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(54) **Title:** CLEANING COMPOSITIONS CONTAINING A CYCLIC AMINE AND A FABRIC SHADING AGENT AND/OR A BRIGHTENER

(57) **Abstract:** The present invention relates generally to cleaning compositions and, more specifically, to cleaning compositions containing a cyclic amine that is suitable for removal of stains from soiled materials and a fabric shading agent and/or a brightener.



CLEANING COMPOSITIONS CONTAINING A CYCLIC AMINE AND A FABRIC SHADING AGENT AND/OR A BRIGHTENER

FIELD OF THE INVENTION

5 The present invention relates generally to cleaning compositions and, more specifically, to cleaning compositions containing a cyclic amine that is suitable for removal of stains from soiled materials and a fabric shading agent.

BACKGROUND OF THE INVENTION

10 Due to the increasing popularity of easy-care fabrics made of synthetic fibers as well as the ever increasing energy costs and growing ecological concerns of detergent users, washing fabrics in cold water (30°C and below) is becoming more prevalent, while the once popular warm and hot water washes are becoming less prevalent. Many commercially available laundry detergents are even advertised as being suitable for washing fabrics at 15°C or even 9°C. To
15 achieve satisfactory washing results at such low temperatures, results comparable to those obtained with hot-water washes, the demands on low-temperature detergents are especially high.

 It is known to include certain additives in detergent compositions to enhance the detergent power of conventional surfactants, so as to improve the removal of grease stains at temperatures of 30°C and below. For example, laundry detergents containing an aliphatic amine
20 compound, in addition to at least one synthetic anionic and/or nonionic surfactant, are known. Also, the use of linear, alkyl-modified (secondary) alkoxypropylamines in laundry detergents to improve cleaning at low temperatures is known. These known laundry detergents, however, are unable to achieve satisfactory cleaning at cold temperatures.

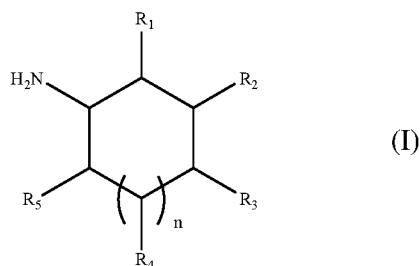
 Furthermore, the use of linear, primary polyoxyalkyleneamines (e.g., Jeffamine® D-230)
25 to stabilize fragrances in laundry detergents and provide longer lasting scent is also known. Also, the use of high-molecular-weight (molecular weight of at least about 1000), branched, trifunctional, primary amines (e.g., Jeffamine® T-5000 polyetheramine) to suppress suds in liquid detergents is known. Additionally, the use of cyclic diamines in hand dish detergents is known.

30 There is a continuing need for a detergent additive that can improve cleaning performance and fabric whitening at low wash temperatures, e.g., at 30°C or even lower, without interfering with the production and the quality of the laundry detergents in any way. More specifically, there is a need for a detergent additive that removes grease stains more completely, as grease stains may become highlighted by a fabric shading dye and incomplete removal may be

highlighted. It has been found that the cleaning compositions of the invention provide more complete grease removal and improved fabric whitening (particularly in cold water).

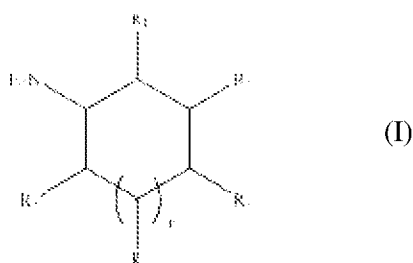
SUMMARY OF THE INVENTION

The present disclosure attempts to solve one more of the needs by providing a cleaning composition (in liquid, powder, unit dose, pouch, or tablet forms) comprising from about 1% to about 70% by weight of a surfactant, from 0.0001% to 0.05% by weight of a fabric shading dye, a brightener, or a mixture thereof, and from about 0.1% to about 10% by weight of a cyclic amine of Formula (I):



where the radicals R_1 , R_2 , R_3 , R_4 and R_5 are independently selected from NH_2 , $-H$, linear or branched alkyl or alkenyl having from about 1 to about 10 carbon atoms and n is from about 0 to about 3 and wherein at least one of the radicals is NH_2 .

The present disclosure further relates to a method of treating a textile, the method comprising the steps of: (a) treating the textile with an aqueous solution of from about 0.1 g/L to about 3 g/L of a surfactant; from about 1 ppb to about 5 ppm of a fabric shading dye suitable for providing a blue or violet shade to white cotton or polyester; and from about 0.1ppm to about 500 ppm of a cyclic amine of Formula (I):



wherein the radicals R_1 , R_2 , R_3 , R_4 and R_5 are independently selected from NH_2 , $-H$, linear or branched alkyl or alkenyl having from about 1 to about 10 carbon atoms and n is from about 0 to about 3 and wherein at least one of the radicals is NH_2 ; and (b) rinsing and drying the textile, wherein the fabric shading dye is selected from azine, anthraquinone, mono-azo, and dis-azo dyes, optionally substituted with polyalkyleneoxy groups.

The present disclosure further relates to methods including pretreatment of a soiled material comprising contacting the soiled material with the cleaning compositions of the disclosure.

DETAILED DESCRIPTION OF THE INVENTION

5 Features and benefits of the various embodiments of the present invention will become apparent from the following description, which includes examples of specific embodiments intended to give a broad representation of the invention. Various modifications will be apparent to those skilled in the art from this description and from practice of the invention. The scope is not intended to be limited to the particular forms disclosed and the invention covers all
10 modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the claims.

As used herein, the articles including “the,” “a” and “an” when used in a claim or in the specification, are understood to mean one or more of what is claimed or described.

As used herein, the terms “include,” “includes” and “including” are meant to be non-
15 limiting.

The term “substantially free of” or “substantially free from” as used herein refers to either the complete absence of an ingredient or a minimal amount thereof merely as impurity or unintended byproduct of another ingredient. A composition that is “substantially free” of/from a component means that the composition comprises less than about 0.5%, 0.25%, 0.1%, 0.05%, or
20 0.01%, or even 0%, by weight of the composition, of the component.

As used herein, the term “soiled material” is used non-specifically and may refer to any type of flexible material consisting of a network of natural or artificial fibers, including natural, artificial, and synthetic fibers, such as, but not limited to, cotton, linen, wool, polyester, nylon, silk, acrylic, and the like, as well as various blends and combinations. Soiled material may
25 further refer to any type of hard surface, including natural, artificial, or synthetic surfaces, such as, but not limited to, tile, granite, grout, glass, composite, vinyl, hardwood, metal, cooking surfaces, plastic, and the like, as well as blends and combinations.

It should be understood that every maximum numerical limitation given throughout this specification includes every lower numerical limitation, as if such lower numerical limitations
30 were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

All cited patents and other documents are, in relevant part, incorporated by reference as if fully restated herein. The citation of any patent or other document is not an admission that the cited patent or other document is prior art with respect to the present invention.

In this description, all concentrations and ratios are on a weight basis of the cleaning composition unless otherwise specified.

Cleaning Composition

As used herein the phrase "cleaning composition" or "detergent composition" includes compositions and formulations designed for cleaning soiled material as well as wash solutions containing such compositions and formulations. Such compositions include but are not limited to, laundry cleaning compositions and detergents, fabric softening compositions, fabric enhancing compositions, fabric freshening compositions, laundry prewash, laundry pretreat, laundry additives, spray products, dry cleaning agent or composition, laundry rinse additive, wash additive, post-rinse fabric treatment, ironing aid, dish washing compositions, hard surface cleaning compositions, unit dose formulation, delayed delivery formulation, detergent contained on or in a porous substrate or nonwoven sheet, and other suitable forms that may be apparent to one skilled in the art in view of the teachings herein. Such compositions may be used as a pre-laundering treatment, a post-laundering treatment, or may be added during the rinse or wash cycle of the laundering operation. The cleaning compositions may have a form selected from liquid, powder, single-phase or multi-phase unit dose, pouch, tablet, gel, paste, bar, or flake.

Surfactant

The cleaning composition comprises one or more surfactants. The cleaning composition may comprise, by weight of the composition, from about 1% to about 70% of a surfactant. The cleaning composition may comprise, by weight of the composition, from about 2% to about 60% of the surfactant. The cleaning composition may comprise, by weight of the composition, from about 5% to about 30% of the surfactant. The surfactant may be selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, ampholytic surfactants, and mixtures thereof. The surfactant may be a deterative surfactant, which encompasses any surfactant or mixture of surfactants that provide cleaning, stain removing, or laundering benefit to soiled material.

