

# (11) EP 2 993 222 A1

(12)

### **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

09.03.2016 Bulletin 2016/10

(51) Int Cl.:

C11D 3/04 (2006.01) C11D 3/20 (2006.01) C11D 3/12 (2006.01) C11D 3/42 (2006.01)

(21) Application number: 14183466.3

(22) Date of filing: 03.09.2014

(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

Designated Extension States:

**BA ME** 

(71) Applicant: Bast, Tim 6318 Walchwil (CH)

(72) Inventors:

Bast, Tim
 6318 Walchwil (CH)

 Leucht, Thomas 36043 Fulda (DE)

(74) Representative: Bast, Tim Zugerstrasse 80a

6318 Walchwil (CH)

# (54) Detergent composition comprising rare earth metal and a stilbene brightening agent

(57) The present invention provides a detergent composition comprising a cleaning agent and a brightening agent. The detergent composition further comprises a brightening booster component. The brightening booster component comprises rare earth metal atoms.

The present invention further provides a method cleaning a textile using the detergent composition. The present invention further provides a method treating a textile using the detergent composition.

EP 2 993 222 A1

### Description

10

15

20

30

35

#### **BACKGROUND**

[0001] The use of stilbene derivatives in detergent compositions as a brightening agent or brightener is well known. For example in EP 0 724 012 A1, a granular detergent composition comprising a stilbene brightener is described.

[0002] It has been found, however, that textiles which have been laundered with detergent compositions comprising the known stilbene brighteners will cause the textiles to exhibit a dull yellowish color after the laundry. This effect is apparent in particular when the textiles is illuminated with a light sources such as F, D65 and TL 84 which resemble the light emitted by neon tubes and energy saving light bulbs.

**[0003]** It is the object of the present invention to enlarge the state of the art. It is another object of the present invention to overcome the disadvantages of prior art detergent compositions.

**[0004]** More specifically, it is one object of the present invention to reduce the yellowish appearance of textiles which have been laundered with a detergent composition comprising a stilbene brightener.

#### SUMMARY OF THE INVENTION

**[0005]** The present invention provides a detergent composition comprising a cleaning agent and a brightening agent. The detergent composition further comprises a brightening booster component. The brightening booster component comprises rare earth metal atoms.

[0006] The present invention further provides a detergent composition wherein the brightening booster component comprises holmium atoms.

[0007] The present invention further provides a detergent composition wherein the brightening agent comprises a salt of a rare earth metal.

[0008] The present invention further provides a detergent composition wherein the brightening agent comprises acetate of a rare earth metal.

**[0009]** The present invention further provides a detergent composition wherein the brightening agent comprises an oxide of a rare earth metal.

[0010] The present invention further provides a detergent composition wherein detergent composition is liquid at ambient conditions.

**[0011]** The present invention further provides a detergent composition wherein the brightening booster component comprises nanoparticles, the nanoparticles comprising the rare earth metal atoms.

[0012] The present invention further provides a detergent composition wherein the nanoparticles comprise rare earth metal oxide nanoparticles.

**[0013]** The present invention further provides a detergent composition wherein the nanoparticles comprise holmium oxide nanoparticles.

**[0014]** The present invention further provides a detergent composition wherein the brightening agent is selected from the group of stilbene and stilbene derivatives.

**[0015]** The present invention further provides a method cleaning a textile comprising the steps of soaking the textile in an aqueous solution of a detergent composition, the detergent composition comprising a brightening agent and nanoparticles, and of drying the textile.

**[0016]** The present invention further provides a method for the treatment of textile fibers comprising the steps of soaking the textile fibers in an aqueous solution of a detergent composition, the detergent composition comprising a brightening agent and nanoparticles, and of drying the textile fibers.

### **DETAILED DESCRIPTION OF THE INVENTION**

**[0017]** The present invention relates to a detergent composition. The detergent composition is useful for cleaning purposes in a dilute solution, preferably dilute aqueous solution. In one aspect, the present invention relates to a laundry detergent composition. The laundry detergent composition is useful cleaning textiles, fabrics, garment, and other implements which are suitable for being laundered in a laundry machine.

**[0018]** "Fabric", "textile" and "garment" are used interchangeably herein to refer to an implement that is made using any suitable means including, but not limited to weaving, felting, knitting, crocheting and combinations thereof, of natural fibers, synthetic fibers and combinations thereof. Nonwovens are also meant to be encompassed by these terms. The implement may be pliable.

