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(54) Title: METHODS OF USING LEUCO COLORANTS AS BLUING AGENTS IN LAUNDRY CARE COMPOSITIONS

(57) Abstract: A method for treating textile articles includes the steps of: (a) providing a laundry care composition comprising a leuco composition; (b) adding the laundry care composition to a liquid medium comprising an converting agent; (c) placing the textile articles in contact with the liquid medium; (d) converting at least some portion of the leuco composition to form an oxidized leuco composition; (e) depositing at least a portion of the oxidized leuco composition onto the textile; (f) optionally, rinsing the textile; and (g) drying the textile articles, wherein the textile article has a Leuco Whiteness Improvement Number (LWIN) of at least 5% after drying.



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## METHODS OF USING LEUCO COLORANTS AS BLUING AGENTS IN LAUNDRY CARE COMPOSITIONS

### TECHNICAL FIELD

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This application describes methods for treating textile articles with laundry care compositions that contain leuco colorants. These types of colorants are provided in a stable, substantially colorless state and then may be transformed to an intense colored state upon exposure to certain physical or chemical changes such as, for example, exposure to oxygen, ion addition, exposure to light, and the like. The methods for treating textile articles laundry care compositions containing the leuco colorants are designed to enhance the apparent or visually perceived whiteness of, or to impart a desired hue to, textile articles over time after washing with the laundry care composition and drying.

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### BACKGROUND

As textile substrates age, their color tends to fade or yellow due to exposure to light, air, soil, and natural degradation of the fibers that comprise the substrates. As such, to visually enhance these textile substrates and counteract the fading and yellowing the use of polymeric colorants for coloring consumer products has become well known in the prior art. For example, it is well known to use whitening agents, either optical brighteners or bluing agents, in textile applications. However, traditional whitening agents have a maximum efficacy upon deposition or exposure to light in the case of optical brighteners.

Leuco dyes are also known in the prior art to exhibit a change from a colorless or slightly colored state to a colored state upon exposure to specific chemical or physical triggers. The change in coloration that occurs is typically visually perceptible to the human eye. All existing compounds have some absorbance in the visible light region (400-700 nm), and thus more or less have some color. In this invention, a dye is considered as a "leuco dye" if it did not render a significant color at its application concentration and conditions, but renders a significant color in its triggered form. The color change upon triggering stems from the change of the molar attenuation coefficient (also known as molar extinction coefficient, molar absorption coefficient, and/or molar absorptivity in some literatures) of the leuco dye molecule in the 400-700 nm range, preferably in the 500-650 nm range, and most preferably in the 530-620 nm range. The increase of the molar attenuation

coefficient of a leuco dye before and after the triggering should be bigger than 50%, more preferably bigger than 200%, and most preferable bigger than 500%.

Thus, it is contemplated to be within the scope of the present invention that the leuco colorants described herein may be ideally suited for use as whitening agents. However, while  
5 traditional leuco colorants may be effective to the extent that they maintain a colorless form on storage in a detergent and undergo a triggered change to a colored or much more highly colored state during or after use by the consumer, it is difficult to control the reaction. Specifically, the difficulty comes in balancing the need to suppress the reaction that leads to the colored form before use, and the need to accelerate the same reaction once the product is used. The reaction on storage  
10 can be suppressed by use of antioxidants, but the use of high levels of antioxidant required to provide the desired stability may lead to issues upon use, such as the undesired yellowing of fabrics from deposition of the antioxidant. This counteracts the very purpose for which the leuco colorants would be used (to provide shading that offsets yellowness on fabrics), and so is counterproductive and tends to reduce the benefit the consumer will experience. As such, there remains a need in  
15 which to slow the conversion during storage and yet retain the ability to convert the molecule once used.

It has now surprisingly been found that the presently claimed leuco colorants provide the desired consumer whiteness benefit onto a textile article when placed in a liquid medium that comprises a converting agent.

20

#### SUMMARY OF THE INVENTION

In one aspect, the present invention provides a method for treating textile articles that includes the steps of: (a) providing a laundry care composition comprising a leuco composition;  
25 (b) adding the laundry care composition to a liquid medium comprising an converting agent; (c) placing the textile articles in contact with the liquid medium; (d) converting at least some portion of the leuco composition to form an oxidized leuco composition; (e) depositing at least a portion of the oxidized leuco composition onto the textile; (f) optionally, rinsing the textile; and (g) drying the textile articles, wherein the textile article has a Leuco Whiteness Improvement Number (LWIN)  
30 of at least 5% after drying.

## DETAILED DESCRIPTION

## Definitions

As used herein, the term "alkoxy" is intended to include C<sub>i</sub>-C<sub>8</sub> alkoxy and alkoxy  
5 derivatives of polyols having repeating units such as butylene oxide, glycidol oxide, ethylene oxide  
or propylene oxide.

As used herein, the interchangeable terms "alkyleneoxy" and "oxyalkylene," and the  
interchangeable terms "polyalkyleneoxy" and "polyoxyalkylene," generally refer to molecular  
structures containing one or more than one, respectively, of the following repeating units: -C<sub>2</sub>H<sub>4</sub>O  
10 -, -C<sub>3</sub>H<sub>6</sub>O-, -C<sub>4</sub>H<sub>8</sub>O-, and any combinations thereof. Non-limiting structures corresponding to  
these groups include -CH<sub>2</sub>CH<sub>2</sub>O-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O -, -CH<sub>2</sub>CH(CH<sub>3</sub>)O-,  
and -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)O-, for example. Furthermore, the polyoxyalkylene constituent may be  
selected from the group consisting of one or more monomers selected from a C<sub>2</sub>-20 alkyleneoxy  
group, a glycidyl group, or mixtures thereof.

15 The terms "ethylene oxide," "propylene oxide" and "butylene oxide" may be shown herein  
by their typical designation of "EO," "PO" and "BO," respectively.

As used herein, the terms "alkyl" and "alkyl capped" are intended to mean any univalent  
group formed by removing a hydrogen atom from a substituted or unsubstituted hydrocarbon.  
Non-limiting examples include hydrocarbyl moieties which are branched or unbranched,  
20 substituted or unsubstituted including C<sub>1</sub>-C<sub>18</sub> alkyl groups, and in one aspect, C<sub>i</sub>-C<sub>6</sub> alkyl groups.

As used herein, unless otherwise specified, the term "aryl" is intended to include C<sub>3</sub>-C<sub>12</sub>  
aryl groups. The term "aryl" refers to both carbocyclic and heterocyclic aryl groups.

As used herein, the term "alkaryl" refers to any alkyl-substituted aryl substituents and aryl-  
substituted alkyl substituents. More specifically, the term is intended to refer to C<sub>7</sub>-16 alkyl-  
25 substituted aryl substituents and C<sub>7</sub>-16 aryl substituted alkyl substituents which may or may not  
comprise additional substituents.

As used herein, the term "detergent composition" is a sub-set of laundry care composition  
and includes cleaning compositions including but not limited to products for laundering fabrics.  
Such compositions may be pre-treatment composition for use prior to a washing step or may be

rinse added compositions, as well as cleaning auxiliaries, such as bleach additives and "stain-stick" or pre-treat types.

As used herein, the term "laundry care composition" includes, unless otherwise indicated, granular, powder, liquid, gel, paste, unit dose, bar form and/or flake type washing agents and/or fabric treatment compositions, including but not limited to products for laundering fabrics, fabric softening compositions, fabric enhancing compositions, fabric freshening compositions, and other products for the care and maintenance of fabrics, and combinations thereof. Such compositions may be pre-treatment compositions for use prior to a washing step or may be rinse added compositions, as well as cleaning auxiliaries, such as bleach additives and/or "stain-stick" or pre-treat compositions or substrate-laden products such as dryer added sheets.

As used herein, the term "leuco" (as used in reference to, for example, a compound, moiety, radical, dye, monomer, fragment, or polymer) refers to an entity (e.g., organic compound or portion thereof) that, upon exposure to specific chemical or physical triggers, undergoes one or more chemical and/or physical changes that results in a shift from a first color state (e.g., uncolored or substantially colorless) to a second more highly colored state. Suitable chemical or physical triggers include, but are not limited to, oxidation, pH change, temperature change, and changes in electromagnetic radiation (e.g., light) exposure. Suitable chemical or physical changes that occur in the leuco entity include, but are not limited to, oxidation and non-oxidative changes, such as intramolecular cyclization. Thus, in one aspect, a suitable leuco entity can be a reversibly reduced form of a chromophore. In one aspect, the leuco moiety preferably comprises at least a first and a second  $\pi$ -system capable of being converted into a third combined conjugated  $\pi$ -system incorporating said first and second  $\pi$ -systems upon exposure to one or more of the chemical and/or physical triggers described above.

As used herein, the terms "leuco composition" or "leuco colorant composition" refers to a composition comprising at least two leuco compounds having independently selected structures as described in further detail herein.

As used herein "average molecular weight" of the leuco colorant is reported as a weight average molecular weight, as determined by its molecular weight distribution: as a consequence of their manufacturing process, the leuco colorants disclosed herein may contain a distribution of repeating units in their polymeric moiety.

As used herein, the terms "maximum extinction coefficient" and "maximum molar extinction coefficient" are intended to describe the molar extinction coefficient at the wavelength of maximum absorption (also referred to herein as the maximum wavelength), in the range of 400 nanometers to 750 nanometers.

5 As used herein, the term "first color" is used to refer to the color of the laundry care composition before triggering, and is intended to include any color, including colorless and substantially colorless.

As used herein, the term "second color" is used to refer to the color of the laundry care composition after triggering, and is intended to include any color that is distinguishable, either  
10 through visual inspection or the use of analytical techniques such as spectrophotometric analysis, from the first color of the laundry care composition.

As used herein, the term "converting agent" refers to any oxidizing agent as known in the art other than molecular oxygen in any of its known forms (singlet and triplet states).

As used herein, the term "triggering agent" refers to a reactant suitable for converting the  
15 leuco composition from a colorless or substantially colorless state to a colored state.

As used herein, the term "whitening agent" refers to a dye or a leuco colorant that may form a dye once triggered that when on white cotton provides a hue to the cloth with a relative hue angle of 210 to 345, or even a relative hue angle of 240 to 320, or even a relative hue angle of 250 to 300 (e.g., 250 to 290).

20 As used herein, "cellulosic substrates" are intended to include any substrate which comprises at least a majority by weight of cellulose. Cellulose may be found in wood, cotton, linen, jute, and hemp. Cellulosic substrates may be in the form of powders, fibers, pulp and articles formed from powders, fibers and pulp. Cellulosic fibers, include, without limitation, cotton, rayon (regenerated cellulose), acetate (cellulose acetate), triacetate (cellulose triacetate), and mixtures  
25 thereof. Articles formed from cellulosic fibers include textile articles such as fabrics. Articles formed from pulp include paper.

As used herein, articles such as "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

As used herein, the terms "include/s" and "including" are meant to be non-limiting.

30 As used herein, the term "solid" includes granular, powder, bar and tablet product forms.

As used herein, the term "fluid" includes liquid, gel, paste and gas product forms.

The test methods disclosed in the Test Methods Section of the present application should be used to determine the respective values of the parameters of Applicants' inventions.

Unless otherwise noted, all component or composition levels are in reference to the active  
5 portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total composition unless otherwise indicated.

10 In one aspect, the molar extinction coefficient of said second colored state at the maximum absorbance in the wavelength in the range 200 to 1,000 nm (more preferably 400 to 750 nm) is preferably at least five times, more preferably 10 times, even more preferably 25 times, most preferably at least 50 times the molar extinction coefficient of said first color state at the wavelength of the maximum absorbance of the second colored state. Preferably, the molar  
15 extinction coefficient of said second colored state at the maximum absorbance in the wavelength in the range 200 to 1,000 nm (more preferably 400 to 750 nm) is at least five times, preferably 10 times, even more preferably 25 times, most preferably at least 50 times the maximum molar extinction coefficient of said first color state in the corresponding wavelength range. An ordinarily skilled artisan will realize that these ratios may be much higher. For example, the first color state  
20 may have a maximum molar extinction coefficient in the wavelength range from 400 to 750 nm of as little as  $10 \text{ M}^{\text{cm}}^{-1}$ , and the second colored state may have a maximum molar extinction coefficient in the wavelength range from 400 to 750 nm of as much as  $80,000 \text{ M}^{\text{cm}}^{-1}$  or more, in which case the ratio of the extinction coefficients would be 8,000:1 or more.

In one aspect, the maximum molar extinction coefficient of said first color state at a  
25 wavelength in the range 400 to 750 nm is less than  $1000 \text{ M}^{\text{cm}}^{-1}$ , and the maximum molar extinction coefficient of said second colored state at a wavelength in the range 400 to 750 nm is more than  $5,000 \text{ M}^{\text{cm}}^{-1}$ , preferably more than 10,000, 25,000, 50,000 or even  $100,000 \text{ M}^{\text{cm}}^{-1}$ . A skilled artisan will recognize and appreciate that a polymer comprising more than one leuco moiety may have a significantly higher maximum molar extinction coefficient in the first color  
30 state (e.g., due to the additive effect of a multiplicity of leuco moieties or the presence of one or more leuco moieties converted to the second colored state). Where more than one leuco moiety is

attached to a molecule, the maximum molar extinction coefficient of said second color state may be more than  $n \times \epsilon$  where  $n$  is the number of leuco moieties plus oxidized leuco moieties present on the molecule, and  $\epsilon$  is selected from  $5,000 \text{ M}^{-1}\text{cm}^{-1}$ , preferably more than 10,000, 25,000, 50,000 or even  $100,000 \text{ M}^{-1}\text{cm}^{-1}$ . Thus for a molecule that has two leuco moieties, the maximum molar extinction coefficient of said second color state may be more than  $10,000 \text{ M}^{-1}\text{cm}^{-1}$ , preferably more than 20,000, 50,000, 100,000 or even  $200,000 \text{ M}^{-1}\text{cm}^{-1}$ . While  $n$  could theoretically be any integer, one skilled in the art appreciates that  $n$  will typically be from 1 to 100, more preferably 1 to 50, 1 to 25, 1 to 10 or even 1 to 5.

The present invention relates to methods for treating textile articles with a class of leuco colorants that may be useful for use in laundry care compositions, such as liquid laundry detergent, to provide a hue to whiten textile substrates. Leuco colorants are compounds that are essentially colorless or only lightly colored but are capable of developing an intense color upon activation. One advantage of using leuco compounds in laundry care compositions is that such compounds, being colorless until activated, allow the laundry care composition to exhibit its own color. The leuco colorant generally does not alter the primary color of the laundry care composition. Thus, manufacturers of such compositions can formulate a color that is most attractive to consumers without concern for added ingredients, such as bluing agents, affecting the final color value of the composition.

The range of textile articles encountered in the consumer home is quite large and often comprises garments constructed from a wide variety of both natural and synthetic fibers, as well as mixtures of these either in the same wash load or even in the same garment. The articles can be constructed in a variety of ways and may comprise any of a vast array of finishes that may be applied by the manufacturer. The amount of any such finish remaining on a consumer's textile article depends on a wide array of factors among which are the durability of the finish under the particular washing conditions employed by the consumer, the particular detergents and additives the consumer may have used as well as the number of cycles that the article has been washed. Depending on the history of each article, finishes may be present to varying degrees or essentially absent, while other materials present in the wash or rinse cycles and contaminants encountered during wearing may start to accumulate on the article.

The skilled artisan is keenly aware that any detergent formulation used by consumers will encounter textile articles that represent the full range of possibilities and expects that there not only may be, but in fact will be, significant differences in the way the formulation performs on some

textiles articles as opposed to others. These differences can be found through routine experimentation.