Anionic Surfactants

The cleaning composition may comprise an anionic surfactant. The cleaning composition may consist essentially of, or even consist of, an anionic surfactant.

Specific, non-limiting examples of suitable anionic surfactants include any conventional anionic surfactant. This may include a sulfate detergent surfactant, for e.g., alkoxyated and/or non-alkoxyated alkyl sulfate materials, and/or sulfonic detergent surfactants, e.g., alkyl benzene sulfonates.

5 Alkoxyated alkyl sulfate materials comprise ethoxyated alkyl sulfate surfactants, also known as alkyl ether sulfates or alkyl polyethoxyate sulfates. Examples of ethoxyated alkyl sulfates include water-soluble salts, particularly the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 30 carbon atoms and a sulfonic acid and its salts.
10 (Included in the term “alkyl” is the alkyl portion of acyl groups. In some examples, the alkyl group contains from about 15 carbon atoms to about 30 carbon atoms. In other examples, the alkyl ether sulfate surfactant may be a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 30 carbon atoms, and in some examples an average carbon chain length of about 25 carbon atoms, and an average
15 (arithmetic mean) degree of ethoxylation of from about 1 mol to 4 mols of ethylene oxide, and in some examples an average (arithmetic mean) degree of ethoxylation of 1.8 mols of ethylene oxide. In further examples, the alkyl ether sulfate surfactant may have a carbon chain length between about 10 carbon atoms to about 18 carbon atoms, and a degree of ethoxylation of from about 1 to about 6 mols of ethylene oxide. In yet further examples, the alkyl ether sulfate
20 surfactant may contain a peaked ethoxyate distribution.

Non-alkoxyated alkyl sulfates may also be added to the disclosed detergent compositions and used as an anionic surfactant component. Examples of non-alkoxyated, e.g., non-ethoxyated, alkyl sulfate surfactants include those produced by the sulfation of higher C8-C20 fatty alcohols. In some examples, primary alkyl sulfate surfactants have the general formula:
25 $\text{ROSO}_3^- \text{M}^+$, wherein R is typically a linear C8-C20 hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. In some examples, R is a C10-C15 alkyl, and M is an alkali metal. In other examples, R is a C12-C14 alkyl and M is sodium.

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
30 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 alkyl benzene sulfonates may

have an average number of carbon atoms in the alkyl group of about 11.8 carbon atoms, which may be abbreviated as C11.8 LAS.

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 deterative surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. A magnesium salt of LAS may be used.

The deterative surfactant may be a mid-chain branched deterative surfactant, e.g., a mid-chain branched anionic deterative surfactant, such as a mid-chain branched alkyl sulphate and/or a mid-chain branched alkyl benzene sulphonate.

Other anionic surfactants useful herein are the water-soluble salts of: paraffin sulfonates and secondary alkane sulfonates containing from about 8 to about 24 (and in some examples about 12 to 18) carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of C8-18 alcohols (e.g., those derived from tallow and coconut oil). Mixtures of the alkylbenzene sulfonates with the above-described paraffin sulfonates, secondary alkane sulfonates and alkyl glyceryl ether sulfonates are also useful. Further suitable anionic surfactants include methyl ester sulfonates and alkyl ether carboxylates.

The anionic surfactants may exist in an acid form, and the acid form may be neutralized to form a surfactant salt. Typical agents for neutralization include metal counterion bases, such as hydroxides, e.g., NaOH or KOH. Further suitable agents for neutralizing anionic surfactants in their acid forms include ammonia, amines, or alkanolamines. Non-limiting examples of alkanolamines include monoethanolamine, diethanolamine, triethanolamine, and other linear or branched alkanolamines known in the art; suitable alkanolamines include 2-amino-1-propanol, 1-aminopropanol, monoisopropanolamine, or 1-amino-3-propanol. Amine neutralization may be done to a full or partial extent, e.g., part of the anionic surfactant mix may be neutralized with sodium or potassium and part of the anionic surfactant mix may be neutralized with amines or alkanolamines.

Nonionic surfactants

The cleaning composition may comprise a nonionic surfactant. The cleaning composition may comprise from about 0.1% to about 50%, by weight of the cleaning composition, of a nonionic surfactant. The cleaning composition may comprise from about 0.1%

to about 25% or about 0.1% to about 15%, by weight of the cleaning composition, of a nonionic surfactants. The cleaning composition may comprise from about 0.3% to about 10%, by weight of the cleaning composition, of a nonionic surfactant. The cleaning composition may comprise from about 1% to about 25%, or about 5% to about 25%, or about 10% to about 25%, by weight of the cleaning composition, of a nonionic surfactant.

Suitable nonionic surfactants useful herein can comprise any conventional nonionic surfactant. These can include, for e.g., alkoxyated fatty alcohols and amine oxide surfactants. In some examples, the detergent compositions may contain an ethoxylated nonionic surfactant. The nonionic surfactant may be selected from the 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. The nonionic surfactant may be selected from ethoxylated alcohols having an average of about 24 carbon atoms in the alcohol and an average degree of ethoxylation of about 9 moles of ethylene oxide per mole of alcohol.

Other non-limiting 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 branched alkyl alkoxyates, BAEx, wherein x is from 1 to 30; alkylpolysaccharides; specifically alkylpolyglycosides; polyhydroxy fatty acid amides; and ether capped poly(oxyalkylated) alcohol surfactants.

Suitable nonionic deterative surfactants also include alkyl polyglucoside and alkyl alkoxyated alcohol. Suitable nonionic surfactants also include those sold under the tradename Lutensol® from BASF.

The nonionic surfactant may be selected from alkyl alkoxyated alcohols, such as a C8-18 alkyl alkoxyated alcohol, for example, a C8-18 alkyl ethoxylated alcohol. The alkyl alkoxyated alcohol may have an average degree of alkoxylation of from about 1 to about 50, or from about 1 to about 30, or from about 1 to about 20, or from about 1 to about 10, or from about 1 to about 7, or from about 1 to about 5, or from about 3 to about 7. The alkyl alkoxyated alcohol can be linear or branched, substituted or unsubstituted.

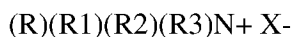
Cationic Surfactants

The cleaning composition may comprise a cationic surfactant. The cleaning composition may comprise from about 0.1% to about 10%, or from about 0.1% to about 7%, or from about 0.1% to about 5%, or from about 1% to about 4%, by weight of the cleaning composition, of a cationic surfactant. The cleaning compositions of the invention may be substantially free of cationic surfactants and surfactants that become cationic below a pH of 7 or below a pH of 6.

Non-limiting examples of cationic surfactants include: the quaternary ammonium surfactants, which can have up to 26 carbon atoms include: alkoxyate quaternary ammonium (AQA) surfactants; dimethyl hydroxyethyl quaternary ammonium; dimethyl hydroxyethyl lauryl ammonium chloride; polyamine cationic surfactants; cationic ester surfactants; and amino surfactants, e.g., amido propyldimethyl amine (APA).

Suitable cationic deterative surfactants also include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

Suitable cationic deterative surfactants are quaternary ammonium compounds having the general formula:



wherein, R is a linear or branched, substituted or unsubstituted C6-18 alkyl or alkenyl moiety, R1 and R2 are independently selected from methyl or ethyl moieties, R3 is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, suitable anions include: halides, for example chloride; sulphate; and sulphonate. Suitable cationic deterative surfactants are mono-C6-18 alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly suitable cationic deterative surfactants are mono-C8-10 alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C10-12 alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C10 alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

Zwitterionic Surfactants

The cleaning composition may comprise a zwitterionic surfactant. Examples of zwitterionic surfactants include: derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Suitable examples of zwitterionic surfactants include betaines, including alkyl dimethyl betaine and cocodimethyl amidopropyl betaine, C8 to

C18 (for example from C12 to C18) amine oxides, and sulfo and hydroxy betaines, such as N-alkyl-N,N-dimethylammino-1-propane sulfonate where the alkyl group can be C8 to C18.