[0019] "Cleaning" is used herein in the broadest sense to mean removal of unwanted substances from fabric. "Cleaning" includes, but is not limited to, the removal of soil from fabric and prevention of re-deposition of soil onto fabric.

[0020] The detergent composition according to the present invention may be a liquid detergent composition. "Liquid

2

40

45

50

detergent composition" as used herein, refers to compositions that are in a form selected from the group of: "pourable liquid"; "gel"; "cream"; and combinations thereof.

**[0021]** "Pourable liquid" as defined herein refers to a liquid having a viscosity of less than about 2000 mPa\*s at 25°C and a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the pourable liquid may be in the range of from about 200 to about 1000 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the pourable liquid may be in the range of from about 200 to about 500 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup>.

**[0022]** "Gel" as defined herein refers to a transparent or translucent liquid having a viscosity of greater than about 2000 mPa\*s at 25°C and at a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the gel may be in the range of from about 3000 to about 10,000 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup> and greater than about 5000 mPa\*s at 25°C at a shear rate of 0.1 sec<sup>-1</sup>.

**[0023]** "Cream" and "paste" are used interchangeably and as defined herein refer to opaque liquid compositions having a viscosity of greater than about 2000 mPa\*s at 25°C and a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the cream may be in the range of from about 3000 to about 10,000 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup>, or greater than about 5000 mPa\*s at 25°C at a shear rate of 0.1 sec<sup>-1</sup>.

**[0024]** The detergent composition of the present invention comprises a cleaning agent. The cleaning agent of the present invention may comprise a surfactant system.

[0025] The cleaning agent may comprise a surfactant system in an amount sufficient to provide desired cleaning properties. In some examples, the liquid cleaning composition comprises, by weight of the composition, from about 0.1% to about 60% of a surfactant system. In other examples, the liquid cleaning composition comprises, by weight of the composition, from about 1% to about 50% of the surfactant system. In further examples, the liquid cleaning composition comprises, by weight of the composition, from about 5% to about 45% of the surfactant system. The surfactant system may comprise a detersive surfactant selected from nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof. In a more specific embodiment, the surfactant system comprises anionic surfactant, nonionic surfactant, or mixtures thereof. Those of ordinary skill in the art will understand that a detersive surfactant encompasses any surfactant or mixture of surfactants that provide cleaning, stain removing, or other laundering benefit to fabrics during the laundering process. A suitable surfactant system for the present invention is for example described in US 2014/0026331 A1. The disclosure of US 2014/0026331 A1 together with any documents directly or indirectly referenced therein is incorporated herein by reference.

20

30

35

45

50

55

**[0026]** The detergent composition of the present invention comprises a brightening agent such as an optical brightener, an optical brightening agent, a fluorescent brightening agent, an optical whitening agent, or a fluorescent whitening agent. The brightening may include chemical compounds that absorb light in the ultraviolet and violet region (usually 340-370 nm) of the electromagnetic spectrum, and re-emit light in the blue region (typically 420-470 nm).

**[0027]** Brightening agents are generally used to enhance the appearance of color of textiles, garments, and fabrics, causing a "whitening" effect, making materials look less yellow by increasing the overall amount of blue light reflected. **[0028]** The brightening agent may be incorporated at levels of from about 0.01% to about 1.2%, by weight of the composition, into the detergent compositions described herein.

[0029] Brightening agents are also referred to as fluorescent whitening agents or fluorescent brightening agents provide optical compensation for the yellow cast in fabric substrates. With brightening agents yellowing is replaced by light emitted from brightening agents present in the area commensurate in scope with yellow color. The violet to blue light supplied by the brightening agents combines with other light reflected from the location to provide a substantially complete or enhanced bright white appearance. This additional light is produced by the brightener through fluorescence. Brightening agents absorb light in the ultraviolet range 275 through 400 nm and emit light in the ultraviolet blue spectrum 400 500 nm. [0030] Fluorescent compounds belonging to the brightening agent family are typically aromatic or aromatic heterocyclic materials often containing condensed ring system. An important feature of these compounds is the presence of an uninterrupted chain of conjugated double bonds associated with an aromatic ring. The number of such conjugated double bonds is dependent on the substituents as well as the planarity of the fluorescent part of the molecule. Most brightener compounds are derivatives of stilbene or 4,4'-diamino stilbene, biphenyl, five membered heterocycles (triazoles, oxazoles, imidazoles, etc.) or six membered heterocycles (cumarins, naphthalamides, triazines, etc.). The choice of Brightening agents for use in detergent compositions will depend upon a number of factors, such as the type of detergent, the nature of other components present in the detergent composition, the temperature of the wash water, the degree of agitation, and the ratio of the material washed to the tub size. The brightener selection is also dependent upon the type of material to be cleaned, e.g., cottons, synthetics, etc. Since most laundry detergent products are used to clean a variety of fabrics, the detergent compositions should contain a mixture of brighteners that are effective for a variety of fabrics. It is of course necessary that the individual components of such a brightener mixture be compatible.