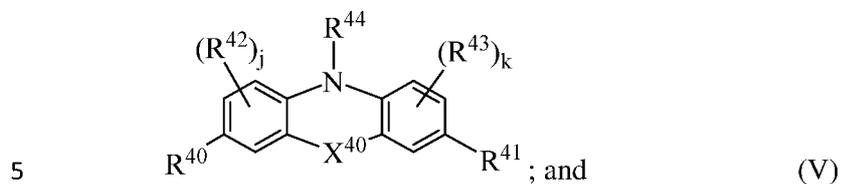
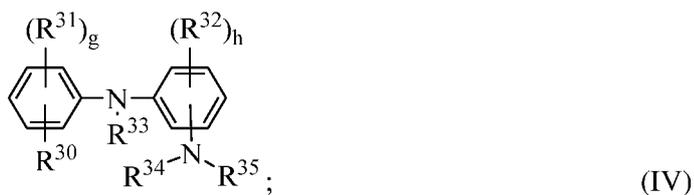
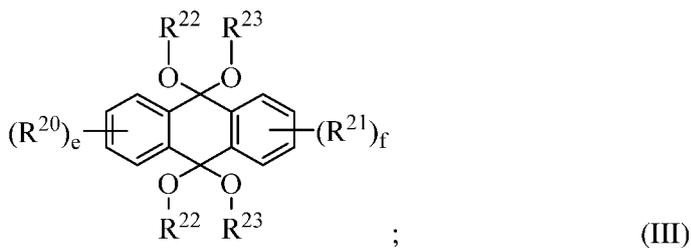
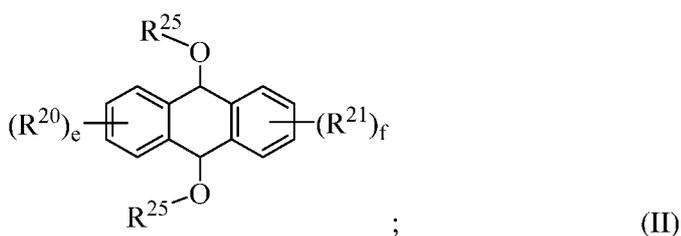
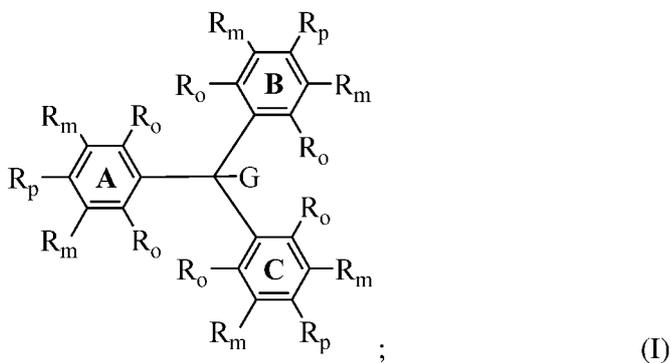
The amount of leuco compounds used in the laundry care compositions of the present invention may be any level suitable to achieve the aims of the invention. In one aspect, the  
5 laundry care composition comprises leuco compounds in an amount from about 0.0001 wt% to about 1.0 wt%, preferably from 0.0005 wt% to about 0.5 wt%, even more preferably from about 0.0008 wt% to about 0.2 wt%, most preferably from 0.004 wt% to about 0.1 wt%.

In another aspect, the laundry care composition comprises leuco compounds in an amount  
10 from 0.0025 to 5.0 milliequivalents/kg, preferably from 0.005 to 2.5 milliequivalents/kg, even more preferably from 0.01 to 1.0 milliequivalents/kg, most preferably from 0.05 to 0.50 milliequivalents/kg, wherein the units of milliequivalents/kg refer to the milliequivalents of leuco moiety per kg of the laundry composition. For leuco compounds comprising more than one leuco moiety, the number of milliequivalents is related to the number of millimoles of the leuco  
15 compound by the following equation: (millimoles of leuco compound) x (no. of milliequivalents of leuco moiety/millimole of leuco compound) = milliequivalents of leuco moiety. In instances where there is only a single leuco moiety per leuco compound, the number of milliequivalents/kg will be equal to the number of millimoles of leuco compound/kg of the laundry care composition.

In one aspect, the invention relates to a leuco composition selected from the group consisting of a diarylmethane leuco, a triarylmethane leuco, an oxazine leuco, a thiazine leuco, a  
20 hydroquinone leuco, an arylaminophenol leuco and mixtures thereof.

Suitable diarylmethane leuco compounds for use herein include, but are not limited to, diarylmethylene derivatives capable of forming a second colored state as described herein. Suitable examples include, but are not limited to, Michler's methane, a diarylmethylene substituted with an -OH group (e.g., Michler's hydrol) and ethers and esters thereof, a  
25 diarylmethylene substituted with a photocleavable moiety, such as a -CN group (bis(para-N,N-dimethyl)phenyl)acetonitrile), and similar such compounds.

In one aspect, the invention relates to methods for treating textile articles with a composition comprising one or more leuco compounds conforming to the group selected from:



(f) mixtures thereof;

wherein the ratio of Formula I-V to its oxidized form is at least 1:19, 1:9, or 1:3, preferably at least 1:1, more preferably at least 3:1, most preferably at least 9:1 or even 19:1.

In the structure of Formula (I), each individual  $R_0$ ,  $R_m$  and  $R_p$  group on each of rings A, B and C is independently selected from the group consisting of hydrogen, deuterium and  $R^5$ ; each  $R^5$  is independently selected from the group consisting of halogens, nitro, alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl,  $-(CH_2)_n-O-R^1$ ,  $-(CH_2)_n-NR^1R^2$ ,  $-C(O)R^1$ ,  $-C(O)OR^1$ ,  $-C(O)O^-$ ,  $-C^{\wedge}NR^1R^2$ ,  $-OC(O)R^1$ ,  $-OC^{\wedge}OR^1$ ,  $-OC^{\wedge}NR^1R^2$ ,  $-S(O)_2R^1$ ,  $-S(O)_2OR^1$ ,  $-S(O)_2O^-$ ,  $-S^{\wedge}NR^1R^2$ ,  $-NR^1C(O)R^2$ ,  $-NR^1C(O)OR^2$ ,  $-NR^1C(O)SR^2$ ,  $-NR^1C(O)NR^2R^3$ ,  $-P(O)_2R^1$ ,  $-P(O)(OR^1)_2$ ,  $-P(O)(OR^1)O^-$ , and  $-P(O)(O^-)_2$ , wherein the index n is an integer from 0 to 4, preferably from 0 to 1, most preferably 0; wherein two  $R_0$  on different A, B and C rings may combine to form a fused ring of five or more members; when the fused ring is six or more members, two  $R_0$  on different A, B and C rings may combine to form an organic linker optionally containing one or more heteroatoms; in one embodiment two  $R_0$  on different A, B and C rings combine to form a heteroatom bridge selected from  $-O-$  and  $-S-$  creating a six member fused ring; an  $R_0$  and  $R_m$  on the same ring or an  $R_m$  and  $R_p$  on the same ring may combine to form a fused aliphatic ring or fused aromatic ring either of which may contain heteroatoms; on at least one of the three rings A, B or C, preferably at least two, more preferably at least three, most preferably all four of the  $R_0$  and  $R_m$  groups are hydrogen, preferably all four  $R_0$  and  $R_m$  groups on at least two of the rings A, B and C are hydrogen; in some embodiments, all  $R_0$  and  $R_m$  groups on rings A, B and C are hydrogen; preferably each  $R_p$  is independently selected from hydrogen,  $-OR^1$  and  $-NR^1R^2$ ; no more than two, preferably no more than one of  $R_p$  is hydrogen, preferably none are hydrogen; more preferably at least one, preferably two, most preferably all three  $R_p$  are  $-NR^1R^2$ ; in some embodiments, one or even two of the Rings A, B and C may be replaced with an independently selected  $C_3-C_9$  heteroaryl ring comprising one or two heteroatoms independently selected from O, S and N, optionally substituted with one or more independently selected  $R^5$  groups; G is independently selected from the group consisting of hydrogen, deuterium,  $C_1-C_{16}$  alkoxide, phenoxide, bisphenoxide, nitrite, nitrile, alkyl amine, imidazole, arylamine, polyalkylene oxide, halides, alkylsulfide, aryl sulfide, or phosphine oxide; in one aspect the fraction  $[(\text{deuterium})/(\text{deuterium} + \text{hydrogen})]$  for G is at least 0.20, preferably at least 0.40, even more preferably at least 0.50 and most preferably at least 0.60 or even at least 0.80; wherein any two of  $R^1$ ,  $R^2$  and  $R^3$  attached to the same heteroatom can combine to form a ring of five or more members optionally comprising one or more additional heteroatoms selected from the group consisting of  $-O-$ ,  $-NR^{15}-$ , and  $-S-$ .

In the structure of Formula (II) - (III), e and f are independently integers from 0 to 4; each  $R^{20}$  and  $R^{21}$  is independently selected from the group consisting of halogens, a nitro group, alkyl groups,

substituted alkyl groups,  $-\text{NC}(0)\text{OR}^1$ ,  $-\text{NC}(0)\text{SR}^1$ ,  $-\text{OR}^1$ , and  $-\text{NR}^1\text{R}^2$ ; each  $\text{R}^{25}$  is independently selected from the group consisting of monosaccharide moiety, disaccharide moiety, oligosaccharide moiety, and polysaccharide moiety,  $-\text{C}(0)\text{R}^1$ ,  $-\text{C}(0)\text{OR}^1$ ,  $-\text{C}(0)\text{NR}^1\text{R}^2$ ; and each  $\text{R}^{22}$  and  $\text{R}^{23}$  is independently selected from the group consisting of hydrogen, alkyl groups, and substituted alkyl groups.

In the structure of Formula (IV),  $\text{R}^{30}$  is positioned ortho or para to the bridging amine moiety and is selected from the group consisting of  $-\text{OR}^{38}$  and  $-\text{NR}^{36}\text{R}^{37}$ , each  $\text{R}^{36}$  and  $\text{R}^{37}$  is independently selected from the group consisting of hydrogen, alkyl groups, substituted alkyl groups, aryl groups, substituted aryl groups, acyl groups,  $\text{R}^4$ ,  $-\text{C}(0)\text{OR}^1$ ,  $-\text{C}(0)\text{R}^1$ , and  $-\text{C}(0)\text{NR}^1\text{R}^2$ ;  $\text{R}^{38}$  is selected from the group consisting of hydrogen, acyl groups,  $-\text{C}(0)\text{OR}^1$ ,  $-\text{C}(0)\text{R}^1$ , and  $-\text{C}(0)\text{NR}^1\text{R}^2$ ; g and h are independently integers from 0 to 4; each  $\text{R}^{31}$  and  $\text{R}^{32}$  is independently selected from the group consisting of alkyl groups, substituted alkyl groups, aryl groups, substituted aryl groups, alkaryl, substituted alkaryl,  $-(\text{CH}_2)_n-\text{O}-\text{R}^1$ ,  $-(\text{CH}_2)_n-\text{NR}^1\text{R}^2$ ,  $-\text{C}(0)\text{R}^1$ ,  $-\text{C}(0)\text{OR}^1$ ,  $-\text{C}(0)\text{O}^-$ ,  $-\text{C}(0)\text{NR}^1\text{R}^2$ ,  $-\text{OC}(0)\text{R}^1$ ,  $-\text{OC}(0)\text{OR}^1$ ,  $-\text{OC}(0)\text{NR}^1\text{R}^2$ ,  $-\text{S}(0)_2\text{R}^1$ ,  $-\text{S}(0)_2\text{OR}^1$ ,  $-\text{S}(0)_2\text{O}^-$ ,  $-\text{S}(0)_2\text{NR}^1\text{R}^2$ ,  $-\text{NR}^1\text{C}(0)\text{R}^2$ ,  $-\text{NR}^1\text{C}(0)\text{OR}^2$ ,  $-\text{NR}^1\text{C}(0)\text{SR}^2$ ,  $-\text{NR}^1\text{C}(0)\text{NR}^2\text{R}^3$ ,  $-\text{OR}^1$ ,  $-\text{NR}^1\text{R}^2$ ,  $-\text{P}(0)_2\text{R}^1$ ,  $-\text{P}(0)(\text{OR}^1)_2$ ,  $-\text{P}(0)(\text{OR}^1)_0$ , and  $-\text{P}(0)(\text{O}^-)_2$ , wherein the index n is an integer from 0 to 4, preferably from 0 to 1, most preferably 0;  $-\text{NR}^{34}\text{R}^{35}$  is positioned ortho or para to the bridging amine moiety and  $\text{R}^{34}$  and  $\text{R}^{35}$  are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl, and  $\text{R}^4$ ;  $\text{R}^{33}$  is independently selected from the group consisting of hydrogen,  $-\text{S}(0)_2\text{R}^1$ ,  $-\text{C}(0)\text{N}(\text{H})\text{R}^1$ ,  $-\text{C}(0)\text{OR}^1$ ; and  $-\text{C}(0)\text{R}^1$ ; when g is 2 to 4, any two adjacent  $\text{R}^{31}$  groups may combine to form a fused ring of five or more members wherein no more than two of the atoms in the fused ring may be nitrogen atoms.

In the structure of Formula (V),  $\text{X}^{40}$  is selected from the group consisting of an oxygen atom, a sulfur atom, and  $\text{NR}^{45}$ ;  $\text{R}^{45}$  is independently selected from the group consisting of hydrogen, deuterium, alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl,  $-\text{S}(0)_2\text{OH}$ ,  $-\text{S}(0)_2\text{O}^-$ ,  $-\text{C}(0)\text{OR}^1$ ,  $-\text{C}(0)\text{R}^1$ , and  $-\text{C}(0)\text{NR}^1\text{R}^2$ ;  $\text{R}^{40}$  and  $\text{R}^{41}$  are independently selected from the group consisting of  $-(\text{CH}_2)_n-\text{O}-\text{R}^1$ ,  $-(\text{CH}_2)_n-\text{NR}^1\text{R}^2$ , wherein the index n is an integer from 0 to 4, preferably from 0 to 1, most preferably 0; j and k are independently integers from 0 to 3;  $\text{R}^{42}$  and  $\text{R}^{43}$  are independently selected from the group consisting of alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl,  $-\text{S}(0)_2\text{R}^1$ ,  $-\text{C}(0)\text{NR}^1\text{R}^2$ ,  $-\text{NC}(0)\text{OR}^1$ ,  $-\text{NC}(0)\text{SR}^1$ ,  $-\text{C}(0)\text{OR}^1$ ,  $-\text{C}(0)\text{R}^1$ ,  $-(\text{CH}_2)_n-\text{O}-\text{R}^1$ ,  $-(\text{CH}_2)_n-\text{NR}^1\text{R}^2$ , wherein the index n is an integer from 0 to 4, preferably from 0 to 1, most preferably 0;  $\text{R}^{44}$  is  $-\text{C}(0)\text{R}^1$ ,  $-\text{C}(0)\text{NR}^1\text{R}^2$ , and  $-\text{C}(0)\text{OR}^1$ .

In the structures of Formula (I) - (V), wherein any charge present in any of the preceding groups is balanced with a suitable independently selected internal or external counterion. Suitable independently selected external counterions may be cationic or anionic. Examples of suitable cations include but are not limited to one or more metals preferably selected from Group I and Group II, the most preferred of these being Na, K, Mg, and Ca, or an organic cation such as iminium, ammonium, and phosphonium. Examples of suitable anions include but are not limited to: fluoride, chloride, bromide, iodide, perchlorate, hydrogen sulfate, sulfate, aminosulfate, nitrate, dihydrogen phosphate, hydrogen phosphate, phosphate, bicarbonate, carbonate, methosulfate, ethosulfate, cyanate, thiocyanate, tetrachlorozincate, borate, tetrafluoroborate, acetate, chloroacetate, cyanoacetate, hydroxyacetate, aminoacetate, methylaminoacetate, di- and tri-chloroacetate, 2-chloro-propionate, 2-hydroxypropionate, glycolate, thioglycolate, thioacetate, phenoxyacetate, trimethylacetate, valerate, palmitate, acrylate, oxalate, malonate, crotonate, succinate, citrate, methylene-bis-thioglycolate, ethylene-bis-iminoacetate, nitrilotriacetate, fumarate, maleate, benzoate, methylbenzoate, chlorobenzoate, dichlorobenzoate, hydroxybenzoate, aminobenzoate, phthalate, terephthalate, indolylacetate, chlorobenzenesulfonate, benzenesulfonate, toluenesulfonate, biphenyl-sulfonate and chlorotoluenesulfonate. Those of ordinary skill in the art are well aware of different counterions which can be used in place of those listed above.

