspartikel polymere und/oder nichtpolymere Reinigungspartikel sind, wobei die polymeren festen Reinigungspartikel eine durchschnittliche Dichte im Bereich von 0,5-2,5 g/cm^3 und ein durchschnittliches Volumen im Bereich von 5-275 mm^3 aufweisen, und wobei das Nachreinigungsmittel mindestens einen Farbstoffübertragungsinhibitor umfasst:

        wobei das Wirtmaterial aus mindestens einem von Polyvinylalkohol, Copolymeren von Poly(vinylalkohol) und Poly(vinylacetat), Poly(ethylvinylalkohol), Hydroxypropylmethylcellulose, Cellulose, Stärke, Hydroxypropylcellulose, Hydroxyethylcellulose, Carboxymethylcellulose, Poly(vinylpyrrolidinon), Poly(ethylenglycol) und Gelatine oder Salzen davon ausgewählt ist; und
        wobei der Farbstoffübertragungsinhibitor aus Chitosan und quervernetzten Polyvinylpyrrolidonpolymeren ausgewählt ist; und
        wobei die nichtpolymeren Reinigungspartikel Glas, Siliciumdioxid, Stein, Holz, Metalle oder Keramikmate-

rialien umfassen und wobei die nichtpolymeren festen Reinigungspartikel eine durchschnittliche Dichte im Bereich von 3,5-12,0 g/cm^3 und ein durchschnittliches Volumen im Bereich von 5-275 mm^3 aufweisen.

2. Formulierung nach Anspruch 1, wobei die polymeren Reinigungspartikel ein Polymer umfassen, das aus Polyalkenen, Polyamiden, Polyestern oder Polyurethanen, bevorzugt Nylon, Polyethylenterephthalat oder Polybutylenterephthalat, ausgewählt ist.

3. Formulierung nach einem der vorhergehenden Ansprüche, wobei die Dosierpartikel in einem Verhältnis von 0,1-50,0 Gew.-% der Gesamtmasse der Formulierung zugegeben werden.

4. Formulierung nach einem der vorhergehenden Ansprüche, wobei die Dosierpartikel eine durchschnittliche Dichte im Bereich von 0,5-2,5 g/cm^3 und ein durchschnittliches Volumen im Bereich von 5-500 mm^3 aufweisen.

5. Formulierung nach einem der vorhergehenden Ansprüche, die zwei oder mehr Arten von Dosierpartikeln umfasst.

6. Formulierung nach einem der vorhergehenden Ansprüche zum Reinigen eines verschmutzten Substrats, wobei das mindestens eine freisetzbare Material mindestens ein Reinigungsmittel umfasst.

7. Formulierung nach einem der vorhergehenden Ansprüche, wobei der Farbstoffübertragungsinhibitor aus Chitosan ausgewählt ist.

8. Formulierung nach einem der vorhergehenden Ansprüche, wobei der mindestens eine weitere Behandlungszusatz mindestens ein antimikrobielles Mittel umfasst, das gegebenenfalls aus ionischen silberhaltigen Zeolithen, Benzalkoniumchlorid, Triclosan®, Silbernitrat und Hexadecyltrimethylammoniumbromid (CTAB) ausgewählt ist.

9. Formulierung nach einem der vorhergehenden Ansprüche, wobei das Reinigungsmittel mindestens ein Detergens und/oder mindestens ein Enzym, ein Oxidationsmittel oder eine Bleiche umfasst, wobei das Detergens gegebenenfalls mindestens ein Tensid umfasst, das aus nichtionischen und/oder anionischen und/oder kationischen Tensiden und/oder ampholytischen und/oder zwitterionischen und/oder semipolaren nichtionischen Tensiden ausgewählt ist, wobei das Tensid gegebenenfalls in einer Menge von 5 % bis 30 % der Dosierpartikelmasse vorhanden ist.