Amphoteric Surfactants

5 The cleaning composition may comprise an amphoteric surfactant. Examples of amphoteric surfactants include aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight or branched-chain and where one of the aliphatic substituents contains at least about 8 carbon atoms, or from about 8 to about 18 carbon atoms, and at least one of the aliphatic
10 substituents contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. Examples of compounds falling within this definition are sodium 3-(dodecylamino)propionate, sodium 3-(dodecylamino) propane-1-sulfonate, sodium 2-(dodecylamino)ethyl sulfate, sodium 2-(dimethylamino) octadecanoate, disodium 3-(N-carboxymethyldodecylamino)propane 1-sulfonate, disodium octadecyl-imminodiacetate, sodium 1-carboxymethyl-2-undecylimidazole,
15 and sodium N,N-bis (2-hydroxyethyl)-2-sulfato-3-dodecoxypropylamine. Suitable amphoteric surfactants also include sarcosinates, glycinate, taurinate, and mixtures thereof.

Branched Surfactants

 The cleaning composition may comprise a branched surfactant. Suitable branched
20 surfactants include anionic branched surfactants selected from branched sulphate or branched sulphonate surfactants, e.g., branched alkyl sulphate, branched alkyl alkoxyated sulphate, and branched alkyl benzene sulphonates, comprising one or more random alkyl branches, e.g., C1-4 alkyl groups, typically methyl and/or ethyl groups.

 The branched deterative surfactant may be a mid-chain branched deterative surfactant, e.g.,
25 a mid-chain branched anionic deterative surfactant, such as a mid-chain branched alkyl sulphate and/or a mid-chain branched alkyl benzene sulphonate.

 The branched anionic surfactant may comprise a branched modified alkylbenzene sulfonate (MLAS).

 The branched anionic surfactant may comprise a C12/13 alcohol-based surfactant
30 comprising a methyl branch randomly distributed along the hydrophobe chain, e.g., Safol®, Marlupal® available from Sasol.

 The branched anionic surfactant may include a 2-alkyl branched primary alkyl sulfates have 100% branching at the C2 position (C1 is the carbon atom covalently attached to the alkoxyated sulfate moiety). 2-alkyl branched alkyl sulfates and 2-alkyl branched alkyl alkoxy

sulfates are generally derived from 2-alkyl branched alcohols (as hydrophobes). 2-alkyl branched alcohols, e.g., 2-alkyl-1-alkanols or 2-alkyl primary alcohols, which are derived from the oxo process, are commercially available from Sasol, as ISALCHEM®.

Additional suitable branched anionic deterative surfactants include surfactant derivatives of isoprenoid-based polybranched detergent alcohols. Isoprenoid-based surfactants and isoprenoid derivatives are also described in the book entitled "Comprehensive Natural Products Chemistry: Isoprenoids Including Carotenoids and Steroids (Vol. two)", Barton and Nakanishi, © 1999, Elsevier Science Ltd and are included in the structure E, and are hereby incorporated by reference. Further suitable branched anionic deterative surfactants include those derived from anteiso and iso-alcohols.

Suitable branched anionic surfactants also include Guerbet-alcohol-based surfactants. Guerbet alcohols are branched, primary monofunctional alcohols that have two linear carbon chains with the branch point always at the second carbon position. Guerbet alcohols are chemically described as 2-alkyl-1-alkanols. Guerbet alcohols generally have from 12 carbon atoms to 36 carbon atoms. The Guerbet alcohols may be represented by the following formula: $(R1)(R2)CHCH_2OH$, where R1 is a linear alkyl group, R2 is a linear alkyl group, the sum of the carbon atoms in R1 and R2 is 10 to 34, and both R1 and R2 are present. Guerbet alcohols are commercially available from Sasol as Isofol® alcohols and from Cognis as Guerbetol.

Fabric Shading Agents

As used herein the term "fabric shading agent" includes dyes or pigments that, when formulated in a detergent composition, can deposit onto a fabric, when the fabric is contacted with a wash liquor comprising the detergent composition, and alter the tint of the fabric. The term "fabric shading agent" and the term "fabric hueing agent" are used interchangeably. For the purposes of the present disclosure, fluorescent optical brighteners are not considered fabric shading agents. Fabric shading agents include fabric shading dyes, pigments, and mixtures thereof.

Without being bound by theory, it is believed that incomplete removal of grease stains may leave regions of a fabric/textile/garment with noticeably different surface characteristics. Fabric shading agents typically deposit to varying degrees on different types of fabric surfaces. Thus, there may be differential deposition of a fabric shading agent on a fabric/textile/garment that has regions with different surface characteristics (due to incomplete removal of grease stains). For example, in the case of a fabric shading agent that is more prone to deposit on more hydrophobic surfaces, a greater concentration of fabric shading agent may deposit on the

remaining grease stain(s) (e.g., shading agents that deposit better on more hydrophobic regions of cotton or synthetics). On the other hand, in the case of shading agents that are less prone to deposit on more hydrophobic surfaces, a greater concentration of fabric shading agent may deposit outside of the remaining grease stain(s) (e.g., shading agents that deposit better on cotton). Regardless, there may be differential deposition of the fabric shading agent and unremoved grease stains may be highlighted, when a shading agents is employed. Therefore, it may be advantageous for formulations that contain shading agents to also provide improved grease stain removal, to reduce differences in surface characteristics.

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. Fabric shading dyes can be used either alone or in combination to create a specific shade of hueing and/or to shade different fabric types. This may be provided for example by mixing a red and green-blue dye to yield a blue or violet shade.

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, triaryl methane, triphenylmethane, xanthenes and mixtures thereof.

The fabric shading dye may be a blue or violet shading dye, providing a blue or violet color to a white cloth or fabric. Such a white cloth treated with the composition will have a hue angle of 240 to 345, more or 260 to 325, or 270 to 310.

The shading dye may have, in the wavelength range of about 400 nm to about 750 nm, in methanol solution, a maximum extinction coefficient greater than about 1000 liter/mol/cm. The shading dye may have, in the wavelength range of about 540 nm to about 630 nm, a maximum extinction coefficient from about 10,000 to about 100,000 liter/mol/cm. The shading dye may have, in the wavelength range of about 560 nm to about 610 nm, a maximum extinction coefficient from about 20,000 to about 70,000 liter/mol/cm or about 90,000 liter/mol/cm.

The Test Methods provided below can be used to determine if a dye, or a mixture of dyes, is a shading dye for the purposes of the present disclosure.

Test Methods

I. Method for Determining Deposition for a Dye

a.) Unbrightened Multifiber Fabric Style 41 swatches (MFF41, 5cm x 10cm, average weight 1.46g) serged with unbrightened thread are purchased from Testfabrics, Inc. (West Pittston, PA). MFF41 swatches are stripped prior to use by washing two full cycles in AATCC heavy duty liquid laundry detergent (HDL) nil brightener at 49°C and washing 3 additional full cycles at 49°C without detergent. Four replicate swatches are placed into each flask.

b.) A sufficient volume of AATCC standard nil brightener HDL detergent solution is prepared by dissolving the detergent in 0 gpg water at room temperature at a concentration of 1.55 g per liter.

c.) A concentrated stock solution of dye is prepared in an appropriate solvent selected from dimethyl sulfoxide (DMSO), ethanol or 50:50 ethanol:water. Ethanol is preferred. The dye stock is added to a beaker containing 400mL detergent solution (prepared in step I.b. above) in an amount sufficient to produce an aqueous solution absorbance at the λ_{max} of 0.1 AU (± 0.01 AU) in a cuvette of path length 1.0 cm. For a mixture of dyes, the sum of the aqueous solution absorbance at the λ_{max} of the individual dyes is 0.1 AU (± 0.01 AU) in a cuvette of path length 1.0 cm. Total organic solvent concentration in a wash solution from the concentrated stock solution is less than 0.5%. A 125mL aliquot of the wash solution is placed into 3 separate disposable 250mL Erlenmeyer flasks (Thermo Fisher Scientific, Rochester, NY).

d.) Four MFF41 swatches are placed into each flask, flasks are capped and manually shaken to wet the swatches. Flasks are placed onto a Model 75 wrist action shaker from Burrell Scientific, Inc. (Pittsburg, PA) and agitated on the highest setting of 10 (390 oscillations per minute with an arc of 14.6°). After 12 minutes, the wash solution is removed by vacuum aspiration, 125mL of 0gpg water is added for a rinse, and the flasks agitated for 4 additional minutes. Rinse solution is removed by vacuum aspiration and swatches are spun in a Mini Countertop Spin Dryer (The Laundry Alternative Inc., Nashua, NH) for 5 minutes, after which they are allowed to air dry in the dark.

e.) L^* , a^* , and b^* values for the 3 most consumer relevant fabric types, cotton and polyester, are measured on the dry swatches using a LabScan XE reflectance spectrophotometer (HunterLabs, Reston, VA; D65 illumination, 10° observer, UV light excluded). The L^* , a^* , and b^* values of the 12 swatches (3 flasks each containing 4 swatches) are averaged and the hueing deposition (HD) of the dye is calculated for each fabric type using the following equation:

$$HD = DE^* = ((L_c^* - L_s^*)^2 + (a_c^* - a_s^*)^2 + (b_c^* - b_s^*)^2)^{1/2}$$

wherein the subscripts c and s respectively refer to the control, i.e., the fabric washed in detergent with no dye, and the fabric washed in detergent containing dye, or a mixture of dyes, according to the method described above.