In the structures of Formula (I) - (V),  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^{15}$  are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl, and  $R^4$ ; wherein  $R^4$  is an organic group composed of one or more organic monomers with said monomer molecular weights ranging from 28 to 500, preferably 43 to 350, even more preferably 43 to 250, wherein the organic group may be substituted with one or more additional leuco colorant moieties conforming to the structure of Formula I-V. In one aspect,  $R^4$  is selected from the group consisting of alkyleneoxy (polyether), oxoalkyleneoxy (polyesters), oxoalkyleneamine (polyamides), epichlorohydrin, quaternized epichlorohydrin, alkyleneamine, hydroxyalkylene, acyloxyalkylene, carboxyalkylene, carboalkoxyalkylene, and sugar. Where any leuco colorant comprises an  $R^4$  group with three or more contiguous monomers, that leuco colorant is defined herein as a "polymeric leuco colorant". One skilled in the art knows that the properties of a compound with regard to any of a number of characteristic attributes such as solubility, partitioning, deposition, removal, staining, etc., are related to the placement, identity and number of such contiguous monomers incorporated therein. The skilled artisan can therefore

adjust the placement, identity and number of such contiguous monomers to alter any particular attribute in a more or less predictable fashion.

Conventional surface water treatment plants are still being used in certain geographies. They typically consist of several steps in the treatment process. These include: (1) Collection ; (2) Screening and Straining ; (3) Chemical Addition ; (4) Coagulation and Flocculation ; (5) Sedimentation and Clarification ; (6) Filtration ; (7) Disinfection ; (8) Storage ; (9) and finally Distribution.

Once the water has gone through the filtration process, it is about as clear and clean as it can get. However, there may still be bacteria and viruses remaining. To ensure these are destroyed, there must be a disinfection process employed.

Many public water systems have to add a disinfectant to the water. The disinfectant should ideally be present in all water found in the pipes that carry the water throughout the community. Most municipalities use either chlorine or chloramines. Some communities switch back and forth between chlorine and chloramines at different times of the year or for other operational reasons. Less commonly, utilities use other disinfectants, such as chlorine dioxide. Some water systems that use water from a groundwater source (like community wells) do not have to add a disinfectant at all.

The most common disinfection process used in the United States, for example, is chlorination. Chlorine comes in many different forms including chlorine gas (most common), chlorine dioxide, hypochlorite (bleach), and others.

Chlorine (*Ch*) is a major disinfectant that is cheap and kills most of the serious disease-causing bacteria in the water. However, chlorine disinfection results in a wide variety of by-products. One class of chlorination by-products, known as trihalomethanes, are suspected carcinogens. Because of concern about these by-products in the water supply, chlorine is now kept to minimum levels, and other methods of disinfection are being used more frequently. In recent years, many water utilities have tried to reduce contamination caused by water treatment by switching from free chlorine to chloramines, compounds made from chlorine and ammonia gases. Chloramines form more stable disinfectants and pose less risk of harmful by-products, but cost more to use.

Whichever method is used, chlorine is added to the water in an amount to ensure all microorganisms are destroyed. Water plants monitor the chlorine levels continuously and very

carefully in the treated water. They must add enough chlorine to ensure thorough disinfection of the water, but avoid adding excesses that can cause taste and odor problems when delivered to the consumer.

In one embodiment, because of the uncertainty of the presence or identity of any converting agent in a liquid medium, it is advantageous to ensure the presence of a converting agent by the addition of supplemental converting agent.

In yet another embodiment, the liquid medium as sourced by the municipality comprises sufficient converting agent such that additional converting agent is not required. Preferably, the liquid medium comprises an active chlorine converting agent resulting from the treatment of the water with an agent selected from the group consisting of chlorine, chlorine dioxide, hypochlorite, and mixtures thereof.

An unappreciated but important aspect of the current invention is that the leuco compositions employed in the laundry care composition scavenge the chlorine from the water supplied by certain municipalities, not only enhancing the bluing effect but serving to improve overall color safety for textile articles that are dyed with chlorine sensitive dyes. The methods of the present invention have surprisingly been found to work even for leuco compositions in laundry care compositions that comprise other chlorine scavengers. Without wishing to be bound by theory, this is believed to be because the leuco compounds are much more reactive chlorine scavengers than are the traditional materials used in laundry care compositions for the same purpose.

The liquid medium is preferably an aqueous medium.

When the liquid medium comprises converting agents the bluing effect is increased. Converting agents can be any oxidizing agent as known in the art other than the singlet or triplet forms of molecular oxygen. Thus, the liquid medium may comprise any suitable oxidizing agent or mixtures thereof known in the art. Converting agents suitable for use in the instant invention to increase the bluing effect include, but are not limited to, oxidizing agents selected from the groups consisting of: quinones (eg. Chlornil, benzoquinone, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone), certain oxygen allotropes (e.g., ozone), peroxides (e.g., hydrogen peroxide, peracetic acid, tert-butyl hydroperoxide, benzoyl peroxide, meta-chloroperoxybenzoic acid, urea hydrogen peroxide, p-cumene hydroperoxide, persulfate, oxone, perborate, percarbonates), nitrogen oxides (e.g., nitrogen monoxide, nitrogen dioxide, nitrous oxide, dinitrogen trioxide, dinitrogen tetroxide, dinitrogen pentoxide, trinitramide), halogens (e.g., chlorine, bromine,

fluorine, iodine), halogen oxides and halogen oxyanions (e.g., hypochlorite, chlorite, chlorate, perchlorate, bromate, iodate, perbromate, periodate, chlorine monoxide, chlorine dioxide, chlorine trioxide, dibromine monoxide, bromine dioxide, dibromine trioxide, diiodine monoxide, iodine monoxide, iodine dioxide, diiodine tetroxide, diiodine pentoxide, tetraiodine nonoxide), metal species at high oxidation state (e.g., lead (IV) oxide, manganese dioxide, manganese(VI) oxide, manganese(VII) oxide, permanganate, chromium trioxide, dichromate, iron (III), meta vanadate, vanadate, sodium bismuthate), and haloamines (e.g., chloramine, bromamine, N-bromo succinimide, N-chloro succinimide, N-iodosuccinimide, N-bromohydantoin, N-chlorohydantoin, N-iodohydantoin, N,N-dibromohydantoin, N,N-dichlorohydantoin, N,N-diiodohydantoin).

Certain oxidizing enzymes, either alone or with a suitable substrate or mediator, may serve as the converting agent. Examples of suitable enzymes include, but are not limited to, peroxidases, oxidases, phenoloxidases, lipoxygenases, and laccase, or mixtures thereof.

Further suitable converting agents described herein include bleaching agents other than bleaching catalysts, including photobleaches, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, pre-formed peracids and mixtures thereof.

In other embodiments, the converting agents may preferably comprise catalytic metal complexes. One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as but not limited to: copper, iron, nickel, chromium, titanium, ruthenium, tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. No. 4,430,243.

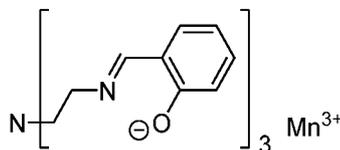
Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. No. 5,246,621 and U.S. Pat. No. 5,244,594. Preferred examples of these catalysts include  $Mn^{II}(u-0)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\text{-}(PF_6)_2$  (often referred to simply as MnTACN),  $Mn^{II}2(u-0)i(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\text{-}(C_{10}_4)_2$ ,  $Mn^{IV}_4(u-0)_6(1,4,7\text{-triazacyclononane})_2\text{-}(C_{10}_4)_2$ ,  $Mn^mMn^{IV}_4(u-0)i(u-OAc)_2\text{-}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\text{-}(C_{10}_4)_3$ , and mixtures thereof. See also European patent application

publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, and mixtures thereof.

Bleach catalysts of particular use in automatic dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. No. 4,246,612 and U.S. Pat. No. 5,227,084. See also U.S. Pat. No. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH<sub>3</sub>)<sub>3</sub> (PF<sub>6</sub>).

Still another type of bleach catalyst, as disclosed in U.S. Pat. No. 5,114,606, is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a noncarboxylate polyhydroxy compound having at least three consecutive C—OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

Catalysts useful in the present invention include metal-containing catalysts such as, but not limited to, Tinocat® TRS KB2 (BASF), which is composed of a manganese ion complexed to three Schiff base ligands as shown in one possible rendering below:



U.S. Pat. No. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



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

bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl<sub>2</sub>, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, Co(2,2'-bispyridylamine)<sub>2</sub>O<sub>2</sub>C<sub>10</sub>F<sub>4</sub>, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

5 Other examples include Mn gluconate, Mn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, Co(NH<sub>3</sub>)<sub>5</sub>Cl, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N<sub>4</sub>Mn<sup>III</sup>(u-0)2Mn<sup>V</sup>(N<sub>4</sub>) and [Bipy<sub>2</sub>Mn<sup>II</sup>(u-0) 2Mn<sup>IV</sup>bipy<sub>2</sub>](C<sub>10</sub>F<sub>4</sub>)<sub>3</sub>.

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

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

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

Other catalysts, such as Fe, Ni, Cr, Cu, etc. could be employed. In addition, U.S. Pat. No.  
30 6,093,343 describes various cobalt catalysts that could be used in the present invention.

Typical amounts of catalyst present in the liquid medium for use in the present invention may be from 0.005% to 5%, preferably 0.05% to 1.5%, more preferably 0.10% to 0.75%, most preferably at about 0.50% by weight based on the weight of the laundry care composition that comprises the leuco compound. If the dose of laundry care composition used is 100 g, then the  
5 typical amount of such a catalyst may be from 5 mg to 5 g, most preferably to about 0.5 g

It is also possible to use anodic oxidation to increase the bluing effect, as long as some electrode were applied during the treatment process.

When supplemental converting agents are provided in the methods of the invention, they may be employed in an amount sufficient to supply a 1.0:1.0 ratio, 5.0:1.0 ratio, a 10:1.0 ratio, a  
10 25:1 ratio, a 100:1 ratio or even a 250:1 ratio of equivalents of the converting agent to the leuco compound present in the wash solution.

In one preferred embodiment, the present invention provides a method for treating textile articles that provides a Leuco Whiteness Improvement Number (LWIN) of at least 5% after drying when washed in a liquid medium that comprises a converting agent. Preferably, the textile article  
15 has a Leuco Whiteness Improvement Number (LWIN), as described in further detail herein, of at least 10% after drying. More preferably the textile article has a Leuco Whiteness Improvement Number (LWIN) of at least 15%, 25% or 50%, most preferably, a Leuco Whiteness Improvement Number (LWIN) of at least 75% or even 100% after drying.

## 20 LAUNDRY CARE INGREDIENTS

### Surfactant system

The products of the present invention may comprise from about 0.00 wt%, more typically from about 0.10 to 80% by weight of a surfactant. In one aspect, such compositions may comprise from about 5% to 50% by weight of surfactant. Surfactants utilized can be of the anionic, nonionic,  
25 amphoteric, ampholytic, zwitterionic, or cationic type or can comprise compatible mixtures of these types. Anionic and nonionic surfactants are typically employed if the fabric care product is a laundry detergent. On the other hand, cationic surfactants are typically employed if the fabric care product is a fabric softener.

### *Anionic surfactant*

30 Useful anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the

compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkyloammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, or even from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Preferred alkyl sulphates are C8-18 alkyl alkoxyated sulphates, preferably a C12-15 alkyl or hydroxyalkyl alkoxyated sulphates. Preferably the alkoxyating group is an ethoxyating group. Typically the alkyl alkoxyated sulphate has an average degree of alkoxylation from 0.5 to 30 or 20, or from 0.5 to 10. The alkyl group may be branched or linear. The alkoxyated alkyl sulfate surfactant may be a mixture of alkoxyated alkyl sulfates, the mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to about 30 carbon atoms, or an average carbon chain length of about 12 to about 15 carbon atoms, and an average (arithmetic mean) degree of alkoxylation of from about 1 mol to about 4 mols of ethylene oxide, propylene oxide, or mixtures thereof, or an average (arithmetic mean) degree of alkoxylation of about 1.8 mols of ethylene oxide, propylene oxide, or mixtures thereof. The alkoxyated alkyl sulfate surfactant may have a carbon chain length from about 10 carbon atoms to about 18 carbon atoms, and a degree of alkoxylation of from about 0.1 to about 6 mols of ethylene oxide, propylene oxide, or mixtures thereof. The alkoxyated alkyl sulfate may be alkoxyated with ethylene oxide, propylene oxide, or mixtures thereof. Alkyl ether sulfate surfactants may contain a peaked ethoxylate distribution. Specific example include C12-C15 EO 2.5 Sulfate, C14-C15 EO 2.5 Sulfate and C12-C15 EO 1.5 Sulfate derived from NEODOL® alcohols from Shell and C12-C14 E03 Sulfate, C12-C16 E03 Sulfate, C12-C14 E02 Sulfate and C12-C14 EO1 Sulfate derived from natural alcohols from Huntsman. The AES may be linear, branched, or combinations thereof. The alkyl group may be derived from synthetic or natural alcohols such as those supplied by the tradename Neodol® by Shell, Safol®, Lial®, and Isalchem® by Sasol or midcut alcohols derived from vegetable oils such as coconut and palm kernel. Another suitable anionic deterative surfactant is alkyl ether carboxylate, comprising a C10-C26 linear or branched, preferably C10-C20 linear, most preferably C16-C18 linear alkyl alcohol and from 2 to 20, preferably 7 to 13, more preferably 8 to 12, most preferably 9.5 to 10.5 ethoxylates. The acid form or salt form, such as sodium or ammonium salt, may be used, and the alkyl chain may contain one cis or trans double bond. Alkyl ether carboxylic acids are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®).

Other useful anionic surfactants can include the alkali metal salts of alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain (linear) or branched chain configuration. In some examples, the alkyl group is linear. Such linear alkylbenzene sulfonates are known as "LAS." In other examples, the linear alkylbenzene sulfonate may have an average number of carbon atoms in the alkyl group of from about 11 to 14. In a specific example, the linear straight chain alkylbenzene sulfonates may have an average number of carbon atoms in the alkyl group of about 11.8 carbon atoms, which may be abbreviated as C 11.8 LAS. Preferred sulphonates are C 10-13 alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) may be obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. A suitable anionic detergent surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. In one aspect a magnesium salt of LAS is used. Suitable anionic sulfonate surfactants for use herein include water-soluble salts of C8-C18 alkyl or hydroxyalkyl sulfonates; C11-C18 alkyl benzene sulfonates (LAS), modified alkylbenzene sulfonate (MLAS) as discussed in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548; methyl ester sulfonate (MES); and alpha-olefin sulfonate (AOS). Those also include the paraffin sulfonates may be monosulfonates and/or disulfonates, obtained by sulfonating paraffins of 10 to 20 carbon atoms. The sulfonate surfactant may also include the alkyl glyceryl sulfonate surfactants.

Anionic surfactants of the present invention may exist in an acid form, and said acid form may be neutralized to form a surfactant salt which is desirable for use in the present detergent compositions. Typical agents for neutralization include the metal counterion base such as hydroxides, e.g., NaOH or KOH. Further preferred agents for neutralizing anionic surfactants of the present invention and adjunct anionic surfactants or cosurfactants in their acid forms include ammonia, amines, or alkanolamines. Alkanolamines are preferred. Suitable non-limiting examples including monoethanolamine, diethanolamine, triethanolamine, and other linear or branched

alkanolamines known in the art; for example, highly preferred alkanolamines include 2-amino-1-propanol, 1-aminopropanol, monoisopropanolamine, or 1-amino-3-propanol.