10. Formulierung nach einem der Ansprüche 1 bis 5, wobei die Dosierpartikel Zusätze umfassen, die frei von Reinigungsmitteln sind.

11. Verfahren zur Behandlung eines Substrats, wobei das Verfahren die Behandlung des Substrats mit einer Formulierung nach einem der Ansprüche 1 bis 10 umfasst.

12. Verfahren nach Anspruch 11 zum Reinigen von Textilfasern und Stoffen, wobei die Behandlung bei Temperaturen zwischen 5 und 95 °C über einen Zeitraum zwischen 10 Minuten und 1 Stunde ausgeführt wird.

13. Verfahren nach Anspruch 11 oder 12, wobei das Verfahren in einer wässrigen Umgebung ausgeführt wird, wobei dem System Wasser zugegeben wird, um ein Wasserzu-Substrat-Verhältnis bereitzustellen, das zwischen 2,5:1 und 0,1:1 w/w oder zwischen 2,0:1 und 0,8:1 liegt.

14. Verfahren nach einem der Ansprüche 11 bis 13, wobei die festen Reinigungspartikel in einer Partikel-zu-Substrat-Zugabemenge von 30:1 bis 0,1:1 nach Substrattrockenmasse zugegeben werden, wobei das Verhältnis fester Reinigungspartikel zum Substrat gegebenenfalls im Bereich von 10:1 bis 0,1:1 w/w oder zwischen 5:1 und 1:1 nach Substrattrockenmasse liegt.

15. Verfahren nach einem der Ansprüche 11 bis 14, wobei das Substrat eine Textilfaser umfasst, wobei die Textilfaser gegebenenfalls eine Naturfaser oder eine Synthesefaser oder eine Mischung davon umfasst.

16. Verfahren nach einem der Ansprüche 11 bis 15, wobei die festen Reinigungspartikel in weiteren Vorgängen gemäß dem beanspruchten Verfahren wiederverwendet werden.

17. Verfahren nach einem der Ansprüche 11 bis 16 zum Reinigen eines verschmutzten Substrats, wobei das Verfahren nacheinander die folgenden Schritte umfasst:

i. Waschen des verschmutzten Substrats mit einer Vielzahl von festen Reinigungspartikeln und einer Vielzahl von Dosierpartikeln;
ii. Durchführen einer ersten Extraktion von überschüssigem Wasser;
iii. Durchführen einer ersten Abtrennung der festen Reinigungspartikel;
iv. Spülen;
v. Durchführen einer zweiten Extraktion von überschüssigem Wasser;
vi. gegebenenfalls mindestens einmaliges Wiederholen der Schritte (iv.) und (v.); und
vii. Durchführen einer zweiten Abtrennung der festen Reinigungspartikel.

Revendications

1. Formule comprenant une multitude de particules de nettoyage solides et une multitude de particules dosantes, où lesdites particules dosantes sont constituées de particules de type noyau-enveloppe comprenant au moins une matière hôte et au moins une matière pouvant être libérée, où ladite matière hôte comprend, au titre d'enveloppe des particules dosantes, au moins une matière polymère partiellement ou entièrement hydrosoluble, et ladite au moins une matière pouvant être libérée constitue la matière de noyau des particules dosantes, comprenant :