**[0031]** Brightening agents useful in the present invention are commercially available and will be appreciated by those skilled in the art. Commercial brightening agents which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles and other miscel-

laneous agents. Examples of these types of brighteners are disclosed in "The Production and Application of Fluorescent BrighteningAgents", M. Zahradnik, Published by John Wiley & Sons, New York (1982), the disclosure of which is incorporated herein by reference.

**[0032]** Stilbene derivatives which may be useful in the present invention include, but are not necessarily limited to, derivatives of bis(triazinyl)amino-stilbene; bisacylamino derivatives of stilbene; triazole derivatives of stilbene; oxadiazole derivatives of stilbene; oxazole derivatives of stilbene; and styryl derivatives of stilbene.

**[0033]** The detergent composition of the present invention can include, for example, about 0 to about 2 weight-%, about 0.05 to about 1 weight-%, about 0.1 to about 0.5 weight-%, or about 0.1 to about 0.2 weight-% brightening agent. In an embodiment, the brightening agent is present at about 0.1 weight-% or at about 0.25 weight-%. The composition can include any of these ranges or any other amount suitable under the circumstances as selected by the skilled practitioner.

[0034] The detergent composition of the present invention further comprises a brightening booster component comprising rare earth metal atoms. The brightening booster component of the present may one comprise one type of rare earth metal atoms, two types of rare earth metal atoms, three types of rare earth metal atoms, or a plurality of rare earth metal atoms. The rare earth metals suitable for the brightening booster component of the present invention include without limitation Sc (Scandium), Y (Yttrium), La (Lanthanum), Ce (Cerium), Pr (Praseodymium), Nd (Neodymium), Pm (Promethium), Sm (Samarium), Eu (Europium), Gd (Gadolinium), Tb (Terbium) Dy (Dysprosium), Ho (Holmium), Er (Erbium), Tm (Thulium), Yb (Ytterbium), and Lu (Lutetium). The rare earth metals suitable for the brightening booster component of the present invention include without limitation Ac (Actinium), Th (Thorium), Pa (Protactinium), U (Uranium), Np (Neptunium), Pt (Plutonium), Am (Americium), Cm (Curium), Bk (Berkelium), Cf (Californium), Es (Einsteinium), Fm (Fermium), Md (Mendelevium), No (Nobelium), and Lf (Lawrencium).

**[0035]** Preferably, the brightening booster component comprises rare earth metal atoms selected from the group of gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium. More preferably, the brightening booster component comprises rare earth metal atoms selected from the group of terbium, dysprosium, holmium, erbium, and thulium. Yet more preferably, the brightening booster component comprises rare earth metal atoms selected from the group of dysprosium, holmium, and erbium. Yet more preferably, the brightening booster component comprises holmium atoms.

[0036] The rare earth metal atoms comprised in the brightening booster component are comprised in the form a salt of the rare earth atoms. Salts are ionic compounds that result from the neutralization reaction of an acid and a base. They are composed of related numbers of cations (positively charged ions) and anions (negative ions) so that the product is electrically neutral (without a net charge). These component ions can be inorganic, such as chloride (Cl<sup>-</sup>), or organic, such as acetate (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>); and can be monatomic, such as fluoride (F<sup>-</sup>), or polyatomic, such as sulfate (SO<sub>4</sub><sup>2-</sup>). The brightening booster agent in the detergent composition of the present invention may comprise an acetate of the rare earth metal (salt formed of a rare earth metal with an acetate ion [CH<sub>3</sub>COO]<sup>-</sup>).