*Nonionic surfactant*

Preferably the composition comprises a nonionic deterative surfactant. Suitable nonionic  
5 surfactants include alkoxyated fatty alcohols. The nonionic surfactant may be selected from ethoxylated alcohols and ethoxylated alkyl phenols of the formula  $R(OC_2H_4)_nOH$ , wherein  $R$  is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of  $n$  is from about 5 to about 15. Other non-limiting  
10 examples of nonionic surfactants useful herein include: C8-C18 alkyl ethoxylates, such as, NEODOL® nonionic surfactants from Shell; C6-C12 alkyl phenol alkoxyates where the alkoxyate units may be ethyleneoxy units, propyleneoxy units, or a mixture thereof; C12-C18 alcohol and C6-C12 alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C14-C22 mid-chain branched alcohols, BA; C14-C22 mid-chain  
15 branched alkyl alkoxyates, BAE $x$ , wherein  $x$  is from 1 to 30; alkylpolysaccharides; specifically alkylpolyglycosides; polyhydroxy fatty acid amides; and ether capped poly(oxyalkylated) alcohol surfactants. Specific example include C12-C15 E07 and C14-C15 E07 NEODOL® nonionic surfactants from Shell, C12-C14 E07 and C12-C14 E09 Surfonic® nonionic surfactants from Huntsman.

20 Highly preferred nonionic surfactants are the condensation products of Guerbet alcohols with from 2 to 18 moles, preferably 2 to 15, more preferably 5-9 of ethylene oxide per mole of alcohol. Suitable nonionic surfactants include those with the trade name Lutensol® from BASF. Lutensol XP-50 is a Guerbet ethoxylate that contains an average of about 5 ethoxy groups. Lutensol XP-80 and containing an average of about 8 ethoxy groups. Other suitable non-ionic surfactants  
25 for use herein include fatty alcohol polyglycol ethers, alkylpolyglucosides and fatty acid glucamides, alkylpolyglucosides based on Guerbet alcohols.

*Amphoteric surfactant*

The surfactant system may include amphoteric surfactant, such as amine oxide. Preferred amine oxides are alkyl dimethyl amine oxide or alkyl amido propyl dimethyl amine oxide, more

preferably alkyl dimethyl amine oxide and especially coco dimethyl amino oxide. Amine oxide may have a linear or mid-branched alkyl moiety.

#### *Ampholytic Surfactants*

The surfactant system may comprise an ampholytic surfactant. Specific, non-limiting  
5 examples of ampholytic surfactants include: aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents may contain at least about 8 carbon atoms, for example from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Pat. No. 3,929,678 at  
10 column 19, lines 18-35, for suitable examples of ampholytic surfactants.

#### *Zwitterionic surfactant*

Zwitterionic surfactants are known in the art, and generally include surfactants which are neutrally charged overall, but carry at least one positive charged atom/group and at least one negatively charged atom/group. Examples of zwitterionic surfactants include: derivatives of  
15 secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants; betaines, including alkyl dimethyl betaine and cocodimethyl amidopropyl betaine, C<sub>s</sub> to C<sub>i8</sub> (for example from C<sub>i2</sub> to C<sub>i8</sub>) amine oxides and sulfo and hydroxy betaines, such  
20 as N-alkyl-N,N-dimethylamino-1-propane sulfonate where the alkyl group can be C<sub>s</sub> to C<sub>i8</sub> and in certain embodiments from C<sub>io</sub> to C<sub>i4</sub>. A preferred zwitterionic surfactant for use in the present invention is the cocoamidopropyl betaine.

#### *Cationic surfactants*

Examples of cationic surfactants include quaternary ammonium surfactants, which can  
25 have up to 26 carbon atoms specific. Additional examples include a) alkoxyate quaternary ammonium (AQA) surfactants as discussed in U.S. Pat. No. 6,136,769; b) dimethyl hydroxyethyl quaternary ammonium as discussed in U.S. Pat. No. 6,004,922; c) polyamine cationic surfactants as discussed in WO 98/35002, WO 98/35003, WO 98/35004, WO 98/35005, and WO 98/35006, which is herein incorporated by reference; d) cationic ester surfactants as discussed in U.S. Pat.  
30 Nos. 4,228,042, 4,239,660 4,260,529 and U.S. Pat. No. 6,022,844, which is herein incorporated by reference; and e) amino surfactants as discussed in U.S. Pat. No. 6,221,825 and WO 00/47708,

which is herein incorporated by reference, and specifically amido propyldimethyl amine (APA). Useful cationic surfactants also include those described in U.S. Pat. No. 4,222,905, Cockrell, issued Sep. 16, 1980, and in U.S. Pat. No. 4,239,659, Murphy, issued Dec. 16, 1980, both of which are also incorporated herein by reference. Quaternary ammonium compounds may be present in fabric enhancer compositions, such as fabric softeners, and comprise quaternary ammonium cations that are positively charged polyatomic ions of the structure  $NR_4^+$ , where **R** is an alkyl group or an aryl group.

#### *Adjunct Cleaning Additives*

The cleaning compositions of the invention may also contain adjunct cleaning additives. The precise nature of the cleaning adjunct additives and levels of incorporation thereof will depend on the physical form of the cleaning composition, and the precise nature of the cleaning operation for which it is to be used.

The adjunct cleaning additives may be selected from the group consisting of builders, structurants or thickeners, clay soil removal/anti-redeposition agents, polymeric soil release agents, polymeric dispersing agents, polymeric grease cleaning agents, enzymes, enzyme stabilizing systems, bleaching compounds, bleaching agents, bleach activators, bleach catalysts, brighteners, dyes, hueing agents, dye transfer inhibiting agents, chelating agents, suds suppressors, softeners, and perfumes. This listing of adjunct cleaning additives is exemplary only, and not by way of limitation of the types of adjunct cleaning additives which can be used. In principle, any adjunct cleaning additive known in the art may be used in the instant invention.

#### *Polymers*

The composition may comprise one or more polymers. Non-limiting examples, all of which may be optionally modified, include polyethyleneimines, carboxymethylcellulose, poly(vinylpyrrolidone), poly(ethylene glycol), poly(vinyl alcohol), poly(vinylpyridine-N-oxide), poly(vinylimidazole), polycarboxylates or alkoxyated substituted phenols (ASP), as described in WO 2016/041676. An example of ASP dispersants, include but are not limited to, HOSTAPAL BV CONC S1000 available from Clariant.

Polyamines may be used for grease, particulate removal or stain removal. A wide variety of amines and polyaklyeneimines can be alkoxyated to various degrees to achieve hydrophobic or hydrophilic cleaning. Such compounds may include, but are not limited to, ethoxyated polyethyleneimine, ethoxyated hexamethylene diamine, and sulfated versions thereof. Useful

examples of such polymers are HP20 available from BASF or a polymer having the following general structure:

bis((C<sub>2</sub>H<sub>5</sub>O)<sub>n</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>(CH<sub>3</sub>)-N+-C<sub>x</sub>H<sub>2x</sub>-N+-(CH<sub>3</sub>)-bis((C<sub>2</sub>H<sub>5</sub>O)(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof. Polypropoxylated-  
5 polyethoxylated amphiphilic polyethyleneimine derivatives may also be included to achieve greater grease removal and emulsification. These may comprise alkoxyated polyalkylenimines, preferably having an inner polyethylene oxide block and an outer polypropylene oxide block. Detergent compositions may also contain unmodified polyethyleneimines useful for enhanced beverage stain removal. PEI's of various molecular weights are commercially available from the  
10 BASF Corporation under the trade name Lupasol®. Examples of suitable PEG's include, but are not limited to, Lupasol FG®, Lupasol G-35®.

The composition may comprise one or more carboxylate polymers, such as a maleate/acrylate random copolymer or polyacrylate homopolymer useful as polymeric dispersing agents. Alkoxyated polycarboxylates such as those prepared from polyacrylates are also useful to  
15 provide clay dispersancy. Such materials are described in WO 91/08281. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub> wherein m is 2-3 and n is 6-12. The side-chains are ester or ether-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure.

20 Preferred amphiphilic graft co-polymer(s) comprise (i) polyethylene glycol backbone; and (ii) at least one pendant moiety selected from polyvinyl acetate, polyvinyl alcohol and mixtures thereof. An example of an amphiphilic graft co-polymer is Sokalan HP22, supplied from BASF.

Alkoxyated substituted phenols as described in WO 2016/041676 are also suitable examples of polymers that provide clay dispersancy. Hostapal BV Cone S1000, available from  
25 Clariant, is one non-limiting example of an ASP dispersant, .

Preferably the composition comprises one or more soil release polymers. Suitable soil release polymers are polyester soil release polymers such as Repel-o-tex polymers, including Repel-o-tex SF, SF-2 and SRP6 supplied by Rhodia. Other suitable soil release polymers include Texcare polymers, including Texcare SRA100, SRA300, SRN100, SRN170, SRN240, SRN260  
30 SRN300 and SRN325 supplied by Clariant. Other suitable soil release polymers are Marloquest polymers, such as Marloquest SL, HSCB, L235M, B, G82 supplied by Sasol. Other suitable soil release polymers include methyl-capped ethoxylated propoxylated soil release polymers as described in US 9,365,806.

Preferably the composition comprises one or more polysaccharides which may in particular be chosen from carboxymethyl cellulose, methylcarboxymethylcellulose, sulfoethylcellulose, methylhydroxyethylcellulose, carboxymethyl xyloglucan, carboxymethyl xylan, sulfoethylgalactomannan, carboxymethyl galactomannan, hydroxyethyl galactomannan, sulfoethyl starch, carboxymethyl starch, and mixture thereof. Other polysaccharides suitable for use in the present invention are the glucans. Preferred glucans are Poly alpha-1,3-glucan which is a polymer comprising glucose monomeric units linked together by glycosidic linkages (i.e., glucosidic linkages), wherein at least about 50% of the glycosidic linkages are alpha- 1,3-glycosidic linkages. Poly alpha-1,3-glucan is a type of polysaccharide. Poly alpha- 1,3-glucan can be enzymatically produced from sucrose using one or more glucosyltransferase enzymes, such as described in U.S. Pat. No. 7,000,000, and U.S. Patent Appl. Publ. Nos. 2013/0244288 and 2013/0244287 (all of which are incorporated herein by reference), for example.

Other suitable polysaccharides for use in the composition are cationic polysaccharides. Examples of cationic polysaccharides include cationic guar gum derivatives, quaternary nitrogen-containing cellulose ethers, and synthetic polymers that are copolymers of etherified cellulose, guar and starch. When used, the cationic polymers herein are either soluble in the composition or are soluble in a complex coacervate phase in the composition formed by the cationic polymer and the anionic, amphoteric and/or zwitterionic surfactant component described hereinbefore. Suitable cationic polymers are described in U.S. Pat. Nos. 3,962,418; 3,958,581; and U.S. Publication No. 2007/0207 109A1.

Polymers can also function as deposition aids for other detergent raw materials. Preferred deposition aids are selected from the group consisting of cationic and nonionic polymers. Suitable polymers include cationic starches, cationic hydroxyethylcellulose, polyvinylformaldehyde, locust bean gum, mannans, xyloglucans, tamarind gum, polyethyleneterephthalate and polymers containing dimethylaminoethyl methacrylate, optionally with one or more monomers selected from the group comprising acrylic acid and acrylamide.

#### *Additional Amines*

Polyamines are known to improve grease removal. Preferred cyclic and linear amines for performance are 1,3-bis (methylamine)-cyclohexane, 4-methylcyclohexane- 1,3-diamine (Baxxodur ECX 210 supplied by BASF) 1,3 propane diamine, 1,6 hexane diamine, 1,3 pentane diamine (Dytek EP supplied by Invista), 2-methyl 1,5 pentane diamine (Dytek A supplied by Invista). US67 10023 discloses hand dishwashing compositions containing said diamines and polyamines containing at least 3 protonable amines. Polyamines according to the invention have

at least one pka above the wash pH and at least two pka's greater than about 6 and below the wash pH. Preferred polyamines with are selected from the group consisting of tetraethylenepentamine, hexaethylhexamine, heptaethylheptamines, octaethyloctamines, nonethylnonamines, and mixtures thereof commercially available from Dow, BASF and Huntman. Especially preferred  
5 polyetheramines are lipophilic modified as described in US9752101, US9487739, US 963 1163

#### *Dye Transfer Inhibitor (DTI)*

The composition may comprise one or more dye transfer inhibiting agents. In one embodiment of the invention the inventors have surprisingly found that compositions comprising polymeric dye transfer inhibiting agents in addition to the specified dye give improved  
10 performance. This is surprising because these polymers prevent dye deposition. Suitable dye transfer inhibitors include, but are not limited to, polyvinylpyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof. Suitable examples include PVP-K15, PVP-K30, ChromaBond S-400, ChromaBond S-403E and Chromabond S-100 from Ashland Aqualon, and  
15 Sokalan HP165, Sokalan HP50, Sokalan HP53, Sokalan HP59, Sokalan® HP 56K, Sokalan® HP 66 from BASF. Other suitable DTIs are as described in WO2012/004134. When present in a subject composition, the dye transfer inhibiting agents may be present at levels from about 0.0001% to about 10%, from about 0.01% to about 5% or even from about 0.1% to about 3% by weight of the composition.

#### *Enzymes*

Enzymes may be included in the cleaning compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, carbohydrases, cellulases, oxidases,  
25 peroxidases, mannanases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal, and yeast origin. Other enzymes that may be used in the cleaning compositions described herein include hemicellulases, peroxidases, proteases, cellulases, endoglucanases, xylanases, lipases, phospholipases, amylases, gluco-amylases, xylanases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases,  
30 pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidases, chondroitinases, laccases, or mixtures thereof., esterases, mannanases, pectate lyases, and or mixtures thereof. Other suitable enzymes include Nuclease enzyme. The composition may comprise a nuclease enzyme. The nuclease enzyme is an enzyme capable of cleaving the

phosphodiester bonds between the nucleotide sub-units of nucleic acids. The nuclease enzyme herein is preferably a deoxyribonuclease or ribonuclease enzyme or a functional fragment thereof. Enzyme selection is influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders, and the like.

5 The enzymes may be incorporated into the cleaning composition at levels from 0.0001% to 5% of active enzyme by weight of the cleaning composition. The enzymes can be added as a separate single ingredient or as mixtures of two or more enzymes.

In some embodiments, lipase may be used. Lipase may be purchased under the trade name Lipex from Novozymes (Denmark). Amylases (Natalase®, Stainzyme®, Stainzyme Plus®) may  
10 be supplied by Novozymes, Bagsvaerd, Denmark. Proteases may be supplied by Genencor International, Palo Alto, Calif., USA (e.g. Purafect Prime®) or by Novozymes, Bagsvaerd, Denmark (e.g. Liquanase®, Coronase®, Savinase®). Other preferred enzymes include pectate lyases preferably those sold under the trade names Pectawash®, Xpect®, Pectaway® and the mannanases sold under the trade names Mannaway® (all from Novozymes A/S, Bagsvaerd,  
15 Denmark), and Purabrite® (Genencor International Inc., Palo Alto, California). A range of enzyme materials and means for their incorporation into synthetic cleaning compositions is disclosed in WO 9307263 A; WO 9307260 A; WO 8908694 A; U.S. Pat. Nos. 3,553,139; 4,101,457; and U.S. Pat. No. 4,507,219. Enzyme materials useful for liquid cleaning compositions, and their incorporation into such compositions, are disclosed in U.S. Pat. No. 4,261,868.

#### 20 *Enzyme Stabilizing System*

The enzyme-containing compositions described herein may optionally comprise from about 0.001% to about 10%, in some examples from about 0.005% to about 8%, and in other examples, from about 0.01% to about 6%, by weight of the composition, of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with  
25 the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, chlorine bleach scavengers and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form  
30 of the cleaning composition. See U.S. Pat. No. 4,537,706 for a review of borate stabilizers.

#### *Chelating Agent.*

Preferably the composition comprises chelating agents and/or crystal growth inhibitor. Suitable molecules include copper, iron and/or manganese chelating agents and mixtures thereof.