II. Method for Determining Relative Hue Angle (vs. Nil Dye Control)

- a) The a^* and b^* values of the 12 swatches from each solution were averaged and the following formulas used to determine Δa^* and Δb^* :

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

wherein the subscripts c and s respectively refer to the fabric washed in detergent with no dye and the fabric washed in detergent containing dye, or mixture of dyes, according to the method described in I. above.

- b.) If the absolute value of both Δa^* and $\Delta b^* < 0.25$, no Relative Hue Angle (RHA) was calculated. If the absolute value of either Δa^* or Δb^* were ≥ 0.25 , the RHA was determined using one of the following formulas:

$$\text{When } \Delta b^* \geq 0, \text{ RHA} = \text{ATAN2}(\Delta a^*, \Delta b^*)$$

$$\text{When } \Delta b^* < 0, \text{ RHA} = 360 + \text{ATAN2}(\Delta a^*, \Delta b^*)$$

III. Method to Determine if a Dye is a Shading Dye

A dye, or mixture of dyes, is considered a shading dye (also known as a hueing dye) for the purposes of the present invention if (a) either the $\text{HD}_{\text{cotton}}$ or the $\text{HD}_{\text{polyester}}$ is greater than or equal to 2.0 DE^* units or preferably greater than or equal to 3.0, or 4.0 or even 5.0, according to the formula above, and (b) the relative hue angle (see Method III. below) on the fabric that meets the DE^* criterion in (a) is within 240 to 345, more preferably 260 to 325, even more preferably 270 to 310. If the value of HD for both fabric types is less than 2.0 DE^* units, or if the relative hue angle is not within the prescribed range on each fabric for which the DE^* meets the criteria the dye is not a shading dye for the purposes of the present invention.

Suitable fabric shading dyes include small molecule dyes, polymeric dyes and dye-clay conjugates.

Small Molecule 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. Such dyes may be classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination with other dyes or in combination with other adjunct ingredients. Reactive dyes may contain small amounts of hydrolyzed dye as sourced, and in detergent formulations or in the wash may undergo additional hydrolysis. Such hydrolyzed dyes and mixtures may also serve as suitable small molecule dyes.

In another aspect, suitable dyes include those selected from the group consisting of dyes denoted by the Colour Index designations such as Direct Violet 5, 7, 9, 11, 31, 35, 48, 51, 66, and 99, Direct Blue 1, 71, 80 and 279, Acid Red 17, 73, 52, 88 and 150, Acid Violet 15, 17, 24, 43, 49 and 50, Acid Blue 15, 17, 25, 29, 40, 45, 48, 75, 80, 83, 90 and 113, Acid Black 1, Basic Violet 1, 3, 4, 10 and 35, Basic Blue 3, 16, 22, 47, 66, 75 and 159, anthraquinone Disperse or Solvent dyes such as Solvent Violet 11, 13, 14, 15, 15, 26, 28, 29, 30, 31, 32, 33, 34, 26, 37, 38, 40, 41, 42, 45, 48, 59; Solvent Blue 11, 12, 13, 14, 15, 17, 18, 19, 20, 21, 22, 35, 36, 40, 41, 45, 59, 59:1, 63, 65, 68, 69, 78, 90; Disperse Violet 1, 4, 8, 11, 11:1, 14, 15, 17, 22, 26, 27, 28, 29, 34, 35, 36, 38, 41, 44, 46, 47, 51, 56, 57, 59, 60, 61, 62, 64, 65, 67, 68, 70, 71, 72, 78, 79, 81, 83, 84, 85, 87, 89, 105; Disperse Blue 2, 3, 3:2, 8, 9, 13, 13:1, 14, 16, 17, 18, 19, 22, 23, 24, 26, 27, 28, 31, 32, 34, 35, 40, 45, 52, 53, 54, 55, 56, 60, 61, 62, 64, 65, 68, 70, 72, 73, 76, 77, 80, 81, 83, 84, 86, 87, 89, 91, 93, 95, 97, 98, 103, 104, 105, 107, 108, 109, 11, 112, 113, 114, 115, 116, 117, 118, 119, 123, 126, 127, 131, 132, 134, 136, 140, 141, 144, 145, 147, 150, 151, 152, 153, 154, 155, 156, 158, 159, 160, 161, 162, 163, 164, 166, 167, 168, 169, 170, 176, 179, 180, 180:1, 181, 182, 184, 185, 190, 191, 192, 196, 197, 198, 199, 203, 204, 213, 214, 215, 216, 217, 218, 223, 226, 227, 228, 229, 230, 231, 232, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 249, 252, 261, 262, 263, 271, 272, 273, 274, 275, 276, 277, 289, 282, 288, 289, 292, 293, 296, 297, 298, 299, 300, 302, 306, 307, 308, 309, 310, 311, 312, 314, 318, 320, 323, 325, 326, 327, 331, 332, 334, 347, 350, 359, 361, 363, 372, 377 and 379, azo Disperse dyes such as Disperse Blue 10, 11, 12, 21, 30, 33, 36, 38, 42, 43, 44, 47, 79, 79:1, 79:2, 79:3, 82, 85, 88, 90, 94, 96, 100, 101, 102, 106, 106:1, 121, 122, 124, 125, 128, 130, 133, 137, 138, 139, 142, 146, 148, 149, 165, 165:1, 165:2, 165:3, 171, 173, 174, 175, 177, 183, 187, 189, 193, 194, 200, 201, 202, 206, 207, 209, 210, 211, 212, 219, 220, 224, 225, 248, 252, 253, 254, 255, 256, 257, 258, 259, 260, 264, 265, 266, 267, 268, 269, 270, 278, 279, 281, 283, 284, 285, 286, 287, 290, 291, 294, 295, 301, 304, 313, 315, 316, 317:319, 321, 322, 324, 328, 330, 333, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 351, 352, 353, 355, 356, 358, 360, 366, 367, 368, 369, 371, 373, 374, 375, 376 and 378, Disperse Violet 2, 3, 5, 6, 7, 9, 10, 12, 3, 16, 24, 25, 33, 39, 42, 43, 45, 48, 49, 50, 53, 54, 55, 58, 60, 63, 66, 69, 75, 76, 77, 82, 86, 88, 91, 92, 93, 93:1, 94, 95, 96, 97, 98, 99, 100, 102, 104, 106 and 107. Small molecule dyes may be selected from the group consisting of C. I. numbers Acid Violet 17, Acid Blue 80, Acid Violet 50, Direct Blue 71, Direct Violet 51, Direct Blue 1, Acid Red 88, Acid Red 150, Acid Blue 29, Acid Blue 113 or mixtures thereof.

Suitable small molecule dyes include dyes with CAS-No's 52583-54-7, 42783-06-2, 210758-04-6, 104366-25-8, 122063-39-2, 167940-11-6, 52239-04-0, 105076-77-5, 84425-43-4, and

87606-56-2, and non-azo dyes Disperse Blue 250, 354, 364, Solvent Violet 8, Solvent blue 43, 57, Lumogen F Blau 650, and Lumogen F Violet 570.

Suitable small molecule dyes include azo dyes, for example, mono-azo dyes covalently bound to phthalocyanine moieties, e.g., Al- and Si-phthalocyanine moieties, via an organic linking moiety.

Polymeric 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.