30

35

40

45

50

**[0037]** Alternatively, the rare earth metal atoms comprised in the brightening booster agent of the present invention may be comprised in the form of an oxide of the rare earth metal. An oxide is a compound comprising one or more oxygen atoms and another element, in the present invention one or more rare earth metal atoms. The rare earth metal in the oxide may have any existing oxidation state for relevant element. The rare earth metal in the oxide may have the +3 oxidation state such as in Holmium (III) Oxide  $Ho_2O_3$ . The brightening booster component of the present invention may comprise one rare earth metal oxide, two rare earth metal oxides, three rare earth metal oxides, or a plurality of rare earth metal oxides. If the brightening booster component comprises more than rare earth metal oxide, the oxides may include the same rare earth metal in different oxidation states or may comprise oxides from different rare earth metals. Suitable oxides for use in the brightening booster component of the present invention include without limitation  $Y_2O_3$ ,  $La_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Eu_2O_3$ ,  $Eu_2$ 

[0038] The laundry detergent composition of the present invention (at ambient conditions) can be in any form, namely, in the form of a liquid; a solid such as a powder, granules, agglomerate, paste, tablet, pouches, bar, gel; an emulsion; types delivered in dual- or multi-compartment containers or pouches; a spray or foam detergent; pre-moistened wipes (i.e., the cleaning composition in combination with a nonwoven material such as that discussed in U.S. Pat. No. 6,121,165); dry wipes (i.e., the cleaning composition in combination with a nonwoven materials, such as that discussed in U.S. Pat. No. 5,980,931) activated with water by a consumer; and other homogeneous or multiphase consumer cleaning product forms.

**[0039]** "Liquid laundry detergent composition" as used herein, refers to compositions that are in a form selected from the group of: "pourable liquid"; "gel"; "cream"; and combinations thereof. "Pourable liquid" as defined herein refers to a liquid having a viscosity of less than about 2000 mPa\*s at 25°C and a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the pourable liquid may be in the range of from about 200 to about 1000 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the pourable liquid may be in the range of from about 200 to about 500 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup>. "Gel" as defined herein refers to a transparent or translucent liquid having

a viscosity of greater than about 2000 mPa\*s at 25°C and at a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the gel may be in the range of from about 3000 to about 10,000 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup> and greater than about 5000 mPa\*s at 25°C at a shear rate of 0.1 sec<sup>-1</sup>. "Cream" and "paste" are used interchangeably and as defined herein refer to opaque liquid compositions having a viscosity of greater than about 2000 mPa\*s at 25°C and a shear rate of 20 sec<sup>-1</sup>. In some embodiments, the viscosity of the cream may be in the range of from about 3000 to about 10,000 mPa\*s at 25°C at a shear rate of 20 sec<sup>-1</sup>, or greater than about 5000 mPa\*s at 25°C at a shear rate of 0.1 sec<sup>-1</sup>.

**[0040]** The laundry detergent composition of the present invention may be in the form of a gel detergent composition comprising an organic solvent selected from the group consisting of low molecular weight aliphatic or aromatic alcohols, low molecular weight alkylene glycols, low molecular weight alkylene glycol ethers, low molecular weight esters, low molecular weight alkylene amines, low molecular weight alkanolamines, and mixtures thereof.

[0041] The laundry detergent composition of the present invention may be in particulate form, such as an agglomerate, a spray-dried powder, an extrudate, a flake, a needle, a noodle, a bead, or any combination thereof. The composition may be in compacted-particulate form, such as in the form of a tablet. The composition may be in some other unit dose form, such as a pouch; typically being at least partially, preferably essentially completely, enclosed by a water-soluble film, such as polyvinyl alcohol. Preferably, the composition is in free-flowing particulate form; by free-flowing particulate form, it is typically meant that the composition is in the form of separate discrete particles. The composition may be made by any suitable method including agglomeration, spray-drying, extrusion, mixing, dry-mixing, liquid spray-on, roller compaction, spheronisation, tabletting or any combination thereof. The composition typically has a bulk density of from 450 g/l to 1,000 g/l, preferred low bulk density detergent compositions have a bulk density of from 550 g/l to 650 g/l and preferred high bulk density detergent compositions have a bulk density of from 750 g/l to 900 g/l. During the laundering process, the composition is typically contacted with water to give a wash liquor having a pH of from above 7 to less than 13, preferably from above 7 to less than 10.5. This is the optimal pH to provide good cleaning whilst also ensuring a good fabric care profile.