au moins un agent post-nettoyage ; et
éventuellement au moins un agent de nettoyage ; et
éventuellement au moins un autre adjuvant de traitement ;
pour le traitement d'un substrat,
où lesdites particules de nettoyage solides sont des particules de nettoyage polymères et/ou non polymères,
où lesdites particules de nettoyage solides polymères présentent une densité moyenne comprise dans l'intervalle allant de 0,5 à 2,5 g/cm^3 et un volume moyen compris dans l'intervalle allant de 5 à 275 mm^3,
et où ledit agent post-nettoyage comprend au moins un agent d'inhibition de transfert de couleur ; où ladite matière hôte est choisie parmi au moins l'un des membres du groupe constitué par les suivants : alcool polyvinylique, copolymères d'alcool polyvinylique et de polyacétate de vinyle, poly(alcool éthylvinylique), hydroxypropylméthylcellulose, cellulose, amidon, hydroxypropylcellulose, hydroxyéthylcellulose, carboxyméthylcellulose, polyvinylpyrrolidinone), poly(éthylène glycol) et gélatine, ou leurs sels ; et,
ledit agent d'inhibition de transfert de couleur est choisi parmi le chitosane et les polymères de polyvinylpyrrolidone réticulés ; et
où lesdites particules de nettoyage non polymères sont constituées de verre, de silice, de pierre, de bois, de métaux ou de matériaux céramiques et où lesdites particules de nettoyage solides non polymères ont une densité moyenne comprise dans l'intervalle allant de 3,5 à 12,0 g/cm^3 et un volume moyen compris dans l'intervalle allant de 5 à 275 mm^3.

2. Formule selon la revendication 1, où lesdites particules de nettoyage polymères comprennent un polymère choisi parmi les suivants : polyalcènes, polyamides, polyesters ou polyuréthanes, préférentiellement nylon, polyéthylène téréphtalate ou polybutylène téréphtalate.

3. Formule selon l'une quelconque des revendications précédentes où lesdites particules dosantes sont ajoutées à un rapport compris entre 0,1 et 50,0 % en masse de la masse totale de ladite formule.

4. Formule selon l'une quelconque des revendications précédentes où lesdites particules dosantes présentent une densité moyenne comprise dans l'intervalle allant de 0,5 à 2,5 g/cm^3 et un volume moyen compris dans l'intervalle allant de 5 à 500 mm^3.

5. Formule selon l'une quelconque des revendications précédentes, qui comprend deux types de particules dosantes ou plus.

6. Formule selon l'une quelconque des revendications précédentes destinée au nettoyage d'un substrat encrassé, où ladite au moins une matière pouvant être libérée comprend au moins un agent de nettoyage.

7. Formule selon l'une quelconque des revendications précédentes, où ledit agent d'inhibition de transfert de couleur est choisi parmi le chitosane.

8. Formule selon l'une quelconque des revendications précédentes, où ledit au moins un autre adjuvant de traitement

comprend au moins un agent antimicrobien,
éventuellement choisi parmi les zéolithes contenant de l'argent ionique, le chlorure de benzalkonium, le Triclosan®, le nitrate d'argent et le bromure d'hexadécyltriméthylammonium (CTAB).

9. Formule selon l'une quelconque des revendications précédentes, où ledit agent de nettoyage comprend au moins un détergent et/ou au moins une enzyme, un agent d'oxydation ou un agent de blanchiment, éventuellement où ledit détergent comprend au moins un tensioactif qui est choisi parmi les tensioactifs non ioniques et/ou anioniques et/ou cationiques et/ou les tensioactifs ampholytiques et/ou zwitterioniques et/ou semi-polaires non ioniques, éventuellement où ledit tensioactif est présent à un niveau compris entre 5 % et 30 % de la masse des particules dosantes.

10. Formule selon l'une quelconque des revendications 1 à 5, où lesdites particules dosantes comprennent des adjuvants qui sont exempts d'agent de nettoyage.

11. Procédé de traitement d'un substrat, ledit procédé comprenant le traitement du substrat par une formule selon l'une quelconque des revendications 1 à 10.

12. Procédé selon la revendication 11 destiné au nettoyage de fibres textiles et de tissus, où ledit traitement est mis en oeuvre à des températures comprises entre 5 et 95 °C pendant une durée comprise entre 10 minutes et 1 heure.

13. Procédé selon la revendication 11 ou 12, où ledit procédé est mis en oeuvre dans un environnement aqueux où de l'eau est ajoutée au système de sorte à fournir un rapport eau sur substrat qui est compris entre 2,5:1 et 0,1:1 en masse, ou entre 2,0:1 et 0,8:1.