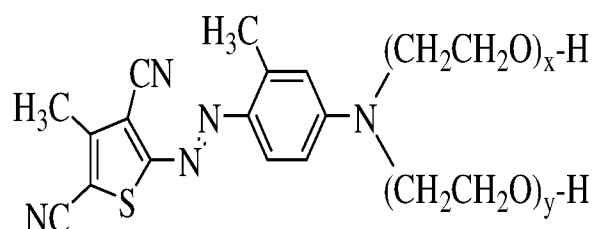
Polymeric dyes include: (a) reactive dyes bound to water soluble polyester polymers via at least one, e.g., two, free -OH groups on the water soluble polyester polymer. The water soluble polyester polymers can be comprised of comonomers of a phenyl dicarboxylate, an oxyalkyleneoxy and a polyoxyalkyleneoxy; (b) reactive dyes bound to polyamines which are polyalkylamines that are generally linear or branched, e.g., polyethyleneimine. The amines in the polymer may be primary, secondary and/or tertiary. The polyamines may be ethoxylated; (c) dye polymers having dye moieties carrying negatively charged groups obtainable by copolymerization of an alkene bound to a dye containing an anionic group and one or more further alkene comonomers not bound to a dye moiety; (d) dye polymers having dye moieties carrying positively charged groups obtainable by copolymerization of an alkene bound to a dye containing an cationic group and one or more further alkene comonomers not bound to a dye moiety; (e) Polymeric thiophene azo polyoxyalkylene dyes containing carboxylate groups; and (f) dye polymer conjugates comprising at least one reactive dye and a polymer comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and combinations thereof (the polymer may be selected from the group consisting of polysaccharides, proteins, polyalkyleneimines, polyamides, polyols, and silicones. For example, carboxymethyl cellulose (CMC) may be covalently bound to one or more reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC,

Other suitable polymeric dyes include polymeric dyes selected from the group consisting of alkoxyated triphenyl-methane polymeric colourants, alkoxyated carbocyclic and alkoxyated heterocyclic azo colourants, including alkoxyated thiophene polymeric colourants, and mixtures thereof. Polymeric dyes may comprise the optionally substituted alkoxyated dyes, such as

alkoxylated triphenyl-methane polymeric colourants, alkoxylated carbocyclic and alkoxylated heterocyclic azo colourants including alkoxylated thiophene polymeric colourants, and mixtures thereof, such as the fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA).

Suitable polymeric bluing agents are illustrated below. As with all such alkoxylated compounds, the organic synthesis may produce a mixture of molecules having different degrees of alkoxylation. During a typical ethoxylation process, for example, the randomness of the ethylene oxide addition results in a mixture of oligomers with different degrees of ethoxylation. As a consequence of its ethylene oxide number distribution, which often follows a Poisson law, a commercial material contains substances with somewhat different properties. For example, in one aspect the product resulting from an ethoxylation is not a single compound containing five (CH₂CH₂O) units as the general structure (Formula A, with x+y = 5) may suggest. Instead, the product is a mixture of several homologs whose total of ethylene oxide units varies from about 2 to about 10. Industrially relevant processes will typically result in such mixtures, which may normally be used directly to provide the fabric shading dye, or less commonly may undergo a purification step.

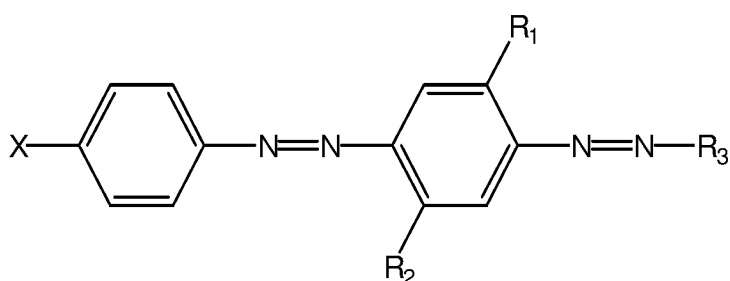
The fabric shading dye may have the structure:



wherein the index values x and y are independently selected from 1 to 10. In some aspects, the average degree of ethoxylation, x + y, sometimes also referred to as the average number of ethoxylate groups, is from about 3 to about 12, or from about 4 to about 8. In some embodiments the average degree of ethoxylation, x + y, can be from about 5 to about 6. The range of ethoxylation present in the mixture varies depending on the average number of ethoxylates incorporated. Typical distributions for ethoxylation of toluidine with either 5 or 8 ethoxylates are shown in Table II on page 42 in the Journal of Chromatography A 1989, volume 462, pp. 39 -47. The whitening agents are synthesized according to the procedures disclosed in U.S. Pat. No. 4,912,203 to Kluger et al.; a primary aromatic amine is reacted with an appropriate amount of ethylene oxide, according to procedures well known in the art. The polyethyleneoxy substituted

m-toluidine useful in the preparation of the colorant can be prepared by a number of well known methods. The polyethyleneoxy groups may be introduced into the m-toluidine molecule by reaction of the m-toluidine with ethylene oxide. Generally the reaction proceeds in two steps, the first being the formation of the corresponding N,N-dihydroxyethyl substituted m-toluidine. In some aspects, no catalyst is utilized in this first step (for example as disclosed at Column 4, lines 16-25 of U.S. Pat. No. 3,927,044 to Foster et al.). The dihydroxyethyl substituted m-toluidine is then reacted with additional ethylene oxide in the presence of a catalyst such as sodium (described in Preparation II of U.S. Pat. No. 3,157,633 to Kuhn), or it may be reacted with additional ethylene oxide in the presence of sodium or potassium hydroxide (described in Example 5 of U.S. Pat. No. 5,071,440 to Hines et al.). The amount of ethylene oxide added to the reaction mixture determines the number of ethyleneoxy groups which ultimately attach to the nitrogen atom. In some aspects, it may be advantageous to dissolve the whitening agent in a solvent which may be protic or aprotic. Typically for ease of handling and formulation such whitening agents may be dissolved in polar protic solvents such as, for example, a low molecular weight polyethyleneglycol such a PEG200. In some aspects, an excess of the polyethyleneoxy substituted m-toluidine coupler may be employed in the formation of the whitening agent and remain as a component in the final colorant mixture. In certain aspects, the presence of excess coupler or diluting solvent may confer advantageous properties to a mixture in which it is incorporated such as the raw material, a pre-mix, a finished product or even the wash solution prepared from the finished product.

The fabric shading dye may have the following structure:



wherein:

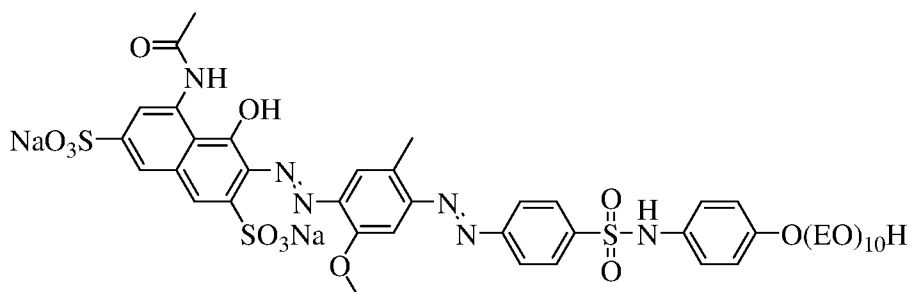
R_1 and R_2 are independently selected from the group consisting of: H; alkyl; alkoxy; alkyleneoxy; alkyl capped alkyleneoxy; urea; and amido;

R_3 is a substituted aryl group;

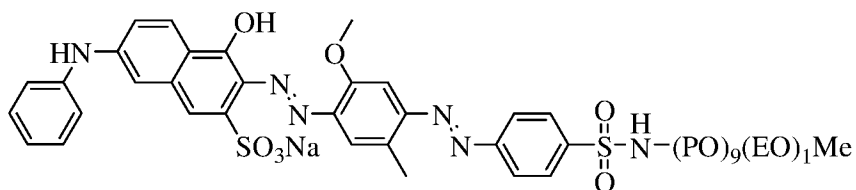
X is a substituted group comprising sulfonamide moiety and optionally an alkyl and/or aryl moiety, and wherein the substituent group comprises at least one alkyleneoxy chain. The hueing dye may be a thiophene dye, such as a thiophene azo dye, which may be alkoxyated. Optionally the dye may be substituted with at least one ionic solubilising group selected from sulphonic, carboxylic or quaternary ammonium groups.