**[0042]** The detergent composition of the present invention may comprise nanoparticles whereby the nanoparticles comprise the rare earth metal atoms.

**[0043]** The term "nanoparticles" as used herein refers to particles defined as a small object that behaves as a whole unit with respect to its transport and properties. A nanoparticle generally comprises more than one individual atom or more than one individual molecule. Nanoparticles may be made up from a plurality of the same individual atoms or the same individual molecules. Alternatively, nanoparticles may be made up from a plurality of different individual atoms and/or different individual molecules.

30

35

45

50

55

**[0044]** The nanoparticles have a size suitable to support achieving the objectives of the present invention. In this connection, size refers to average cross-section of a particle, such as diameter. The nanoparticles may have a size where at least about 70% by weight, more preferably at least about 80%, yet more preferably at least about 90%, yet more preferably at least about 95% of the nanoparticles have a size from about 1 nm to about 200 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 80%, yet more preferably at least about 95% of the nanoparticles have a size from about 1 nm to about 150 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 80%, yet more preferably at least about 95% of the nanoparticles have a size from about 1 nm to about 100 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 100 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 100 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 100 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 100 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 100 nm. Alternatively, the nanoparticles may have a size where at least about 70% by weight, more preferably at least about 90%, yet more preferably at least about 90%, yet more preferably at least about 90%, of the nanoparticles have a size from about 1 nm to about 80 nm.

[0045] The nanoparticles have a surface area suitable to support achieving the objectives of the present invention. Increased surface area may be better achieved via small sized particles rather than particles with high porosity. The nanoparticles may have a surface area of at least about 5 m²/g. Alternatively, The nanoparticles may have a surface area of at least about 10 m²/g. Alternatively, The nanoparticles may have a surface area of at least about 25 m²/g. Alternatively, The nanoparticles may have a surface area of at least about 20 m²/g. Alternatively, The nanoparticles may have a surface area of at least about 30 m²/g.

**[0046]** The nanoparticles have a morphology suitable for the objectives of the present invention. Suitable examples of the one or more morphologies the nanoparticles include without limitation spherical, substantially spherical, oval, popcorn-like, plate-like, cubic, pyramidal, cylindrical, and the like. The nanoparticles may be crystalline, partially crystalline, or amorphous.

**[0047]** Nanoparticles suitable for the present invention are commercially available. Alternative, the nanoparticles can be obtained through a variety of processes known in the state of the art, including attrition, pyrolysis, radiolysis, and a sol-gel process.

**[0048]** The nanoparticles comprised in the detergent composition of the present invention may comprise rare earth metal oxide nanoparticles. The detergent composition of the present invention may comprise holmium oxide nanopar-

ticles.

10

25

30

40

45

50

**[0049]** Holmium Oxide (Ho2O3) nanopowder or nanoparticles, nanodots or nanocrystals may be spherical or faceted high surface area oxide magnetic nanostructure particles. The holmium oxide nanoparticles may be 20-80 nanometers (nm) in diameter with specific surface area in the 10 - 50 m<sup>2</sup>/g range. Alternatively, the holmium oxide nanoparticles may have a diameter in the 100 nm range with a specific surface area of approximately 7-10 m 2/g.

**[0050]** The brightening agent for the detergent composition of the present invention may be selected from the group of stilbene and stilbene derivatives.

**[0051]** Stilbene derivatives which may be useful in the present invention include, but are not necessarily limited to, derivatives of bis(triazinyl)amino-stilbene; bisacylamino derivatives of stilbene; triazole derivatives of stilbene; oxadiazole derivatives of stilbene; oxazole derivatives of stilbene; and styryl derivatives of stilbene.

[0052] The brightening agents suitable for the present invention include those belonging to the class of triazine-stilbenes (di-, tetra- or hexa-sulfonated). The brightening agents suitable for the present invention include those belonging to the class of biphenyl-stilbenes. The brightening agents suitable for the present invention include those belonging to the class of diaminostilbene-sulphonic acid derivatives. Typical fluorescent whitening agents are Parawhite KX, supplied by Paramount Minerals and Chemicals, Mumbai, India; Tinopal® DMS and Tinopal® CBS available from Ciba-GeigyAG, Basel, Switzerland. Tinopal® DMS is the disodium salt of 4,4'-bis-(2-morpholino-4 anilino-s-triazin-6-ylamino)stilbene disulphonate.