14. Procédé selon l'une quelconque des revendications 11 à 13, où lesdites particules de nettoyage solides sont ajoutées à un niveau d'addition de particules sur substrat compris entre 30:1 et 0,1:1 par rapport à la masse sèche du substrat, éventuellement le rapport des particules de nettoyage solides sur le substrat est compris dans l'intervalle allant de 10:1 à 0,1:1 en masse ou de 5:1 à 1:1 par rapport à la masse sèche du substrat.

15. Procédé selon l'une quelconque des revendications 11 à 14, où ledit substrat solide comprend une fibre textile, éventuellement où ladite fibre textile comprend une fibre naturelle ou une fibre synthétique ou l'un de leurs mélanges.

16. Procédé selon l'une quelconque des revendications 11 à 15, où lesdites particules de nettoyage solides sont réutilisées dans des procédures ultérieures en fonction du procédé selon l'invention.

17. Procédé selon l'une quelconque des revendications 11 à 16 destiné au nettoyage d'un substrat encrassé, ledit procédé comprenant, à la suite, les étapes consistant à :

i. laver le substrat encrassé à l'aide d'une multitude de particules de nettoyage solides et d'une multitude de particules dosantes ;
ii. mettre en oeuvre une première extraction de l'eau en excès ;
iii. mettre en oeuvre une première séparation desdites particules de nettoyage solides ;
iv. rincer ;
v. mettre en oeuvre une deuxième extraction de l'eau en excès ;
vi. éventuellement répéter les étapes (iv.) et (v.) au moins une fois ; et
vii. mettre en oeuvre une deuxième séparation desdites particules de nettoyage solides.

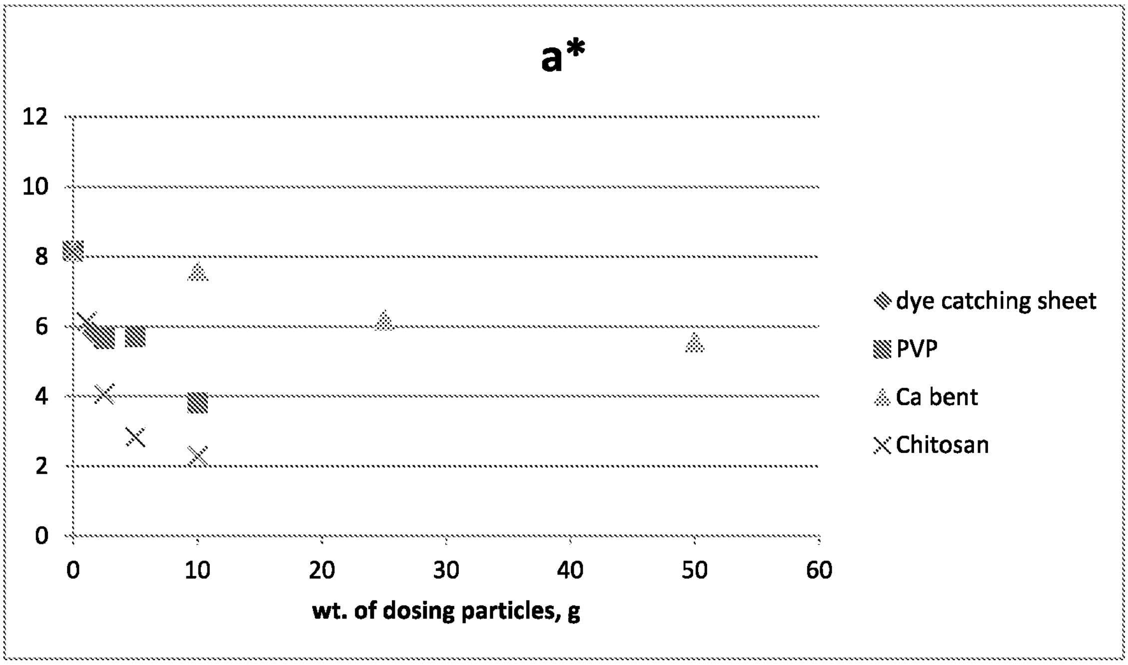

FIGURE 1 EFFECT OF QUANTITY OF DOSING PARTICLES ON VALUES OF A* (1.4 KG WASHLOAD)