Non-limiting examples of suitable fabric shading dyes are:

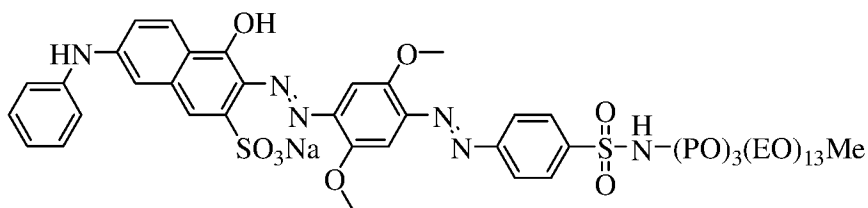
Dye Formula 1



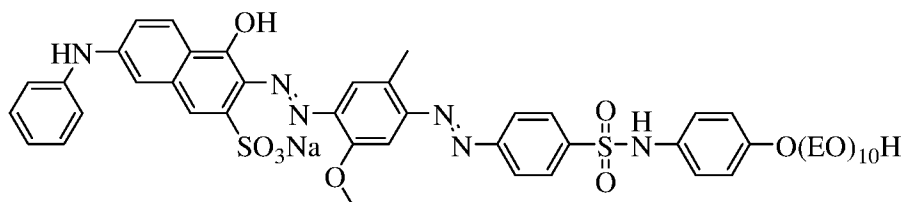
Dye Formula 2



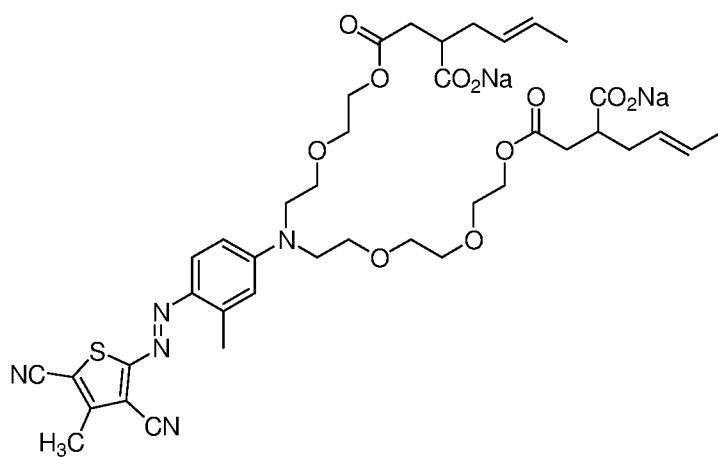
Dye Formula 3



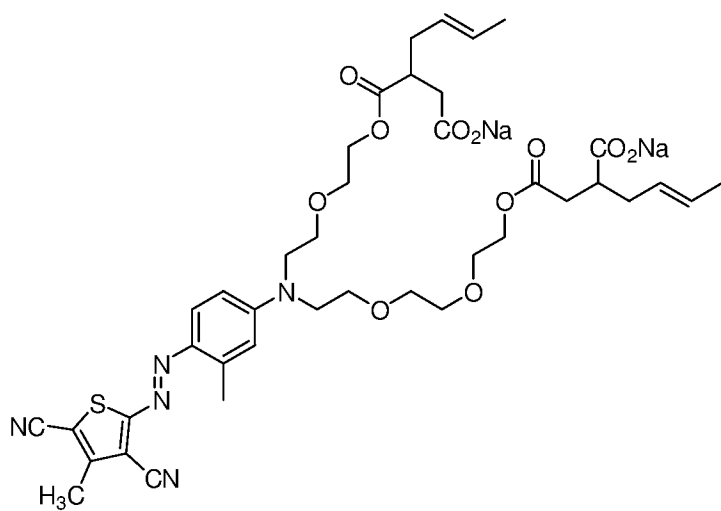
Dye Formula 4



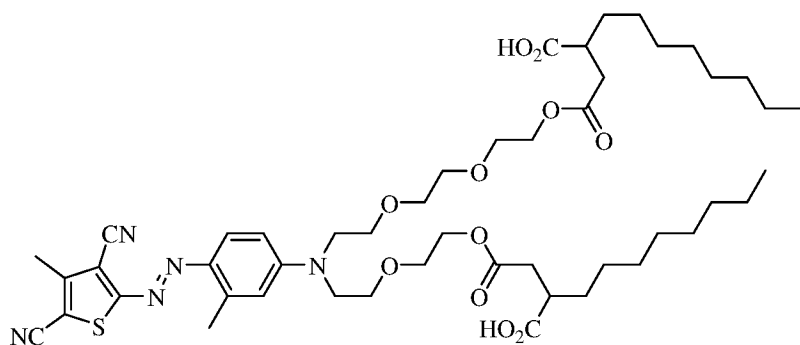
5 Dye Formula 5



Dye Formula 6

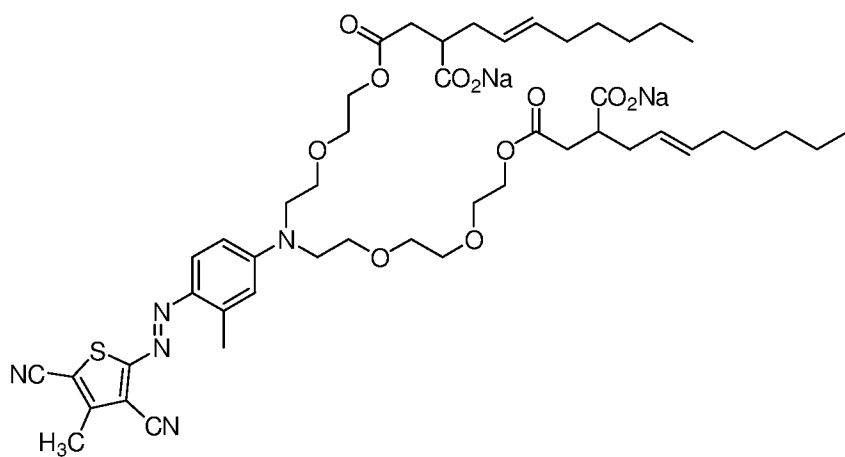


Dye Formula 7

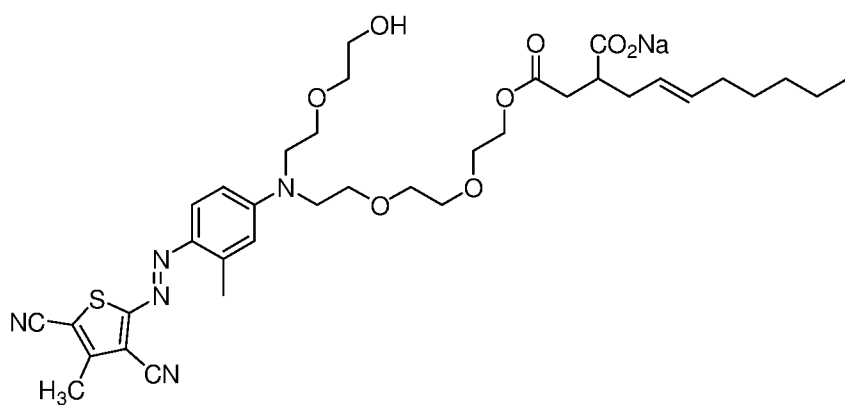


Dye Formula 8

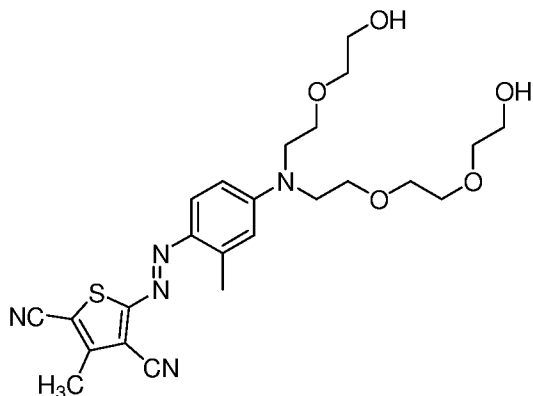
5



Dye Formula 9



Dye Formula 10



Dye-Clay Conjugates

5 Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay; the clay may be selected from the group consisting of Montmorillonite clay, Hectorite clay, Saponite clay and mixtures thereof. In another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of a clay and one cationic/basic dye selected from the group consisting of C.I. Basic

10 Yellow 1 through 108, C.I. Basic Orange 1 through 69, C.I. Basic Red 1 through 118, C.I. Basic Violet 1 through 51, C.I. Basic Blue 1 through 164, C.I. Basic Green 1 through 14, C.I. Basic Brown 1 through 23, CI Basic Black 1 through 11 In still another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of: Montmorillonite Basic Blue B7 C.I. 42595 conjugate, Montmorillonite Basic Blue B9 C.I. 52015 conjugate,

15 Montmorillonite Basic Violet V3 C.I. 42555 conjugate, Montmorillonite Basic Green G1 C.I. 42040 conjugate, Montmorillonite Basic Red R1 C.I. 45160 conjugate, Montmorillonite C.I. Basic Black 2 conjugate, Hectorite Basic Blue B7 C.I. 42595 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Green G1 C.I. 42040 conjugate, Hectorite Basic Red R1 C.I. 45160 conjugate, Hectorite C.I. Basic Black 2

20 conjugate, Saponite Basic Blue B7 C.I. 42595 conjugate, Saponite Basic Blue B9 C.I. 52015 conjugate, Saponite Basic Violet V3 C.I. 42555 conjugate, Saponite Basic Green G1 C.I. 42040 conjugate, Saponite Basic Red R1 C.I. 45160 conjugate, Saponite C.I. Basic Black 2 conjugate and mixtures thereof.