**[0053]** Usually, the brightening agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the brightening agent or agents used in laundry treatment composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt%.

[0054] Suitable stilbene derivatives include without limitation:

- benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl) amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl) amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt
- Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(2-hydroxyethyl) methylamino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-(4-morpholinyl)-6-(phenylamino)-1,3,5-triazin-2-yilamino]-, disodium salt
- Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(3-amino-3-oxopropyl) (2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt
- Benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(3-amino-3-oxopropyl) (2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt

[0055] Other suitable stilbene derivatives include without limitation the stilbene derivatives disclosed in WO 2001/066681 A1, incorporated herein by reference.

- [0056] The detergent composition of present invention may further comprise additional components including without limitation cleaning enzymes (such as amylases, proteases, and other enzymes), fatty acids, other adjunct cleaning additives, chelating agents, builders, structurants, thickeners, clay soil removal agents, anti-redeposition agents, polymeric soil release agents, alkoxylated polyamine polymers, polymeric grease cleaning agents, enzyme stabilizing systems, bleaching compounds, bleaching agents, bleach activators, bleach catalysts, fabric hueing agents, dye transfer inhibiting agents, suds suppressors, fabric softeners, conditioning agents, humectants, suspending agents, suds boosters, fillers, and carriers. Suitable additional components for the present invention such as the aforementioned are for example described in US 2014/0026331 A1 and in US8716208B1. The disclosures of US 2014/0026331 A1 and US8716208 together with any documents directly or indirectly referenced therein are incorporated herein by reference. [0057] The present invention further provides a method for the preparation of a detergent composition comprising the steps of providing the components of the detergent composition of the present invention and combining the components to form the detergent composition of the present invention. Suitable processes for providing and combining the components are known in the state of the art and may be selected as appropriate under the circumstances by the skilled artisan. [0058] The present invention further provides a method cleaning a textile comprising the steps of
- soaking the textile in an aqueous solution of a detergent composition, the detergent composition comprising a brightening agent and nanoparticles
  - drying the textile

[0059] The present invention further provides a method for the treatment of textile fibers

- soaking the textile fibers in an aqueous solution of a detergent composition, the detergent composition comprising a brightening agent and nanoparticles
- drying the textile fibers

5

10

15

20

25

30

35

40

45

50

55

**[0060]** Also described herein is a method for cleaning fabrics. Such method includes the steps of providing one or more fabrics to which stains are adhered, and contacting said fabrics with a wash solution. The wash solution comprises water; and a detergent composition as described herein. The cleaning fabrics may optionally be rinsed after contact with the wash solution. The compositions may be employed at concentrations of from about 200 ppm to about 10,000 ppm in solution. The water temperatures may range from about 5° C. to about 100° C. The water to fabric ratio may be from about 1:1 to about 20:1.

**[0061]** The following four inventive detergent compositions (examples A1, A2, B1, and B2) have been prepared and tested. All four compositions comprise a brightening booster in accordance with the present invention and exhibit certain inventive benefits described herein.

### **EXAMPLE A1**

[0062] The exemplary detergent composition A1 is a solid composition comprising about

Components (exemplary detergent composition A1)	Weight%
Linear sodium alkylbenzene sulfonate	8.8 (± 0.5)
Fatty alcohol ethoxylate C <sub>12-14</sub> (7EO)	4.7 (± 0.3)
Sodium soap	3.2 (± 0.2)
Foam inhibitor concentrate (12% silicone supported on inorganic su bstrate)	3.9 (± 0.3)
Sodium aluminosilicate zeolite 4a (80% active material)	28.3 (± 1.0)
Sodium carbonate	11.6 (± 1.0)
Poly(acrylic acid-co-maleic acid), sodium salt	2.4 (± 0.2)
Sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 3.3:1)	3.0 (± 0.2)
Carboxymethyl cellulose	1.2 (± 0.1)
Phosphonate (commercial designation "Dequest® 2066", 25 % active acid)	2.8 (± 0.2)
Optical brightener for cotton (stilbene derivative, commercially designated "RUCO-BLANC ADS" available from Rudolf GmbH, Altvaterstraße 58 - 64, 82538 Geretsried, Germany)	0.2 (± 0.02)
Brightening booster (holmium oxide)	0.08 (± 0.01)
Sodium sulfate	6.5 (± 0.5)
Protease (Savinase® 8.0)	0.4 (± 0.04)
Sodium perborate tetrahydrate (10% to 10.4% available oxygen) (separate additive)	20.0
Tetra acetyl ethylene diamine (active content 90.0% to 94.0%) (separate additive)	3.0