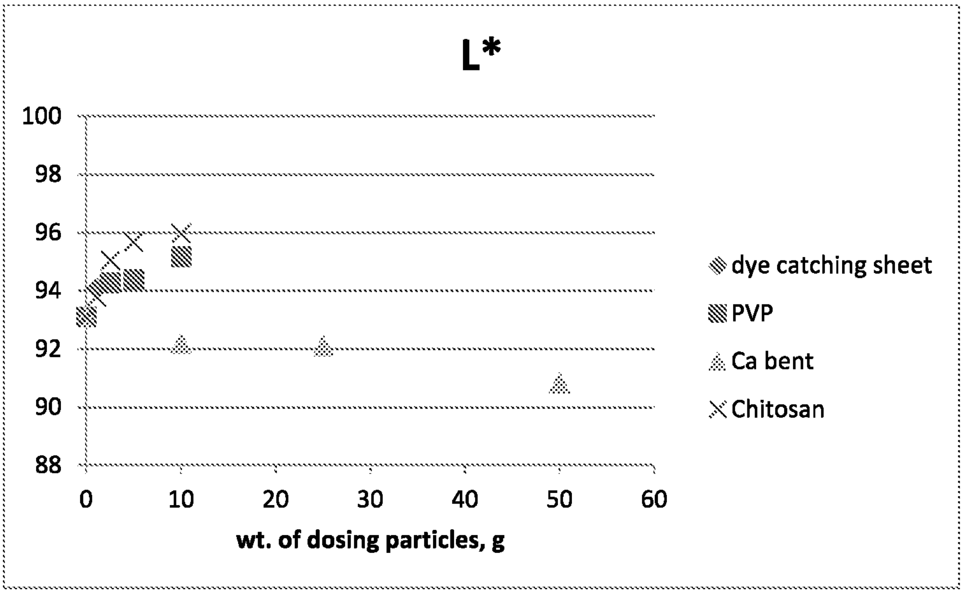

FIGURE 2 EFFECT OF QUANTITY OF DOSING PARTICLES ON VALUES OF L* (1.4 KG WASHLOAD)