Suitable molecules include aminocarboxylates, aminophosphonates, succinates, salts thereof, and mixtures thereof. Non-limiting examples of suitable chelants for use herein include ethylenediaminetetracetates, N-(hydroxyethyl)-ethylene-diamine-triacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylene-tetraamine-hexacetates, diethylenetriamine-  
5 pentaacetates, ethanoldiglycines, ethylenediaminetetrakis (methylenephosphonates), diethylenetriamine penta(methylene phosphonic acid) (DTPMP), ethylenediamine disuccinate (EDDS), hydroxy ethanedimethylenephosphonic acid (HEDP), methylglycinediacetic acid (MGDA), diethylenetriaminepentaacetic acid (DTPA), and 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron), salts thereof, and mixtures thereof. Tiron as well as other sulphonated catechols may  
10 also be used as effective heavy metal chelants. Other non-limiting examples of chelants of use in the present invention are found in U.S. Patent Nos. 7445644, 7585376 and 2009/0176684A1. Other suitable chelating agents for use herein are the commercial DEQUEST series, and chelants from Monsanto, DuPont, and Nalco Inc.

#### *Brighteners*

15 Optical brighteners or other brightening or whitening agents may be incorporated at levels of from about 0.01% to about 1.2%, by weight of the composition, into the cleaning compositions described herein. Commercial optical brighteners, which may be used herein, can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphene-5,5-dioxide, azoles, 5-  
20 and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents," M. Zahradnik, John Wiley & Sons, New York (1982). Specific, non-limiting examples of optical brighteners which may be useful in the present compositions are those identified in U.S. Pat. No. 4,790,856 and U.S. Pat. No. 3,646,015. Highly preferred Brighteners include Disodium 4,4'-  
25 bis{[4-anilino-6-[bis(2-hydroxyethyl)amino-s-triazin-2-yl]-amino]-2,2'-stilbenedisulfonate, 4,4'-bis{[4-anilino-6-morpholino-s-triazin-2-yl]-amino}-2,2'-stilbenedisulfonate, Disodium 4,4"-bis[(4,6-di-anilino-s-triazin-2-yl)-amino]-2,2'-stilbenedisulfonate and disodium 4,4'-bis-(2-sulfostyryl)biphenyl.

#### *Bleaching Agents.*

30 It may be preferred for the composition to comprise one or more bleaching agents. Suitable bleaching agents include photobleaches, hydrogen peroxide, sources of hydrogen peroxide, pre-formed peracids and mixtures thereof.

(1) photobleaches for example sulfonated zinc phthalocyanine sulfonated aluminium phthalocyanines, xanthene dyes and mixtures thereof;

(2) pre-formed peracids: Suitable preformed peracids include, but are not limited to compounds selected from the group consisting of pre-formed peroxyacids or salts thereof typically a percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, for example, Oxone®, and mixtures thereof. Suitable examples include peroxydicarboxylic acids or salts thereof, or peroxydisulfonic acids or salts thereof. Particularly preferred peroxyacids are phthalimido-peroxy-alkanoic acids, in particular  $\epsilon$ -phthalimido peroxy hexanoic acid (PAP). Preferably, the peroxyacid or salt thereof has a melting point in the range of from 30°C to 60°C.

(3) sources of hydrogen peroxide, for example, inorganic perhydrate salts, including alkali metal salts such as sodium salts of perborate (usually mono- or tetra-hydrate), percarbonate, persulphate, perphosphate, persilicate salts and mixtures thereof.

#### Fabric Shading Dyes

The fabric shading dye (sometimes referred to as hueing, bluing or whitening agents) typically provides a blue or violet shade to fabric. Such dye(s) are well known in the art and may be used either alone or in combination to create a specific shade of hueing and/or to shade different fabric types. The fabric shading dye may be selected from any chemical class of dye as known in the art, including but not limited to acridine, anthraquinone (including polycyclic quinones), azine, azo (e.g., monoazo, disazo, trisazo, tetrakisazo, polyazo), benzodifurane, benzodifuranone, carotenoid, coumarin, cyanine, diazahemicyanine, diphenylmethane, formazan, hemicyanine, indigoids, methane, naphthalimides, naphthoquinone, nitro, nitroso, oxazine, phthalocyanine, pyrazoles, stilbene, styryl, triarylmethane, triphenylmethane, xanthenes and mixtures thereof. The amount of adjunct fabric shading dye present in a laundry care composition of the invention is typically from 0.0001 to 0.05 wt% based on the total cleaning composition, preferably from 0.0001 to 0.005 wt%. Based on the wash liquor, the concentration of fabric shading dye typically is from 1 ppb to 5 ppm, preferably from 10 ppb to 500 ppb.

Suitable fabric shading dyes include small molecule dyes, polymeric dyes and dye-clay conjugates. Preferred fabric shading dyes are selected from small molecule dyes and polymeric dyes. Suitable small molecule dyes may be selected from the group consisting of dyes falling into the Colour Index (C.I., Society of Dyers and Colourists, Bradford, UK) classifications of Acid, Direct, Basic, Reactive, Solvent or Disperse dyes.

Suitable polymeric dyes include dyes selected from the group consisting of polymers containing covalently bound (sometimes referred to as conjugated) chromogens, (also known as dye-polymer conjugates), for example polymers with chromogen monomers co-polymerized into the backbone of the polymer and mixtures thereof. Preferred polymeric dyes comprise the  
5 optionally substituted alkoxyated dyes, such as alkoxyated triphenyl-methane polymeric colourants, alkoxyated carbocyclic and alkoxyated heterocyclic azo colourants including alkoxyated thiophene polymeric colourants, and mixtures thereof, such as the fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA).

Suitable dye clay conjugates include dye clay conjugates selected from the group  
10 comprising at least one cationic/basic dye and a smectite clay; a preferred clay may be selected from the group consisting of Montmorillonite clay, Hectorite clay, Saponite clay and mixtures thereof.

Pigments are well known in the art and may also be used in the laundry care compositions herein. Suitable pigments include C.I Pigment Blues 15 to 20, especially 15 and/or 16, C.I. Pigment  
15 Blue 29, C.I. Pigment Violet 15, Monastral Blue and mixtures thereof.

#### *Builders*

The cleaning compositions of the present invention may optionally comprise a builder. Builders selected from aluminosilicates and silicates assist in controlling mineral hardness in wash water, or to assist in the removal of particulate soils from surfaces. Suitable builders may be  
20 selected from the group consisting of phosphates polyphosphates, especially sodium salts thereof; carbonates, bicarbonates, sesquicarbonates, and carbonate minerals other than sodium carbonate or sesquicarbonate; organic mono-, di-, tri-, and tetracarboxylates, especially water-soluble non-surfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and  
25 aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing cleaning compositions.

#### *pH Buffer System*

The compositions may also include a pH buffer system. The cleaning compositions herein  
30 may be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.0 and about 12, and in some examples, between about 7.0 and 11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, or acids, and are well known to those skilled in the art. These include, but are not limited to, the use

of sodium carbonate, citric acid or sodium citrate, monoethanol amine or other amines, boric acid or borates, and other pH-adjusting compounds well known in the art. The cleaning compositions herein may comprise dynamic in-wash pH profiles by delaying the release of citric acid.

#### *Structurant/ Thickeners*

5            Structured liquids can either be internally structured, whereby the structure is formed by primary ingredients (e.g. surfactant material) and/or externally structured by providing a three dimensional matrix structure using secondary ingredients (e.g. polymers, clay and/or silicate material). The composition may comprise from about 0.01% to about 5%, by weight of the composition, of a structurant, and in some examples, from about 0.1% to about 2.0%, by weight of  
10 the composition, of a structurant. The structurant may be selected from the group consisting of diglycerides and triglycerides, ethylene glycol distearate, microcrystalline cellulose, cellulose-based materials, microfiber cellulose, biopolymers, xanthan gum, gellan gum, and mixtures thereof. In some examples, a suitable structurant includes hydrogenated castor oil, and non-ethoxylated derivatives thereof. Other suitable structurants are disclosed in US Patent No.  
15 6,855,680. Such structurants have a thread-like structuring system having a range of aspect ratios. Further suitable structurants and the processes for making them are described in WO 2010/034736.

#### *Suds Suppressors*

Compounds for reducing or suppressing the formation of suds can be incorporated into the cleaning compositions described herein. Suds suppression can be of particular importance in the  
20 so-called "high concentration cleaning process" as described in U.S. Pat. No. 4,489,455, 4,489,574, and in front-loading style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). Examples  
25 of suds suppressors include monocarboxylic fatty acid, and soluble salts therein, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C18-C40 ketones (e.g., stearone), N-alkylated amino triazines, waxy hydrocarbons preferably having a melting point below about 100 °C, silicone suds suppressors, and secondary alcohols. Suds suppressors are described in U.S. Pat. Nos. 2,954,347;  
30 4,075,118; 4,265,779; 4,265,779; 3,455,839; 3,933,672; 4,652,392; 4,978,471; 4,983,316; 5,288,431; 4,639,489; 4,749,740; and 4,798,679.

The cleaning compositions herein may comprise from 0% to about 10%, by weight of the composition, of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids,

and salts thereof, may be present in amounts up to about 5% by weight of the cleaning composition, and in some examples, may be from about 0.5% to about 3% by weight of the cleaning composition. Silicone suds suppressors may be utilized in amounts up to about 2.0% by weight of the cleaning composition, although higher amounts may be used. Monostearyl phosphate suds suppressors may be utilized in amounts ranging from about 0.1% to about 2% by weight of the cleaning composition. Hydrocarbon suds suppressors may be utilized in amounts ranging from about 0.01% to about 5.0% by weight of the cleaning composition, although higher levels can be used. Alcohol suds suppressors may be used at about 0.2% to about 3% by weight of the cleaning composition.

#### 10 *Suds Boosters*

If high sudsing is desired, suds boosters such as the C10-C16 alkanolamides may be incorporated into the cleaning compositions from about 1% to about 10% by weight of the cleaning composition. Some examples include the C10-C14 monoethanol and diethanol amides. If desired, water-soluble magnesium and/or calcium salts such as MgCh, MgSO<sub>4</sub>, CaCh, CaSO<sub>4</sub>, and the like, may be added at levels of about 0.1% to about 2% by weight of the cleaning composition, to provide additional suds and to enhance grease removal performance.

#### *Fillers and Carriers*

Fillers and carriers may be used in the cleaning compositions described herein. As used herein, the terms "filler" and "carrier" have the same meaning and can be used interchangeably. Liquid cleaning compositions, and other forms of cleaning compositions that include a liquid component (such as liquid-containing unit dose cleaning compositions), may contain water and other solvents as fillers or carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, isopropanol, and phenoxyethanol are suitable. Monohydric alcohols may be used in some examples for solubilizing surfactants, and polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,2-propanediol, 1,3-propanediol, 2,3-butanediol, ethylene glycol, and glycerine may be used). Amine-containing solvents may also be used.

#### *Methods of Use*

The present invention includes methods for whitening fabric. Compact fluid detergent compositions that are suitable for sale to consumers are suited for use in laundry pretreatment applications, laundry cleaning applications, and home care applications. Such methods include, but are not limited to, the steps of contacting detergent compositions in neat form or diluted in wash

liquor, with at least a portion of a fabric which may or may not be soiled and then optionally rinsing the fabric. The fabric material may be subjected to a washing step prior to the optional rinsing step. Machine laundry methods may comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry  
5 detergent composition in accord with the invention. An "effective amount" of the detergent composition means from about 20 g to about 300g of product dissolved or dispersed in a wash solution of volume from about 5L to about 65L. The water temperatures may range from about 5° C. to about 100° C. The water to soiled material (e.g., fabric) ratio may be from about 1:1 to about 30: 1. The compositions may be employed at concentrations of from about 500 ppm to about 15,000  
10 ppm in solution. In the context of a fabric laundry composition, usage levels may also vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water, and the type of washing machine (e.g., top-loading, front-loading, vertical-axis Japanese-type automatic washing machine).

The detergent compositions herein may be used for laundering of fabrics at reduced wash  
15 temperatures. These methods of laundering fabric comprise the steps of delivering a laundry detergent composition to water to form a wash liquor and adding a laundering fabric to said wash liquor, wherein the wash liquor has a temperature of from about 0 °C to about 20° C, or from about 0° C to about 15° C, or from about 0° C to about 9° C. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the laundry detergent composition with water.  
20 Another method includes contacting a nonwoven substrate, which is impregnated with the detergent composition, with a soiled material. As used herein, "nonwoven substrate" can comprise any conventionally fashioned nonwoven sheet or web having suitable basis weight, caliper (thickness), absorbency, and strength characteristics. Non-limiting examples of suitable commercially available nonwoven substrates include those marketed under the trade names  
25 SONTARA® by DuPont and POLY WEB® by James River Corp.

Hand washing/soak methods, and combined hand washing with semi-automatic washing machines, are also included.

#### *Packaging for the Compositions*

The cleaning compositions described herein can be packaged in any suitable container  
30 including those constructed from paper, cardboard, plastic materials, and any suitable laminates. An optional packaging type is described in European Application No. 94921505.7.

#### *Multi-Compartment Pouch*

The cleaning compositions described herein may also be packaged as a multi-compartment cleaning composition.

#### *Other Adjunct Ingredients*

A wide variety of other ingredients may be used in the cleaning compositions herein, including, for example, other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid or other liquid fillers, erythrosine, colloidal silica, waxes, probiotics, surfactin, aminocellulosic polymers, Zinc Ricinoleate, perfume microcapsules, rhamnolipids, sphorolipids, glycopeptides, methyl ester ethoxylates, sulfonated estolides, cleavable surfactants, biopolymers, silicones, modified silicones, aminosilicones, deposition aids, hydrotropes (especially cumene-sulfonate salts, toluene-sulfonate salts, xylene-sulfonate salts, and naphalene salts), PVA particle-encapsulated dyes or perfumes, pearlescent agents, effervescent agents, color change systems, silicone polyurethanes, opacifiers, tablet disintegrants, biomass fillers, fast-dry silicones, glycol distearate, starch perfume encapsulates, emulsified oils including hydrocarbon oils, polyolefins, and fatty esters, bisphenol antioxidants, micro-fibrous cellulose structurants, properfumes, styrene/acrylate polymers, triazines, soaps, superoxide dismutase, benzophenone protease inhibitors, functionalized TiO<sub>2</sub>, dibutyl phosphate, silica perfume capsules, and other adjunct ingredients, choline oxidase, triarylmethane blue and violet basic dyes, methine blue and violet basic dyes, anthraquinone blue and violet basic dyes, azo dyes basic blue 16, basic blue 65, basic blue 66 basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48, oxazine dyes, basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141, Nile blue A and xanthene dye basic violet 10, an alkoxyated triphenylmethane polymeric colorant; an alkoxyated thiopene polymeric colorant; thiazolium dye, mica, titanium dioxide coated mica, bismuth oxychloride, and other actives.

Anti-oxidant: The composition may optionally contain an anti-oxidant present in the composition from about 0.001 to about 2% by weight. Preferably the antioxidant is present at a concentration in the range 0.01 to 0.08% by weight. Mixtures of anti-oxidants may be used.

One class of anti-oxidants used in the present invention is alkylated phenols. Hindered phenolic compounds are a preferred type of alkylated phenols having this formula. A preferred hindered phenolic compound of this type is 3,5-di-tert-butyl-4-hydroxytoluene (BHT).

Furthermore, the anti-oxidant used in the composition may be selected from the group consisting of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -tocopherol, ethoxyquin, 2,2,4-trimethyl-1,2-dihydroquinoline, 2,6-di-tert-butyl hydroquinone, tert-butyl hydroxyanisole, lignosulphonic acid and salts thereof, and mixtures thereof.

The cleaning compositions described herein may also contain vitamins and amino acids such as: water soluble vitamins and their derivatives, water soluble amino acids and their salts and/or derivatives, water insoluble amino acids viscosity modifiers, dyes, nonvolatile solvents or diluents (water soluble and insoluble), pearlescent aids, pediculocides, pH adjusting agents, 5 preservatives, skin active agents, sunscreens, UV absorbers, niacinamide, caffeine, and minoxidil.