### **EXAMPLE A2**

[0063] The exemplary detergent composition A2 is a solid composition comprising about

Components (exemplary detergent composition A2)	Weight%
Linear sodium alkylbenzene sulfonate	8.8 (± 0.5)
Fatty alcohol ethoxylate C <sub>12-14</sub> (7EO)	4.7 (± 0.3)
Sodium soap	3.2 (± 0.2)

(continued)

	Components (exemplary detergent composition A2)	Weight%
5	Foam inhibitor concentrate (12% silicone supported on inorganic su bstrate)	3.9 (± 0.3)
Ü	Sodium aluminosilicate zeolite 4a (80% active material)	28.3 (± 1.0)
	Sodium carbonate	11.6 (± 1.0)
10	Poly(acrylic acid-co-maleic acid), sodium salt	2.4 (± 0.2)
	Sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 3.3:1)	3.0 (± 0.2)
	Carboxymethyl cellulose	1.2 (± 0.1)
	Phosphonate (commercial designation "Dequest® 2066", 25 % active acid)	2.8 (± 0.2)
15	Optical brightener for cotton (stilbene derivative, commercially designated "RUCO-BLANC ADS" available from Rudolf GmbH, Altvaterstraße 58 - 64, 82538 Geretsried, Germany)	0.2 (± 0.02)
	Brightening booster (holmium acetate)	0.12 (± 0.02)
	Sodium sulfate	6.5 (± 0.5)
20	Protease (Savinase® 8.0)	0.4 (± 0.04)
	Sodium perborate tetrahydrate (10% to 10.4% available oxygen) (separate additive)	20.0
	Tetra acetyl ethylene diamine (active content 90.0% to 94.0%) (separate additive)	3.0

# EXAMPLE B1: STILBENDERIVAT + 0,12% HOLMIUMACETAT

[0064] The exemplary detergent composition B1 is a liquid composition comprising about

Components (exemplary detergent composition B1)	Weight%
Linear sodium alkylbenzene sulfonate	12.0 (± 0.6)
Anionic surfactant	8.0 (± 0.8)
Citric acid (sodium citrate)	1.2 (± 0.12)
Fatty acid (C24 sodium salt)	4.0 (± 0.6)
Alkali (NaOH)	2.65
Chelating agent (diethylene triamine pentaacetic acid)	0.3 (± 0.05)
Stabilizer (propanediol/neutralizing agent)	8.13 (± 1.2)
Preservative (borax)	1.0 (± 0.1)
Optical brightener for cotton (stilbene derivative, commercially designated "RUCO-BLANC ADS" available from Rudolf GmbH, Altvaterstraße 58 - 64, 82538 Geretsried, Germany)	0.04 (± 0.01)
Brightening booster (holmium oxide)	0.08 (± 0.01)
Water / other additives	rest

# **EXAMPLE B2**

50

55

[0065] The exemplary detergent composition B2 is a liquid composition comprising about

Components (exemplary detergent composition B2)	Weight%
Linear sodium alkylbenzene sulfonate	12.0 (± 0.6)
Anionic surfactant	8.0 (± 0.8)
Citric acid (sodium citrate)	1.2 (± 0.12)

(continued)

	Components (exemplary detergent composition B2)	Weight%
5	Fatty acid (C24 sodium salt)	4.0 (± 0.6)
	Alkali (NaOH)	2.65
0	Chelating agent (diethylene triamine pentaacetic acid)	0.3 (± 0.05)
	Stabilizer (propanediol/neutralizing agent)	8.13 (± 1.2)
	Preservative (borax)	1.0 (± 0.1)
	Optical brightener for cotton (stilbene derivative, commercially designated "RUCO-BLANC ADS" available from Rudolf GmbH, Altvaterstraße 58 - 64, 82538 Geretsried, Germany)	0.04 (± 0.01)
5	Brightening booster (holmium acetate)	0.12 (± 0.01)
	Water / other additives	rest

[0066] Every document cited herein, including any cross referenced or related patent or application is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

[0067] While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

### 30 Claims

5

10

15

20

25

35

40

45

50

55

- 1. Detergent composition comprising
  - a cleaning agent

and

- a brightening agent

### characterized in that

the detergent composition further comprises

- a brightening booster component,

the brightening booster component comprising a rare earth metal atoms.