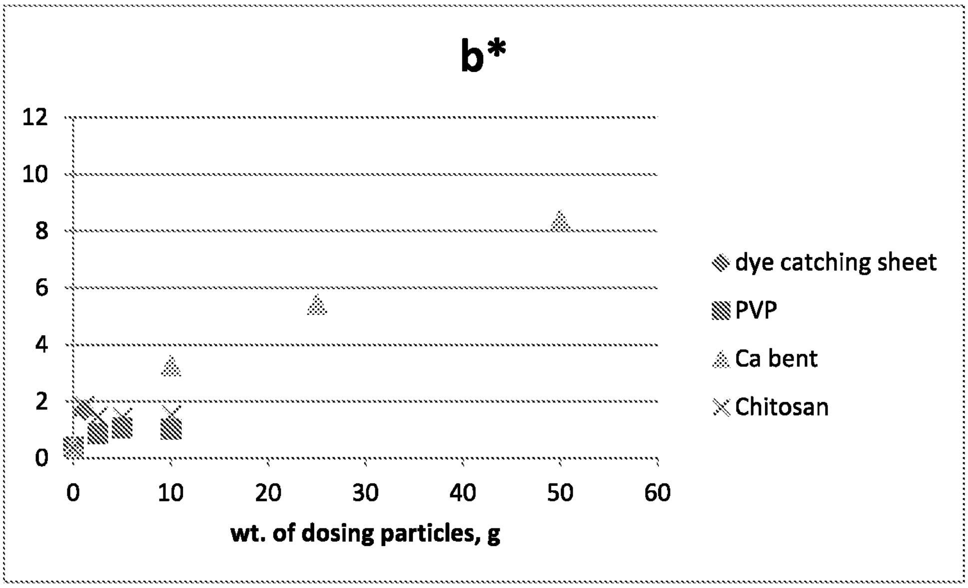

FIGURE 3 EFFECT OF QUANTITY OF DOSING PARTCLES ON VALUES OF B* (1.4 KG WASHLOAD)

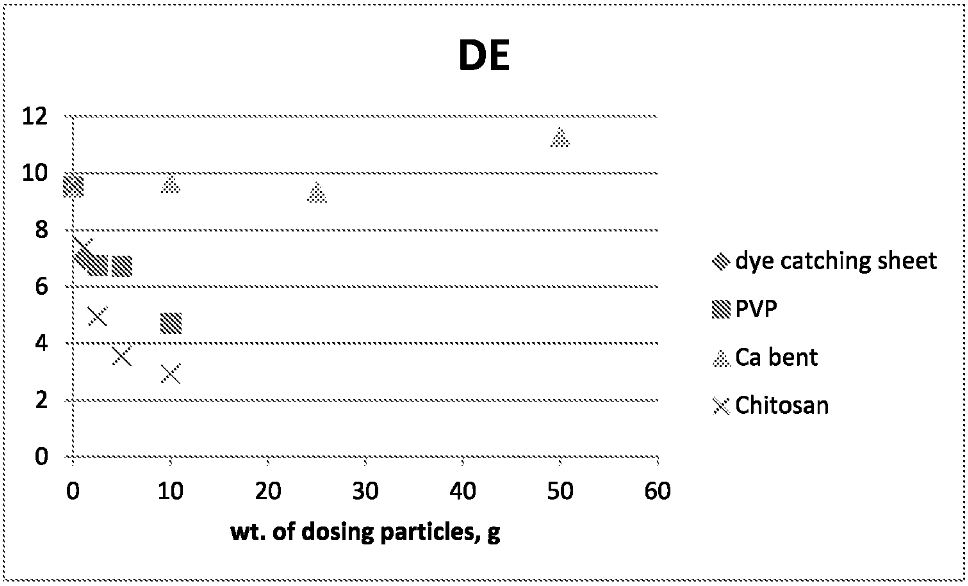

FIGURE 4 DE VALUES (1.4 KG WASHLOAD)