The cleaning compositions of the present invention may also contain pigment materials such as nitroso, monoazo, disazo, carotenoid, triphenyl methane, triaryl methane, xanthene, quinoline, oxazine, azine, anthraquinone, indigoid, thionindigoid, quinacridone, phthalocyanine, botanical, and natural colors, including water soluble components such as those having C.I. Names.

10 The cleaning compositions of the present invention may also contain antimicrobial agents. Cationic active ingredients may include but are not limited to n-alkyl dimethyl benzyl ammonium chloride, alkyl dimethyl ethyl benzyl ammonium chloride, dialkyl dimethyl quaternary ammonium compounds such as didecyl dimethyl ammonium chloride, N,N-didecyl-Nmethyl-poly(oxyethyl) ammonium propionate, dioctyl didecyl ammonium chloride, also including quaternary species 15 such as benzethonium chloride and quaternary ammonium compounds with inorganic or organic counter ions such as bromine, carbonate or other moieties including dialkyl dimethyl ammonium carbonates, as well as antimicrobial amines such as Chlorhexidine Gluconate, PHMB (Polyhexamethylene biguanide), salt of a biguanide, a substituted biguanide derivative, an organic salt of a quaternary ammonium containing compound or an inorganic salt of a quaternary 20 ammonium containing compound or mixtures thereof.

In one aspect, such method comprises the steps of optionally washing and/or rinsing said surface or fabric, contacting said surface or fabric with any composition disclosed in this specification then optionally washing and/or rinsing said surface or fabric is disclosed, with an optional drying step.

25 Drying of such surfaces or fabrics may be accomplished by any one of the common means employed either in domestic or industrial settings. The fabric may comprise any fabric capable of being laundered in normal consumer or institutional use conditions, and the invention is suitable for cellulosic substrates and in some aspects also suitable for synthetic textiles such as polyester and nylon and for treatment of mixed fabrics and/or fibers comprising synthetic and cellulosic 30 fabrics and/or fibers. As examples of synthetic fabrics are polyester, nylon, these may be present in mixtures with cellulosic fibers, for example, polycotton fabrics. The solution typically has a pH of from 7 to 11, more usually 8 to 10.5. The compositions are typically employed at concentrations

from 500 ppm to 5,000 ppm in solution. The water temperatures typically range from about 5°C to about 90°C. The water to fabric ratio is typically from about 1:1 to about 30:1.

### Test Methods

Fabric swatches used in the test methods herein are obtained from Testfabrics, Inc. West Pittston, PA, and are 100% Cotton, Style 403 (cut to 2" x 2") and/or Style 464 (cut to 4" x 6"), and an unbrightened multifiber fabric, specifically Style 41 (5cm x 10cm).

All reflectance spectra and color measurements, including L\*, a\*, b\*, K/S, and Whiteness Index (WI CIE) values on dry fabric swatches, are made using one of four spectrophotometers: (1) a Konica-Minolta 3610d reflectance spectrophotometer (Konica Minolta Sensing Americas, Inc., Ramsey, NJ, USA; D65 illumination, 10° observer, UV light excluded), (2) a LabScan XE reflectance spectrophotometer (HunterLabs, Reston, VA; D65 illumination, 10° observer, UV light excluded), (3) a Color-Eye® 7000A (GretagMacbeth, New Windsor, NY, USA; D65 light, UV excluded), or (4) a Color i7 spectrophotometer (X-rite, Inc., Grand Rapids, MI, USA; D65 light, UV excluded). Measurements are performed using two layers of fabric, obtained by stacking smaller internal replicates (e.g., 2" x 2" Style 403) or folding of larger fabric swatches (e.g., 4" x 6" style 464).

Where fabrics are irradiated, unless otherwise indicated, the specified fabrics post-dry are exposed to simulated sunlight with irradiance of 0.77 W/m<sup>2</sup> @ 420 nm in an Atlas Xenon Fade-Ometer Q3000+ (Atlas Material Testing Technology, Mount Prospect, Illinois, USA) equipped with Type S Borosilicate inner (Part no. 20277300) and outer (Part no. 20279600) filters, set at 37 °C maximum cabinet temperature, 57 °C maximum black panel temperature (BPT black panel geometry), and 35% RH (relative humidity). Unless otherwise indicated, irradiation is continuous over the stated duration.

#### I. Method for Determining Leuco Colorant Efficiency from a Wash Solution

Cotton swatches (Style 403) are stripped prior to use by washing at 49°C two times with heavy duty liquid laundry detergent nil brightener (1.55 g/L in aqueous solution). A concentrated stock solution of each leuco colorant to be tested is prepared in a solvent selected from ethanol or 50:50 ethanol:water, preferably ethanol.

### A. Liquid medium without converting agent

A base wash solution is prepared by dissolving AATCC heavy duty liquid laundry detergent nil brightener (5.23 g/1.0 L) in deionized water. Four stripped cotton swatches are weighed together and placed in a 250mL Erlenmeyer flask along with two 10mm glass marbles. A total of three such flasks are prepared for each wash solution to be tested. The base wash solution is dosed with the leuco colorant stock to achieve a wash solution with the desired  $2.0 \times 10^{-6} N$  wash concentration of the leuco colorant. (By way of example, a 1.0 ppm wash solution of a leuco colorant with equivalent weight of 493.65 g/equivalent, or a 1.5 ppm wash solution of a leuco colorant with equivalent weight of 757.97 g/equivalent, provides a wash solution that is  $2.0 \times 10^{-6} N$  leuco.)

An aliquot of this wash solution sufficient to provide a 10.0:1.0 liquor:fabric (w/w) ratio is placed into each of the three 250mL Erlenmeyer flasks. Each flask is dosed with a 1000 gpg stock hardness solution to achieve a final wash hardness of 6 gpg (3:1 Ca:Mg).

The flasks are placed on a Model 75 wrist action shaker (Burrell Scientific, Inc., Pittsburg, PA) and agitated at the maximum setting for 12 minutes, after which the wash solution is removed by aspiration, and a volume of rinse water (0 gpg) equivalent to the amount of wash solution used is added. Each flask is dosed with a 1000 gpg stock hardness solution to achieve a final rinse hardness of 6 gpg (3:1 Ca:Mg) before agitating 4 more minutes. The rinse is removed by aspiration and the fabric swatches are spun dry (Mini Countertop Spin Dryer, The Laundry Alternative Inc., Nashua, NH) for 1 minute, then placed in a food dehydrator set at 135 °F to dry in the dark for 2 hours.

$L^*$ ,  $a^*$ ,  $b^*$  and Whiteness Index (WI CIE) values for the cotton fabrics are measured on the dry swatches at 0, 6, 24 and 48 hours after drying using a LabScan XE reflectance spectrophotometer. The  $L^*$ ,  $a^*$ , and  $b^*$  values of the 12 swatches generated for each leuco colorant (three flasks with four swatches each) are averaged and the leuco colorant efficiency (LCE) of each leuco colorant is calculated based on the data collected at 48 hours using the following equation:

$$LCE = DE^* = ((L^*_c - L^*_s)^2 + (a^*_c - a^*_s)^2 + (b^*_c - b^*_s)^2)^{1/2}$$

wherein the subscripts c and s respectively refer to the control, i.e., the fabric washed in detergent with no leuco colorant, and the sample, i.e., the fabric washed in detergent containing leuco colorant.

**B. Liquid medium with converting agent (no supplemental converting agent)**

A base wash solution is prepared by dissolving heavy duty liquid laundry detergent nil brightener (5.23 g/1.0 L) in municipal water where the municipal water has been treated with chlorine. The level of free chlorine and total chlorine in the municipal water may be measured according to the manufacturer's instructions using CHEMetrics' chlorine Vacu-vials® (CHEMetrics, Inc., Midland, VA). Four stripped cotton swatches are weighed together and placed in a 250mL Erlenmeyer flask along with two 10mm glass marbles. A total of three such flasks are prepared for each wash solution to be tested. The base wash solution is dosed with the leuco colorant stock to achieve a wash solution with the desired  $2.0 \times 10^{-6} N$  wash concentration of the leuco colorant.

An aliquot of this wash solution sufficient to provide a 10.0:1.0 liquor:fabric (w/w) ratio is placed into each of the three 250mL Erlenmeyer flasks.

The flasks are placed on a Model 75 wrist action shaker (Burrell Scientific, Inc., Pittsburg, PA) and agitated at the maximum setting for 12 minutes, after which the wash solution is removed by aspiration. A volume of municipal water equivalent to the amount of wash solution used is added before agitating 4 more minutes. The rinse is removed by aspiration and the fabric swatches are spun dry (Mini Countertop Spin Dryer, The Laundry Alternative Inc., Nashua, NH) for 1 minute, then placed in a food dehydrator set at 135 °F to dry in the dark for 2 hours.

$L^*$ ,  $a^*$ ,  $b^*$ , and Whiteness Index (WI CIE) values for the cotton fabrics are measured on the dry swatches at 0, 6, 24 and 48 hours after drying using a LabScan XE reflectance spectrophotometer. The  $L^*$ ,  $a^*$ , and  $b^*$  values of the 12 swatches generated for each leuco colorant (three flasks with four swatches each) are averaged and the leuco colorant efficiency (LCE) of each leuco colorant is calculated based on the data collected at 48 hours using the following equation:

$$LCE = DE^* = ((L^*_c - L^*_s)^2 + (a^*_c - a^*_s)^2 + (b^*_c - b^*_s)^2)^{1/2}$$

wherein the subscripts c and s respectively refer to the control, i.e., the fabric washed in detergent with no leuco colorant, and the sample, i.e., the fabric washed in detergent containing leuco colorant.

### C. Liquid medium with converting agent plus supplemental converting agent

A base wash solution is prepared by dissolving heavy duty liquid laundry detergent nil brightener (5.23 g/1.0 L) in municipal water where the municipal water has been treated with chlorine. The level of free chlorine and total chlorine in the municipal water may be measured according to the manufacturer's instructions using CHEMetrics' chlorine Vacu-vials® (CHEMetrics, Inc., Midland, VA). Four stripped cotton swatches are weighed together and placed in a 250mL Erlenmeyer flask along with two 10mm glass marbles. A total of three such flasks are prepared for each wash solution to be tested.

The base wash solution is dosed with the leuco colorant stock to achieve a wash solution with the desired  $2.0 \times 10^{-6} N$  wash concentration of the leuco colorant. Thereafter the wash solution is dosed with a stock solution containing the supplemental converting agent in an amount sufficient to supply a minimum of 2.0:1.0 ratio of equivalents of the converting agent to the leuco compound present in the wash solution. Other methods that may be employed ensure the supplemental converting agent is present in an amount sufficient to supply a minimum of a 5.0:1.0 ratio, a 10:1.0 ratio or even a 25:1 ratio.

An aliquot of this wash solution sufficient to provide a 10.0:1.0 liquor:fabric (w/w) ratio is placed into each of the three 250mL Erlenmeyer flasks.

The flasks are placed on a Model 75 wrist action shaker (Burrell Scientific, Inc., Pittsburg, PA) and agitated at the maximum setting for 12 minutes, after which the wash solution is removed by aspiration. A volume of municipal water equivalent to the amount of wash solution used is added before agitating 4 more minutes. The rinse is removed by aspiration and the fabric swatches are spun dry (Mini Countertop Spin Dryer, The Laundry Alternative Inc., Nashua, NH) for 1 minute, then placed in a food dehydrator set at 135 °F to dry in the dark for 2 hours.

$L^*$ ,  $a^*$ ,  $b^*$ , and Whiteness Index (WI CIE) values for the cotton fabrics are measured on the dry swatches at 0, 6, 24 and 48 hours after drying using a LabScan XE reflectance spectrophotometer. The  $L^*$ ,  $a^*$ , and  $b^*$  values of the 12 swatches generated for each leuco colorant (three flasks with four swatches each) are averaged and the leuco colorant efficiency (LCE) of each leuco colorant is calculated based on the data collected at 48 hours using the following equation:

$$LCE = DE^* = ((L^*_c - L^*_s)^2 + (a^*_c - a^*_s)^2 + (b^*_c - b^*_s)^2)^{1/2}$$

wherein the subscripts c and s respectively refer to the control, i.e., the fabric washed in detergent with no leuco colorant, and the sample, i.e., the fabric washed in detergent containing leuco colorant.

## II. Method for Determining Relative Hue Angle (vs. Nil Leuco Colorant)

5 The relative hue angle delivered by a leuco colorant to cotton fabrics treated according to Method I described above is determined as follows.

- a) The  $a^*$  and  $b^*$  values of the 12 swatches at 48 hours from each solution are averaged and the following formulas used to determine  $Aa^*$  and  $Ab^*$ :

$$Aa^* = a^*_s - a^*_c \quad \text{and} \quad Ab^* = b^*_s - b^*_c$$

10 wherein the subscripts c and s respectively refer to the fabric washed in detergent with no leuco colorant and the fabric washed in detergent containing leuco colorant.

- b) If the absolute value of both  $Aa^*$  and  $Ab^* < 0.25$ , no Relative Hue Angle (RHA) is calculated. If the absolute value of either  $Aa^*$  or  $Ab^*$  is  $\geq 0.25$ , the RHA is determined using one of the following formulas:

15 
$$RHA = \text{ATAN2}(Aa^*, Ab^*) \text{ for } Ab^* \geq 0$$

$$RHA = 360 + \text{ATAN2}(Aa^*, Ab^*) \text{ for } Ab^* < 0$$

A relative hue angle can be calculated for each time point where data is collected in either the dark post-dry or light post-dry assessments. Any of these points may be used to satisfy the requirements of a claim.

## 20 III. Method for Determining Leuco Whiteness Improvement Number (LWIN)

The Leuco Whiteness Improvement Number (LWIN) represents the change in whiteness improvement between a textile article washed with a laundry care composition comprising a leuco composition and a textile article washed with a laundry care composition lacking a leuco composition. The liquid medium is the same for both treatments and may be a liquid medium  
25 without supplemental converting agent or one with supplemental converting agent.

The change in Whiteness Index for the cotton fabrics washed in a composition according to Method I above is calculated according to the following equation:

$$AWI = WI_{CIE \text{ after wash}} - WI_{CIE \text{ before wash}}$$

Wherein the textile article "control" is washed in a laundry care composition lacking a leuco composition and the textile article "sample" is washed in a laundry care composition comprising a leuco composition.

The LWIN is calculated according to the following equation:

$$LWIN = [(AWI_{\text{sample}} - AWI_{\text{control}}) / AWI_{\text{control}}] \times 100\%$$

As is apparent, the three different liquid media used in Method I above can give rise to three separate LWIN values, one for deionized water (lacking any converting agent), one for municipal water (comprising some converting agent), and one for municipal water plus supplemental converting agent.

In the event that the value of the  $AWI_{\text{control}}$  turns out to be 0.0, the positive value of the standard deviation for the measurement of that value in that test may be supplied as the value for the  $AWI_{\text{control}}$ , so that the LWIN may be calculated (note the denominator ( $AWI_{\text{control}}$ ) cannot be zero or the value is undefined).

### Application Examples 1-10

#### Bluing effect of leuco compounds in different liquid medium

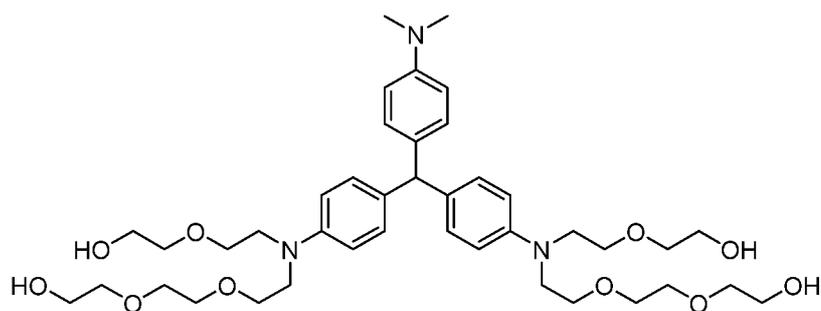
Tap water is often treated with chlorine species to disinfect. Commonly used disinfecting agents include, but are not limited to, chlorine, chlorine dioxide, chloramine, and combinations thereof. The method of measuring the chlorine level in water is well known to those skilled in the art. One method uses a chlorine kit and colorimeter commercialized by Hach. Since disinfecting agents are oxidizing in nature, different water sources will have an influence on the bluing efficacy of the leuco compound. The effect of chlorine species on bluing is dependent on the formulation of the detergent. Some detergent formulations contain a "chlorine scavenger" which acts to deactivate the active chlorine in the tap water. Other additives in detergent formulations, such as the anti-oxidant and reducing agent, may also have effect on the chlorine species.