2. Detergent composition according to Claim 1

wherein

the brightening booster component comprises holmium atoms.

3. Detergent composition according to Claim 1 or 2 wherein

the brightening agent comprises a salt of a rare earth metal.

4. Detergent composition according to Claim 3

wherein

the brightening agent comprises an acetate of a rare earth metal.

5. Detergent composition according to Claim 1 or 2

wherein

the brightening agent comprises an oxide of a rare earth metal.

6. Detergent composition according to Claim 1

wherein detergent composition is liquid at ambient conditions. 7. Detergent composition according to Claim 1 5 wherein the brightening booster component comprises nanoparticles, the nanoparticles comprising the rare earth metal atoms. 8. Detergent composition according to Claim 1 10 wherein the nanoparticles comprise rare earth metal oxide nanoparticles. 9. Detergent composition according to Claim 6 15 the nanoparticles comprise holmium oxide nanoparticles. 10. Detergent composition according to Claim 1 wherein the brightening agent is selected from the group of stilbene and stilbene derivatives. 20 11. Method for cleaning a textile comprising the steps of - soaking the textile in an aqueous solution of a detergent composition according to any of Claim 1 through Claim 10 25 - drying the textile 12. Method for the treatment of textile fibers comprising the step of - soaking the textile fibers in an aqueous solution of a detergent composition accordingto any of Claim 1 through 30 Claim 10 13. Method for the treatment of textile fibers wherein the method further comprises the step of - drying the textile fibers 35 40 45

50

55



# **EUROPEAN SEARCH REPORT**

Application Number

EP 14 18 3466

10	
15	
20	
25	
30	
35	
40	
45	

50

55

5

	DOCUMENTS CONSIDER			
Category	Citation of document with indica of relevant passages		Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Х	AT 388 928 B (LANG CHI 25 September 1989 (198 * claims; examples 1-6	39-09-25)	1-13	INV. C11D3/04 C11D3/12 C11D3/20
X	EP 2 762 556 A1 (SONG 6 August 2014 (2014-08 * paragraphs [0032] - claims; example 1 *	3-06)	1-13	C11D3/42
Х	GB 1 247 997 A (UNILEY 29 September 1971 (197 * page 1, line 81 - page	71-09-29)	1,3,4,	
Х	US 2012/115767 A1 (VAI [US] ET AL) 10 May 20: * paragraphs [0060] - claims *	12 (2012-05-10)	1-3,5-8, 10-13	
A	US 7 012 053 B1 (BARN/[US] ET AL) 14 March 2 * column 47, lines 21 * columns 77-78 *	2006 (2006-03-14)	1-13	TECHNICAL FIELDS SEARCHED (IPC) C11D
	The present search report has been drawn up for all claims		1	
	Place of search  Munich	Date of completion of the search  5 March 2015	Pfa	Examiner Innenstein, Heide
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 principl E : earlier patent do after the filing da D : document cited i L : document cited f	cument, but publiste in the application or other reasons	
		& : member of the s document		

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

EP 14 18 3466

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.

05-03-2015

· [	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
	AT 388928 B	25-09-1989	NONE	
;	EP 2762556 A1	06-08-2014	EP 2762556 A1 JP 2014528992 A KR 20140106498 A US 2014235523 A1 WO 2013044466 A1	06-08-2014 30-10-2014 03-09-2014 21-08-2014 04-04-2013
	GB 1247997 A	29-09-1971	GB 1247997 A US 3640875 A	29-09-1971 08-02-1972
	US 2012115767 A1	10-05-2012	US 2012115767 A1 US 2014302107 A1	10-05-2012 09-10-2014
	US 7012053 B1	14-03-2006	NONE	
:				
P0459				
DRM 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

- EP 0724012 A1 [0001]
- US 20140026331 A1 [0025] [0056]
- US 6121165 A [0038]
- US 5980931 A [0038]

- WO 2001066681 A1 [0055]
- US 8716208 B1 [0056]
- US 8716208 B [0056]

# Non-patent literature cited in the description

 M. ZAHRADNIK. The Production and Application of Fluorescent BrighteningAgents. John Wiley & Sons, 1982 [0031]