Pigments

25 Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pyranthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone,

tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by C1-C3 -alkyl or a phenyl or heterocyclic radical, and wherein the phenyl and heterocyclic radicals may additionally carry substituents, anthrapyrimidinecarboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polybromochloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof. Other suitable pigments are described in WO2008/090091. In another aspect, suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof. Suitable pigments include Pigment Blues 15 to 20, especially Pigment Blue 15 and/or 16. Other suitable pigments include those selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof.

The concentration of fabric shading agent present in the cleaning composition of the invention is from about 0.0001 to about 0.05 wt% based on the total cleaning composition, or from about 0.0001 to about 0.005 wt%. Based on the wash liquor, the concentration of fabric shading agent is from about 1 ppb to about 5 ppm, or from about 10 ppb to about 500 ppb. The concentration of the fabric shading agent may depend on the equivalent weight of the fabric shading agent. The equivalent weight (EW) of the fabric shading agent, the molecular weight (MW) divided by the number of dye chromophores in the shading agent, may be between 200 and 2000. When the equivalent weight of the shading agent is greater than 2000, these ranges should be multiplied by the equivalent weight of the shading agent divided by 2000. Thus if a shading agent has a MW of 1,000 with a single dye chromophore, its EW is the same as its MW. If the MW is 5,000 and the shading agent has two chromophores, its EW would be 2,500 and the ranges indicated above should be multiplied by (2,500/2,000), so that for example the amount of such a fabric shading dye present in the cleaning composition of the invention is typically from 0.00125 to 0.0625 wt% based on the total cleaning composition. Such corrections to levels may be required depending on the number of chromophores attached to a polymer of high MW, for example. For the purposes of this disclosure, a chromophore is considered a dye chromophore if it has an extinction coefficient of at least 1,000 L/mol/cm, or at least 5,000 L/mol/cm, at the maximum absorbance in the visible range between 400 nm and 750 nm.

The fabric shading agent may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for the agent, with optional purification step(s). Such reaction mixtures generally comprise the fabric shading agent

molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route.

Brighteners

5 Brighteners (also referred to as fluorescent optical brighteners) emit at least some visible light. In contrast, fabric hueing agents can alter the tint of a surface as they absorb at least a portion of the visible light spectrum.

Without being bound by theory, it is believed that brighteners may deposit on dingy areas of fabric. When brighteners deposit on such dingy areas, such as grease stains, the brighteners
10 may not work as effectively. The dingy area may contain compounds that also absorb UV light, thereby competing with the brighteners for the UV light. To the extent that these compounds absorb the UV light, the UV light is not used to activate the brighteners and the brighteners fluoresce less. Therefore, it is believed that improved grease cleaning may contribute to more even distribution of brightener efficiency across a fabric.

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 detergent compositions described herein. Commercial fluorescent brighteners suitable for the present invention can be classified into subgroups, including but not limited to: derivatives of stilbene, pyrazoline, coumarin, benzoxazoles, carboxylic acid, methinecyanines, dibenzothiophene-5,5-
20 dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents.

In some examples, the fluorescent brightener is selected from the group consisting of disodium 4,4'-bis{[4-anilino-6-morpholino-s-triazin-2-yl]-amino}-2,2'-stilbenedisulfonate (brightener 15, commercially available under the tradename Tinopal AMS-GX by Ciba Geigy Corporation), disodium 4,4'-bis{[4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl]-amino}-
25 2,2'-stilbenedisulfonate (commercially available under the tradename Tinopal UNPA-GX by Ciba-Geigy Corporation), disodium 4,4'-bis{[4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl]-amino}-2,2'-stilbenedisulfonate (commercially available under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation). The fluorescent brightener may be disodium 4,4'-bis{[4-anilino-6-morpholino-s-triazin-2-yl]-amino}-2,2'-stilbenedisulfonate.

30 The brighteners may be added in particulate form or as a premix with a suitable solvent, for example nonionic surfactant, monoethanolamine, propane diol.

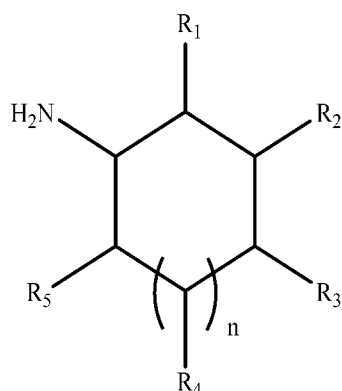
The brightener may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for the brightener molecule, with optional

purification step(s). Such reaction mixtures generally comprise the brightener molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route.

Cyclic Amine

- 5 The cleaning compositions described herein may include from about 0.1% to about 10%, or from about 0.2% to about 5%, or from about 0.5% to about 3%, by weight the composition, of a cyclic amine.

The cyclic amine may be represented by the structure of Formula (I):



- 10 The substituents “Rs” can be independently selected from NH₂, H and linear, branched alkyl or alkenyl from 1 to 10 carbon atoms. For the purpose of this invention “Rs” includes R1-R5. At least one of the “Rs” needs to be NH₂. The remaining “Rs” can be independently selected from NH₂, H and linear, branched alkyl or alkenyl having from 1 to 10 carbon atoms. n is from 0 to 3, or n is 1.
- 15 The amine of the disclosure is a cyclic amine with at least two primary amine functionalities. The primary amines can be in any position in the cycle but it has been found that in terms of grease cleaning, better performance may be obtained when the primary amines are in positions 1,3. It has also been found advantageous in terms of grease cleaning amines in which one of the substituents is -CH₃ and the rest are H.

- 20 The term “cyclic amine” herein encompasses a single cyclic amine and a mixture thereof.

The cyclic amine can be subjected to protonation depending on the pH of the cleaning medium in which it is used.

Adjuncts

- 25 The cleaning compositions of the invention may also contain an adjunct. Suitable adjuncts include 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.

Enzymes

The cleaning compositions described herein may comprise one or more enzymes which
5 provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase,
10 and amylases, or mixtures thereof. A typical combination is an enzyme cocktail that may comprise, for example, a protease and lipase in conjunction with amylase. When present in a detergent composition, the aforementioned additional enzymes may be present at levels from about 0.00001% to about 2%, from about 0.0001% to about 1% or even from about 0.001% to about 0.5% enzyme protein by weight of the detergent composition.

Enzyme Stabilizing System

The cleaning compositions may 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 the detergent enzyme. Such a
20 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 of the detergent
25 composition. In the case of aqueous detergent compositions comprising protease, a reversible protease inhibitor, such as a boron compound, including borate, 4-formyl phenylboronic acid, phenylboronic acid and derivatives thereof, or compounds such as calcium formate, sodium formate and 1,2-propane diol may be added to further improve stability.

Builders

30 The cleaning compositions may comprise a builder. Built detergent compositions typically comprise at least about 1% builder, based on the total weight of the composition. Liquid detergent compositions may comprise up to about 10% builder, and in some examples up to about 8% builder, of the total weight of the composition. Granular detergent compositions

may comprise up to about 30% builder, and in some examples up to about 5% builder, by weight of the composition.

Suitable builders include aluminosilicates (e.g., zeolite builders, such as zeolite A, zeolite P, and zeolite MAP), silicates, phosphates, such as polyphosphates (e.g., sodium tri-
5 polyphosphate), 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 nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. Additional
10 suitable builders may be selected from citric acid, lactic acid, fatty acid, polycarboxylate builders, for example, copolymers of acrylic acid, copolymers of acrylic acid and maleic acid, and copolymers of acrylic acid and/or maleic acid, and other suitable ethylenic monomers with various types of additional functionalities. Alternatively, the composition may be substantially free of builder.