Table 1 lists some application examples using leuco colorant in water with different chlorine source and concentration. The total chlorine level was measured using Hach total chlorine kit and colorimeter.

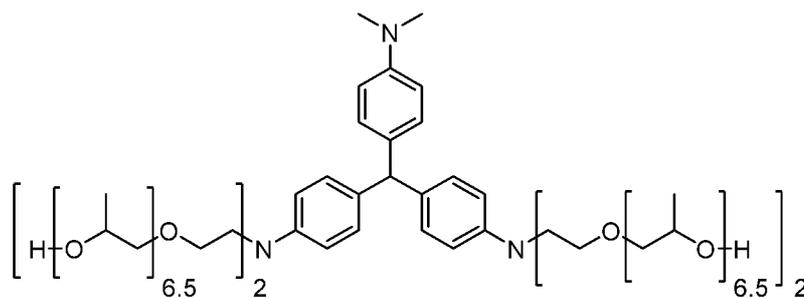
In a 1 liter beaker, 500 mL of water, 0.5 gram of detergent (Tide® Free and Gentle liquid  
 5 detergent, pH about 8-9), and the leuco dye to be tested (loading of the leuco dye was included in  
 Table 1 below) were mixed. The leuco dye can be introduced into the wash water by either 1)  
 premixing with the detergent or 2) pre-dissolving in about 1 mL of organic solvent and then add  
 directly into the wash water. Six pieces of bleached cotton t-shirt fabric (purchased from  
 Testfabrics, Inc., style number 437W-60, cut to 6" by 6" size) were added to the wash water and  
 10 washed with tergotometer at room temperature for 15 minutes. The fabric/water ratio was about  
 40 gram/liter. After wash, the fabric samples were rinsed by hand with 500 mL testing water twice  
 and then dried in a dryer for 1 hour. The CIE L\*, a\*, and b\* values were read with a color eye  
 spectrophotometer.

The delta b\* values of the cotton washed with different leuco colorants are reported in  
 15 Table 1 below. The delta b\* values were obtained by subtraction with the b\* value of the same  
 kind of fabrics washed with no leuco colorants following the same procedure described above.

The leuco dyes tested are shown below.

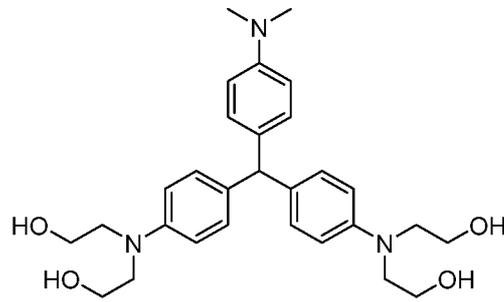


Leuco A

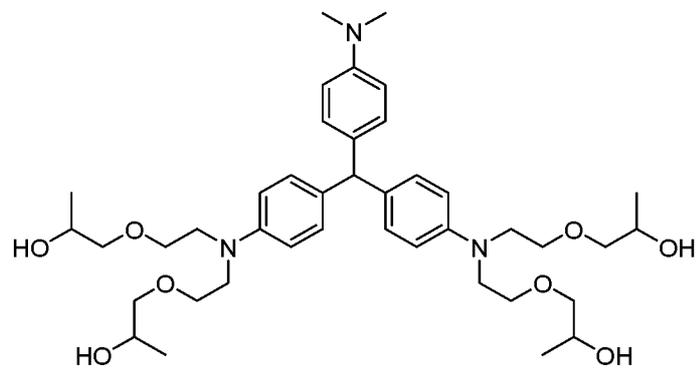


Leuco B

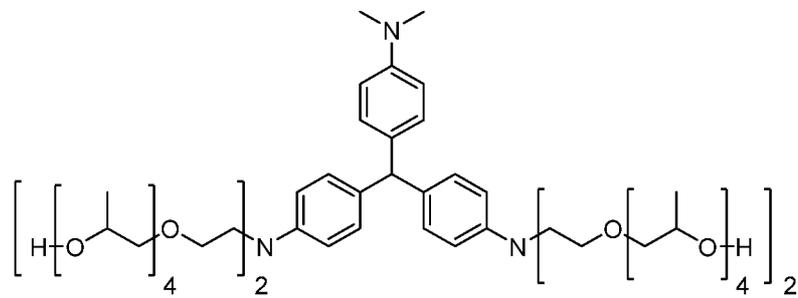
43



Leuco C



Leuco D



Leuco E

5

Table 1. Results for Application Examples 1-10

Ex	Leuco		Total Chlorine		
	Compound	(ppm)	(ppm)	Species	delta b*
1	C	1	0	-	-0.5
2	C	1	2.82	Chloramine	-1.1
3	C	1	1.16	Chlorine	-1.0
4	D	1	0	-	-0.5
5	A	0.2	1.58	Chlorine and ClO <sub>2</sub>	-1.6

6	<b>A</b>	0.2	0	–	0
7	<b>A</b>	0.2	2.82	Chloramine	-0.1
8	<b>A</b>	0.2	1.16	Chlorine	-0.2
9	<b>B</b>	1	0	–	-0.1
10	<b>E</b>	1	0	–	-0.3

Leuco colorants **A** and **C** both demonstrate enhanced bluing when used in a liquid medium that comprises a converting agent versus the bluing achieved in a liquid medium without converting agent.

5

**Formulation Examples**

The following are illustrative examples of cleaning compositions according to the present disclosure and are not intended to be limiting.

Examples 1-7: Heavy Duty Liquid laundry detergent compositions.

<b><u>Ingredients</u></b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
	% weight						
AE <sub>1</sub> S	6.77	5.16	1.36	1.30	-	-	-
AE <sub>3</sub> S	-	-	-	-	0.45	-	-
LAS	0.86	2.06	2.72	0.68	0.95	1.56	3.55
HSAS	1.85	2.63	1.02	-	-	-	-
AE9	6.32	9.85	10.20	7.92			
AE8							35.45
AE7					8.40	12.44	
C <sub>12-14</sub> dimethyl Amine Oxide	0.30	0.73	0.23	0.37	-	-	-
C <sub>12-18</sub> Fatty Acid	0.80	1.90	0.60	0.99	1.20	-	15.00
Citric Acid	2.50	3.96	1.88	1.98	0.90	2.50	0.60
Optical Brightener 1	1.00	0.80	0.10	0.30	0.05	0.50	0.001
Optical Brightener 3	0.001	0.05	0.01	0.20	0.50	-	1.00
Sodium formate	1.60	0.09	1.20	0.04	1.60	1.20	0.20
DTI	0.32	0.05	-	0.60	-	0.60	0.01
Sodium hydroxide	2.30	3.80	1.70	1.90	1.70	2.50	2.30
Monoethanolamine	1.40	1.49	1.00	0.70	-	-	-

Diethylene glycol	5.50	-	4.10	-	-	-	-
Chelant 1	0.15	0.15	0.11	0.07	0.50	0.11	0.80
4-formyl-phenylboronic acid	-	-	-	-	0.05	0.02	0.01
Sodium tetraborate	1.43	1.50	1.10	0.75	-	1.07	-
Ethanol	1.54	1.77	1.15	0.89	-	3.00	7.00
Polymer 1	0.10	-	-	-	-	-	2.00
Polymer 2	0.30	0.33	0.23	0.17	-	-	-
Polymer 3	-	-	-	-	-	-	0.80
Polymer 4	0.80	0.81	0.60	0.40	1.00	1.00	-
1,2-Propanediol	-	6.60	-	3.30	0.50	2.00	8.00
Structurant	0.10	-	-	-	-	-	0.10
Perfume	1.60	1.10	1.00	0.80	0.90	1.50	1.60
Perfume encapsulate	0.10	0.05	0.01	0.02	0.10	0.05	0.10
Protease	0.80	0.60	0.70	0.90	0.70	0.60	1.50
Mannanase	0.07	0.05	0.045	0.06	0.04	0.045	0.10
Amylase 1	0.30	-	0.30	0.10	-	0.40	0.10
Amylase 2	-	0.20	0.10	0.15	0.07	-	0.10
Xyloglucanase	0.20	0.10	-	-	0.05	0.05	0.20
Lipase	0.40	0.20	0.30	0.10	0.20	-	-
Polishing enzyme	-	0.04	-	-	-	0.004	-
Nuclease	0.05	-	-	-	-	-	0.003
Dispersin B	-	-	-	0.05	0.03	0.001	0.001
Liquitint® V200	0.01	-	-	-	-	-	0.005
Leuco colorant	0.05	0.035	0.01	0.02	0.004	0.002	0.004
Dye control agent	-	0.3	-	0.03	-	0.3	0.3
Water, dyes & minors	Balance						
pH	8.2						

Based on total cleaning and/or treatment composition weight. Enzyme levels are reported as raw material.

Examples 8 to 18: Unit Dose Compositions.

These examples provide various formulations for unit dose laundry detergents. Compositions 8 to 12 comprise a single unit dose compartment. The film used to encapsulate the compositions is polyvinyl- alcohol-based film.

<b><u>Ingredients</u></b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
	<b>% weight</b>				
LAS	19.09	16.76	8.59	6.56	3.44
AE3S	1.91	0.74	0.18	0.46	0.07
AE7	14.00	17.50	26.33	28.08	31.59
Citric Acid	0.6	0.6	0.6	0.6	0.6
C12-15 Fatty Acid	14.8	14.8	14.8	14.8	14.8
Polymer 3	4.0	4.0	4.0	4.0	4.0
Chelant 2	1.2	1.2	1.2	1.2	1.2
Optical Brightener 1	0.20	0.25	0.01	0.01	0.50
Optical Brightener 2	0.20	-	0.25	0.03	0.01
Optical Brightener 3	0.18	0.09	0.30	0.01	-
DTI	0.10	-	0.20	-	-
Glycerol	6.1	6.1	6.1	6.1	6.1
Monoethanol amine	8.0	8.0	8.0	8.0	8.0
Tri-isopropanol amine	-	-	2.0	-	-
Tri-ethanol amine	-	2.0	-	-	-
Cumene sulfonate	-	-	-	-	2.0
Protease	0.80	0.60	0.07	1.00	1.50
Mannanase	0.07	0.05	0.05	0.10	0.01
Amylase 1	0.20	0.11	0.30	0.50	0.05
Amylase 2	0.11	0.20	0.10	-	0.50
Polishing enzyme	0.005	0.05	-	-	-
Nuclease	0.-	0.05	-	-	0.005
Dispersin B	0.010	0.05	0.005	0.005	-
Cyclohexyl dimethanol	-	-	-	2.0	-
Leuco Colorant	0.06	0.03	0.10	0.02	0.04
Liquitint <sup>®</sup> V200	-	-	0.01	0.05	-

Structurant	0.14	0.14	0.14	0.14	0.14
Perfume	1.9	1.9	1.9	1.9	1.9
Dye control agent	0.1	0.3	0.2	0.5	0.3
Water and miscellaneous	To 100%				
pH	7.5-8.2				

Based on total cleaning and/or treatment composition weight. Enzyme levels are reported as raw material.

In the following examples the unit dose has three compartments, but similar compositions can be made with two, four or five compartments. The film used to encapsulate the compartments is polyvinyl alcohol.

<b><u>Base compositions</u></b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>
<b><u>Ingredients</u></b>	<b>% weight</b>			
HLAS	26.82	16.35	7.50	3.34
AE7	17.88	16.35	22.50	30.06
Citric Acid	0.5	0.7	0.6	0.5
C12-15 Fatty acid	16.4	6.0	11.0	13.0
Polymer 1	2.9	0.1	-	-
Polymer 3	1.1	5.1	2.5	4.2
Cationic cellulose polymer	-	-	0.3	0.5
Polymer 6	-	1.5	0.3	0.2
Chelant 2	1.1	2.0	0.6	1.5
Optical Brightener 1	0.20	0.25	0.01	0.005
Optical Brightener 3	0.18	0.09	0.30	0.005
DTI	0.1	-	0.05	-
Glycerol	5.3	5.0	5.0	4.2
Monoethanolamine	10.0	8.1	8.4	7.6
Polyethylene glycol	-	-	2.5	3.0
Potassium sulfite	0.2	0.3	0.5	0.7
Protease	0.80	0.60	0.40	0.80
Amylase 1	0.20	0.20	0.200	0.30
Polishing enzyme	-	-	0.005	0.005

Nuclease	0.05	-	-	-
Dispersin B	-	0.010	0.010	0.010
MgCl <sub>2</sub>	0.2	0.2	0.1	0.3
Structurant	0.2	0.1	0.2	0.2
Acid Violet 50	0.04	0.03	0.05	0.03
Perfume / encapsulates	0.10	0.30	0.01	0.05
Dye control agent	0.2	0.03	0.4	-
Solvents and misc.	To 100%			
pH	7.0-8.2			

<b><u>Finishing compositions</u></b>	<b>17</b>			<b>18</b>		
Compartment	A	B	C	A	B	C
Volume of each compartment	40 ml	5 ml	5 ml	40 ml	5 ml	5 ml
<b><u>Ingredients</u></b>	Active material in Wt.%					
Perfume	1.6	1.6	1.6	1.6	1.6	1.6
Liquitint V200™	0	0.006	0	0	0.004	-
Leuco colorant		0.02		0.04	-	-
TiO <sub>2</sub>	-	-	0.1	-		0.1
Sodium Sulfite	0.4	0.4	0.4	0.1	0.3	0.3
Polymer 5	-			2	-	-
Hydrogenated castor oil	0.14	0.14	0.14	0.14	0.14	0.14
Base Composition 13, 14, 15 or 16	Add to 100%					

Based on total cleaning and/or treatment composition weight, enzyme levels are reported as raw material.

- AE1.8S is C12-15 alkyl ethoxy (1.8) sulfate
- 5 AE3S is C12-15 alkyl ethoxy (3) sulfate
- AE7 is C<sub>i2-i3</sub> alcohol ethoxylate, with an average degree of ethoxylation of 7
- AE8 is C<sub>i2-i3</sub> alcohol ethoxylate, with an average degree of ethoxylation of 8
- AE9 is C<sub>i2-i3</sub> alcohol ethoxylate, with an average degree of ethoxylation of 9
- Amylase 1 is Stainzyme®, 15 mg active/g, supplied by Novozymes

	Amylase 2	is Natalase®, 29 mg active/g, supplied by Novozymes
	Xyloglucanase	is Whitezyme®, 20mg active/g, supplied by Novozymes
	Chelant 1	is diethylene triamine pentaacetic acid
	Chelant 2	is 1-hydroxy ethane 1,1-diphosphonic acid
5	Dispersin B	is a glycoside hydrolase, reported as 1000mg active/g
	DTI	is either poly(4-vinylpyridine- 1-oxide) (such as Chromabond S-403E®), or poly(1-vinylpyrrolidone-co-1-vinylimidazole) (such as Sokalan HP56®).
10	Dye control agent	Dye control agent in accordance with the invention, for example Suparex® O.IN (M1), Nylofixan® P (M2), Nylofixan® PM (M3), or Nylofixan® HF (M4)
	HSAS	is mid-branched alkyl sulfate as disclosed in US 6,020,303 and US6,060,443
15	LAS	is linear alkylbenzenesulfonate having an average aliphatic carbon chain length C <sub>9</sub> -C <sub>15</sub> (HLAS is acid form).
	Leuco colorant	Any suitable leuco colorant or mixtures thereof according to the instant invention.
	Lipase	is Lipex®, 18 mg active/g, supplied by Novozymes
	Liquitint® V200	is a thiophene azo dye provided by Milliken
20	Mannanase	is Mannaway®, 25 mg active/g, supplied by Novozymes
	Nuclease	is a Phosphodiesterase SEQ ID NO 1, reported as 1000mg active/g
	Optical Brightener 1	is disodium 4,4'-bis{[4-anilino-6-morpholino-s-triazin-2-yl]-amino} -2,2'-stilbenedisulfonate
	Optical Brightener 2	is disodium 4,4'-bis-(2-sulfostryl)biphenyl (sodium salt)
25	Optical Brightener 3	is Optiblanc SPL10® from 3V Sigma
	Perfume encapsulate	is a core-shell melamine formaldehyde perfume microcapsules.