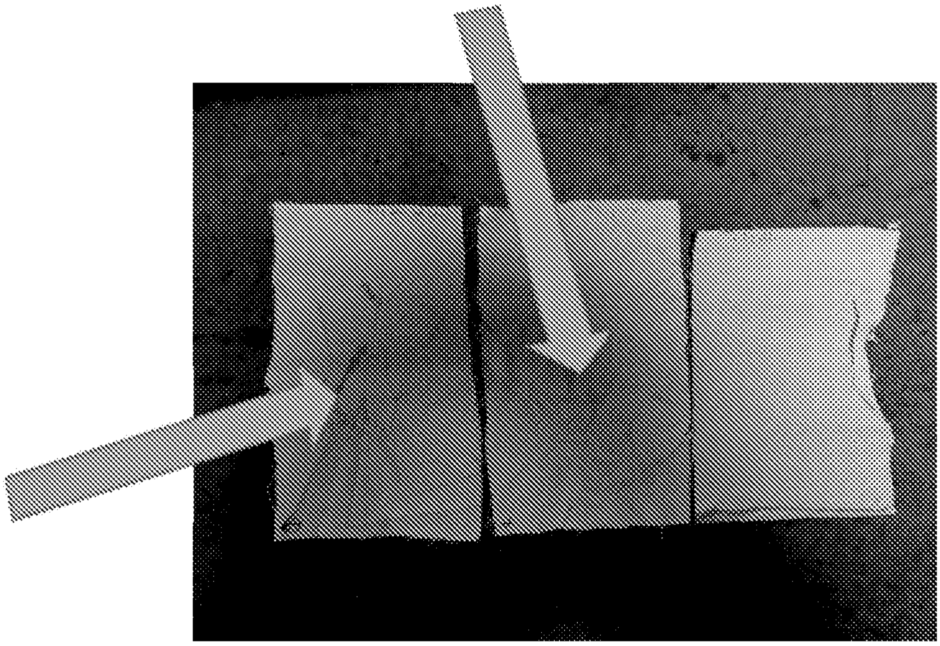

FIGURE 5 PHOTOGRAPHS OF CLOTHS

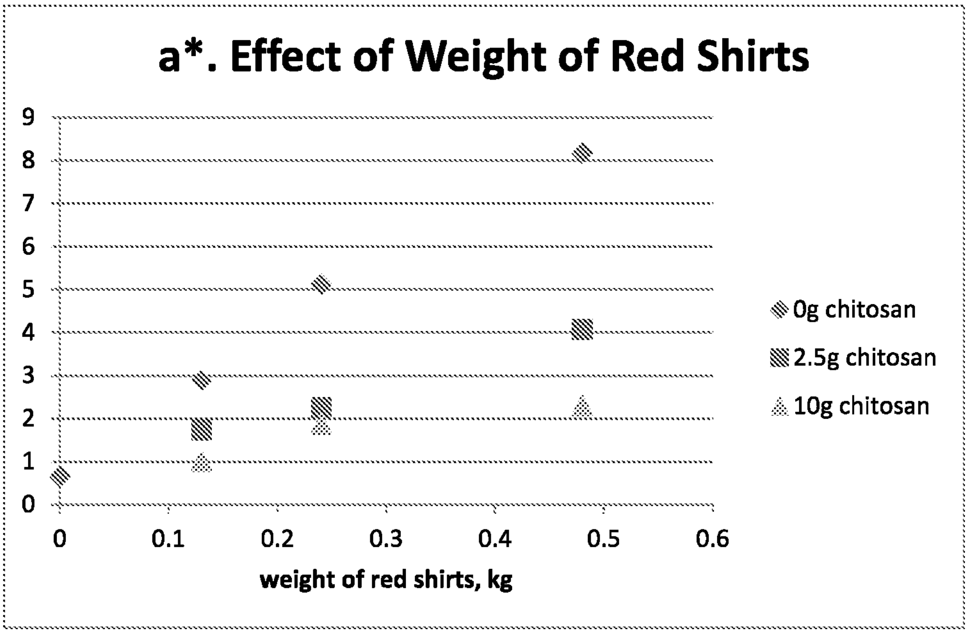

FIGURE 6 EFFECT ON DTI OF VARIATIONS IN WEIGHT OF DYE ELUTING MATERIAL AND OF CHITOSAN CORE-SHELL PARTICLES

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2007128962 A **[0005] [0009]**
- WO 2012056252 A **[0005] [0009]**
- WO 2012095677 A **[0005] [0009]**
- WO 2010094959 A **[0006] [0009] [0079]**
- WO 2011064581 A **[0007] [0009] [0079]**
- WO 2011098815 A **[0008] [0009] [0079]**
- WO 2011128680 A **[0009] [0010]**
- WO 2011128676 A **[0011]**
- WO 2011150138 A **[0014]**
- US 2004242133 A **[0015]**
- US 2011245136 A **[0016]**
- WO 2010079466 A **[0017]**
- GB 2432844 A **[0018]**
- WO 9842818 A **[0019]**
- US 2004242133 A1 **[0019]**
- WO 2014006425 A1 **[0019]**