Polishing enzyme	is Para-nitrobenzyl esterase, reported as 1000mg active/g
Polymer 1	is bis((C <sub>2</sub> H <sub>5</sub> O)(C <sub>2</sub> H <sub>4</sub> ) <sub>n</sub> )(CH <sub>3</sub> -N <sup>+</sup> -C <sub>x</sub> H <sub>2x</sub> -N <sup>+</sup> -(CH <sub>3</sub> )-bis((C <sub>2</sub> H <sub>5</sub> O)(C <sub>2</sub> H <sub>4</sub> ) <sub>n</sub> ), wherein n = 20-30, x = 3 to 8 or sulphated or sulfonated variants thereof
5 Polymer 2	is ethoxylated (EO <sub>15</sub> ) tetraethylene pentamine
Polymer 3	is ethoxylated polyethylenimine
Polymer 4	is ethoxylated hexamethylene diamine
Polymer 5	is Acusol 305, provided by Rohm&Haas
10 Polymer 6	is a polyethylene glycol polymer grafted with vinyl acetate side chains, provided by BASF.
Protease	is Purafect Prime®, 40.6 mg active/g, supplied by DuPont
Structurant	is Hydrogenated Castor Oil

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

Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, 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.

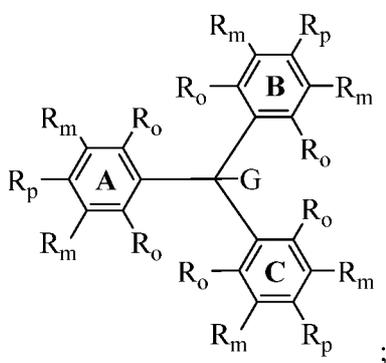
While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be

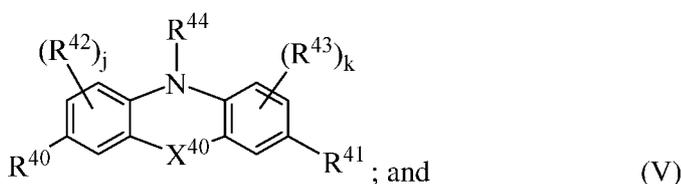
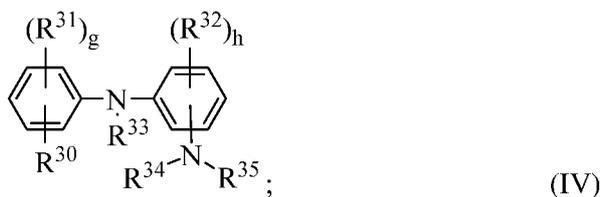
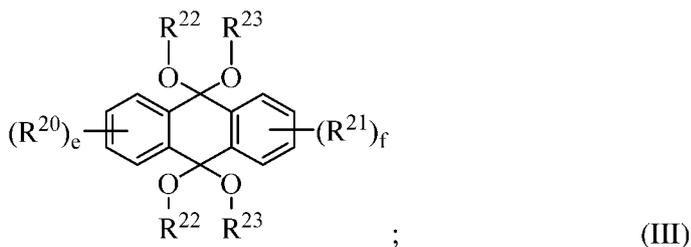
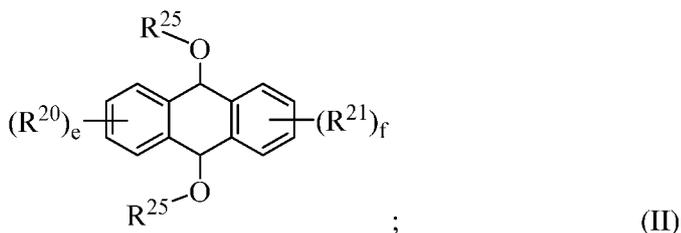
made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

## CLAIMS

We claim:

1. A method for treating textile articles comprising the steps of: (a) providing a laundry care composition comprising a leuco composition; (b) adding the laundry care composition to a liquid medium comprising an converting agent; (c) placing the textile articles in contact with the liquid medium; (d) converting at least some portion of the leuco composition to form an oxidized leuco composition; (e) depositing at least a portion of the oxidized leuco composition onto the textile; (f) optionally, rinsing the textile; and (g) drying the textile articles, wherein the textile article has a Leuco Whiteness Improvement Number (LWIN) of at least 5% after drying.
2. The method for treating textile articles of any proceeding claim, wherein the textile article has a Leuco Leuco Whiteness Improvement Number (LWIN) of at least 10% after drying.
3. The method for treating textile articles of any proceeding claim , wherein the converting agent is selected from the group consisting of chlorine, chlorine dioxide, hypochlorite and mixtures thereof.
4. The method for treating textile articles of any proceeding claim, wherein the leuco composition is selected from the group consisting of a diarylmethane leuco, a triarylmethane leuco, an oxazine leuco, a thiazine leuco, a hydroquinone leuco, an arylaminophenol leuco and mixtures thereof.
5. The method for treating textile articles of any proceeding claim, wherein the leuco composition is selected from one or more compounds selected from the group consisting of:





5 (f) mixtures thereof;

wherein the ratio of Formula I-V to its oxidized form is at least 1:3; wherein each individual  $R_0$ ,  $R_m$  and  $R_p$  group on each of rings A, B and C is independently selected from the group consisting of hydrogen, deuterium and  $R^5$ ; wherein each  $R^5$  is independently selected from the group consisting of halogens, nitro, alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl,  $-C(O)R^1$ ,  $-C(O)OR^1$ ,  $-C(O)O^-$ ,  $-C(O)NR^1R^2$ ,  $-OC(O)R^1$ ,  $-OC(O)OR^1$ ,  $-OC(O)NR^1R^2$ ,  $-S(O)_2R^1$ ,  $-S(O)_2OR^1$ ,  $-S(O)_2O^-$ ,  $-S(O)_2NR^1R^2$ ,  $-NR^1C(O)R^2$ ,  $-NR^1C(O)OR^2$ ,  $-NR^1C(O)SR^2$ ,  $-NR^1C(O)NR^2R^3$ ,  $-OR^1$ ,  $-NR^1R^2$ ,  $-P(O)_2R^1$ ,  $-P(O)(OR^1)_2$ ,  $-P(O)(OR^1)O^-$ , and  $-P(O)(O^-)_2$ ; ; wherein at least one of the  $R_0$  and  $R_m$  groups on at least one of the three rings A, B  
 10 or C is hydrogen; each  $R_p$  is independently selected from hydrogen,  $-OR^1$  and  $-NR^1R^2$ ;  
 15

wherein G is independently selected from the group consisting of hydrogen, deuterium, C1-C16 alkoxide, phenoxide, bisphenoxide, nitrite, nitrile, alkyl amine, imidazole, arylamine, polyalkylene oxide, halides, alkylsulfide, aryl sulfide, and phosphine oxide;

wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl, and R<sup>4</sup>; R<sup>4</sup> is a organic group  
5 substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl, and R<sup>4</sup>; R<sup>4</sup> is a organic group composed of one or more organic monomers with said monomer molecular weights ranging from 28 to 500;

wherein e and f are independently integers from 0 to 4;

wherein each R<sup>20</sup> and R<sup>21</sup> is independently selected from the group consisting of a halogen, a nitro  
10 group, alkyl groups, substituted alkyl groups, -NC(O)OR<sup>1</sup>, -NC(O)SR<sup>1</sup>, -OR<sup>1</sup>, and -NR<sup>2</sup>;

wherein each R<sup>25</sup> is independently selected from the group consisting of a monosaccharide moiety, a disaccharide moiety, an oligosaccharide moiety, a polysaccharide moiety, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -C(O)NR<sup>1</sup>R<sup>2</sup>;

wherein each R<sup>22</sup> and R<sup>23</sup> is independently selected from the group consisting of hydrogen, an alkyl  
15 group, and substituted alkyl groups;

wherein R<sup>30</sup> is positioned ortho or para to the bridging amine moiety and is selected from the group consisting of -OR<sup>38</sup> and -NR<sup>36</sup>R<sup>37</sup>, wherein each R<sup>36</sup> and R<sup>37</sup> is independently selected from the group consisting of hydrogen, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an acyl group, R<sup>4</sup>, -C(O)OR<sup>1</sup>, -C(O)R<sup>1</sup>, and -C(O)NR<sup>1</sup>R<sup>2</sup>;

wherein R<sup>38</sup> is selected from the group consisting of hydrogen, an acyl group, -C(O)OR<sup>1</sup>,  
20 -C(O)R<sup>1</sup>, and -C(O)NR<sup>1</sup>R<sup>2</sup>;

wherein g and h are independently integers from 0 to 4;

wherein each R<sup>31</sup> and R<sup>32</sup> is independently selected from the group consisting of an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an alkaryl, substituted alkaryl,  
25 -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -C(O)O-, -C(O)NR<sup>1</sup>R<sup>2</sup>, -OC<sup>1</sup>R<sup>1</sup>, -OC(O)OR<sup>1</sup>, -OC(O)NR<sup>1</sup>R<sup>2</sup>, -S(O)<sub>2</sub>R<sup>1</sup>, -S(O)<sub>2</sub>OR<sup>1</sup>, -S(O)<sub>2</sub>O-, -S(O)<sub>2</sub>NR<sup>1</sup>R<sup>2</sup>, -NR<sup>1</sup>C(O)R<sup>2</sup>, -NR<sup>1</sup>C(O)OR<sup>2</sup>, -NR<sup>1</sup>C(O)SR<sup>2</sup>, -NR<sup>1</sup>C(O)NR<sup>2</sup>R<sup>3</sup>, -OR<sup>1</sup>, -NR<sup>1</sup>R<sup>2</sup>, -P(O)<sub>2</sub>R<sup>1</sup>, -P(O)(OR<sup>1</sup>)<sub>2</sub>, -P(O)(OR<sup>1</sup>)O<sup>-</sup>, and -P(O)(O<sup>-</sup>)<sub>2</sub>;

wherein  $-NR^{34}R^{35}$  is positioned ortho or para to the bridging amine moiety and  $R^{34}$  and  $R^{35}$  are independently selected from the group consisting of hydrogen, an alkyl, a substituted alkyl, an aryl, a substituted aryl, an alkaryl, a substituted alkaryl, and  $R^4$ ;

wherein  $R^{33}$  is independently selected from the group consisting of hydrogen,  $-S(O)_2R^1$ ,  
 5  $-C(O)N(H)R^1$ ;  $-C(O)OR^1$ ; and  $-C(O)R^1$ ; wherein when  $g$  is 2 to 4, any two adjacent  $R^{31}$  groups may combine to form a fused ring of five or more members wherein no more than two of the atoms in the fused ring may be nitrogen atoms;

wherein  $X^{40}$  is selected from the group consisting of an oxygen atom, a sulfur atom, and  $NR^{45}$ ;  
 wherein  $R^{45}$  is independently selected from the group consisting of hydrogen, deuterium, an alkyl,  
 10 a substituted alkyl, an aryl, a substituted aryl, an alkaryl, a substituted alkaryl,  $-S(O)_2H$ ,  
 $-S(O)_2O$ ,  $-C(O)OR^1$ ,  $-C(O)R^1$ , and  $-C^*NR^1R^2$ ;

wherein  $R^{40}$  and  $R^{41}$  are independently selected from the group consisting of  $-OR^1$  and  $-NR^1R^2$ ;

wherein  $j$  and  $k$  are independently integers from 0 to 3;

wherein  $R^{42}$  and  $R^{43}$  are independently selected from the group consisting of an alkyl, a substituted  
 15 alkyl, an aryl, a substituted aryl, an alkaryl, a substituted alkaryl,  $-S(O)_2R^1$ ,  $-C(O)NR^1R^2$ ,  
 $-NC(O)OR^1$ ,  $-NC(O)SR^1$ ,  $-C(O)OR^1$ ,  $-C^*R^1$ ,  $-OR^1$ ,  $-NR^{3/4}R^2$ ;

wherein  $R^{44}$  is  $-C(O)R^1$ ,  $-C(O)NR^1R^2$ , and  $-C(O)OR^1$ ;

wherein any charge present in any of the compounds is balanced with a suitable independently selected internal or external counterion.

20 6. The method for treating textile articles of any preceding claim, wherein two  $R_0$  groups on different A, B and C rings combine to form a fused ring of five or more members.

7. The method for treating textile articles of any preceding claim, wherein the fused ring is six or more members and two  $R_0$  groups on different A, B and C rings combine to form an organic linker containing one or more heteroatoms.

25 8. The method for treating textile articles of any preceding claim, wherein two  $R_0$  on different A, B and C rings combine to form a heteroatom bridge selected from  $-O-$  and  $-S-$  to create a six member fused ring.

9. The method for treating textile articles of any preceding claim, wherein either an  $R_0$  and  $R_m$  on the same ring or an  $R_M$  and  $R_P$  on the same ring combine to form a fused aliphatic ring or fused aromatic ring.
10. The method for treating textile articles of any preceding claim, wherein all four of the  $R_0$  and  $R_M$  groups on at least one of the three rings A, B or C is hydrogen.
11. The method for treating textile articles of any preceding claim, wherein all of the  $R_0$  and  $R_m$  groups on all three rings A, B or C is hydrogen.
12. The method for treating textile articles of any preceding claim, wherein all three  $R_P$  are  $-NR^1R^2$ .
13. The method for treating textile articles of any preceding claim, wherein the organic group may be substituted with one or more additional leuco colorant moieties conforming to the structure of Formula I.
14. The method for treating textile articles of any preceding claim, wherein  $R^4$  is selected from the group consisting of alkyleneoxy, oxoalkyleneoxy, oxoalkyleneamine, epichlorohydrin, quaternized epichlorohydrin, alkyleneamine, hydroxyalkylene, acyloxyalkylene, carboxyalkylene, carboalkoxyalkylene, and sugar.
15. The method for treating textile articles of any preceding claim, wherein the laundry care ingredient is selected from the group consisting of surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, enzyme stabilizers, catalytic materials, bleach activators, polymeric dispersing agents, clay soil removal agents, anti-redeposition agents, brighteners, suds suppressors, dyes, perfume, perfume delivery systems, structurants, fabric softeners, carriers, hydrotropes, processing aids, pigments, antioxidants and mixtures thereof.

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2017/059413

A. CLASSIFICATION OF SUBJECT MATTER  
**INV. C11D3/40 C11D3/42 CIIDII/00**  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
**C11D**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
**EPO-Internal , WPI Data**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	wo 2008/100445 A2 (MI LLI KEN & CO [US] ) 21 August 2008 (2008-08-21) page 4, lines 4-24 page 5, lines 7-12 page 24, line 5 - page 26, line 12 claims; examples; tabl es 1,2 -----	1-15
A	US 3 133 036 A (ULTEE ARNOLDUS J) 12 May 1964 (1964-05-12) claims -----	1-15
A	US 3 341 539 A (MAX STAEUBLE ET AL) 12 September 1967 (1967-09-12) claims -----	1-15
A, P	wo 2016/178668 A1 (MI LLI KEN & CO [US] ) 10 November 2016 (2016-11-10) claims; examples; tabl es IA,IB -----	1-15

Further documents are listed in the continuation of Box C.  See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search <b>2 February 2018</b>	Date of mailing of the international search report <b>13/02/2018</b>
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