15 Structurant / Thickeners

Suitable structurants/thickeners include di-benzylidene polyol acetal derivative. The fluid detergent composition may comprise from about 0.01% to about 1% by weight of a dibenzylidene polyol acetal derivative (DBPA), or from about 0.05% to about 0.8%, or from
20 about 0.1% to about 0.6%, or even from about 0.3% to about 0.5%. The DBPA derivative may comprise a dibenzylidene sorbitol acetal derivative (DBS).

Suitable structurants/thickeners also include bacterial cellulose. The fluid detergent composition may comprise from about 0.005 % to about 1 % by weight of a bacterial cellulose network. The term "bacterial cellulose" encompasses any type of cellulose produced via
25 fermentation of a bacteria of the genus Acetobacter such as CELLULON® by CPKelco U.S. and includes materials referred to popularly as microfibrillated cellulose, reticulated bacterial cellulose, and the like.

Suitable structurants/thickeners also include coated bacterial cellulose. The bacterial cellulose may be at least partially coated with a polymeric thickener. The at least partially coated
30 bacterial cellulose may comprise from about 0.1 % to about 5 %, or even from about 0.5 % to about 3 %, by weight of bacterial cellulose; and from about 10 % to about 90 % by weight of the polymeric thickener. Suitable bacterial cellulose may include the bacterial cellulose described above and suitable polymeric thickeners include: carboxymethylcellulose, cationic hydroxymethylcellulose, and mixtures thereof.

Suitable structurants/thickeners also include cellulose fibers. The composition may comprise from about 0.01 to about 5% by weight of the composition of a cellulosic fiber. The cellulosic fiber may be extracted from vegetables, fruits or wood. Commercially available examples are Avicel® from FMC, Citri-Fi from Fiberstar or Betafib from Cosun.

5 Suitable structurants/thickeners also include non-polymeric crystalline hydroxyl-functional materials. The composition may comprise from about 0.01 to about 1% by weight of the composition of a non-polymeric crystalline, hydroxyl functional structurant. The non-polymeric crystalline, hydroxyl functional structurants generally may comprise a crystallizable glyceride which can be pre-emulsified to aid dispersion into the final fluid detergent composition.

10 The crystallizable glycerides may include hydrogenated castor oil or "HCO" or derivatives thereof, provided that it is capable of crystallizing in the liquid detergent composition.

Suitable structurants/thickeners also include polymeric structuring agents. The compositions may comprise from about 0.01 % to about 5 % by weight of a naturally derived and/or synthetic polymeric structurant. Examples of naturally derived polymeric structurants of

15 use in the present invention include: hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives and mixtures thereof. Suitable polysaccharide derivatives include: pectine, alginate, arabinogalactan (gum Arabic), carrageenan, gellan gum, xanthan gum, guar gum and mixtures thereof. Examples of synthetic polymeric structurants of use in the present invention include: polycarboxylates,

20 polyacrylates, hydrophobically modified ethoxylated urethanes, hydrophobically modified non-ionic polyols and mixtures thereof.

Suitable structurants/thickeners also include di-amido-gellants. The external structuring system may comprise a di-amido gellant having a molecular weight from about 150 g/mol to about 1,500 g/mol, or even from about 500 g/mol to about 900 g/mol. Such di-amido gellants

25 may comprise at least two nitrogen atoms, wherein at least two of said nitrogen atoms form amido functional substitution groups. The amido groups may be different or the same. Non-limiting examples of di-amido gellants are: N,N'-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; dibenzyl (2S,2'S)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)dicarbamate; dibenzyl

30 (2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)dicarbamate.

Polymeric Dispersing Agents

The cleaning composition may comprise one or more polymeric dispersing agents. Examples are carboxymethylcellulose, poly(vinyl-pyrrolidone), poly(ethylene glycol),

poly(vinyl alcohol), poly(vinylpyridine-N-oxide), poly(vinylimidazole), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid co-polymers.

The cleaning composition may comprise one or more amphiphilic cleaning polymers such as the compound having the following general structure: bis((C₂H₅O)(C₂H₄O)_n)(CH₃)-N⁺-C_xH_{2x}-N⁺-(CH₃)-bis((C₂H₅O)(C₂H₄O)_n), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof.

The cleaning composition may comprise amphiphilic alkoxyated grease cleaning polymers which have balanced hydrophilic and hydrophobic properties such that they remove grease particles from fabrics and surfaces. The amphiphilic alkoxyated grease cleaning polymers may comprise a core structure and a plurality of alkoxyate groups attached to that core structure. These may comprise alkoxyated polyalkylenimines, for example, having an inner polyethylene oxide block and an outer polypropylene oxide block. Such compounds may include, but are not limited to, ethoxylated polyethyleneimine, ethoxylated hexamethylene diamine, and sulfated versions thereof. Polypropoxylated derivatives may also be included. A wide variety of amines and polyalkyleneimines can be alkoxyated to various degrees. A useful example is 600g/mol polyethyleneimine core ethoxylated to 20 EO groups per NH and is available from BASF. The detergent compositions described herein may comprise from about 0.1% to about 10%, and in some examples, from about 0.1% to about 8%, and in other examples, from about 0.1% to about 6%, by weight of the detergent composition, of alkoxyated polyamines.

Carboxylate polymer - The detergent composition may also include one or more carboxylate polymers, which may optionally be sulfonated. Suitable carboxylate polymers include a maleate/acrylate random copolymer or a poly(meth)acrylate homopolymer. In one aspect, the carboxylate polymer is a poly(meth)acrylate homopolymer having a molecular weight from 4,000 Da to 9,000 Da, or from 6,000 Da to 9,000 Da.

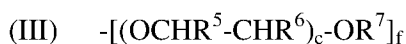
Alkoxyated polycarboxylates may also be used in the detergent compositions herein to provide grease removal. Such materials are described in WO 91/08281 and PCT 90/01815. Chemically, these materials comprise poly(meth)acrylates having one ethoxy side-chain per every 7-8 (meth)acrylate units. The side-chains are of the formula -(CH₂CH₂O)_m (CH₂)_nCH₃ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but may be in the range of about 2000 to about 50,000. The detergent compositions described herein may comprise from about 0.1% to about 10%, and in some examples, from about 0.25% to about 5%, and in

other examples, from about 0.3% to about 2%, by weight of the detergent composition, of alkoxylated polycarboxylates.

The detergent compositions may include an amphiphilic graft co-polymer. A suitable amphiphilic graft co-polymer comprises (i) a polyethylene glycol backbone; and (ii) and at least one pendant moiety selected from polyvinyl acetate, polyvinyl alcohol and mixtures thereof. A suitable amphilic graft co-polymer is Sokalan® HP22, supplied from BASF. Suitable polymers include random graft copolymers, for example, a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is typically about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units.

Soil release polymer

The detergent compositions of the present invention may also include one or more soil release polymers having a structure as defined by one of the following structures (I), (II) or (III):



wherein:

a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with SO₃Me;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium wherein the alkyl groups are C₁-C₁₈ alkyl or C₂-C₁₀ hydroxyalkyl, or mixtures thereof;

R¹, R², R³, R⁴, R⁵ and R⁶ are independently selected from H or C₁-C₁₈ n- or iso-alkyl; and

R⁷ is a linear or branched C₁-C₁₈ alkyl, or a linear or branched C₂-C₃₀ alkenyl, or a
5 cycloalkyl group with 5 to 9 carbon atoms, or a C₈-C₃₀ aryl group, or a C₆-C₃₀ arylalkyl group.

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, SRN300 and SRN325 supplied by Clariant. Other suitable soil release
10 polymers are Marloquest polymers, such as Marloquest SL supplied by Sasol.

Cellulosic polymer

The cleaning compositions of the present invention may also include one or more cellulosic polymers including those selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose. In one aspect, the cellulosic polymers are
15 selected from the group comprising carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixtures thereof. In one aspect, the carboxymethyl cellulose has a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

Additional Amines

20 Additional amines may be used in the cleaning compositions described herein for added removal of grease and particulates from soiled materials. The detergent compositions described herein may comprise from about 0.1% to about 10%, in some examples, from about 0.1% to about 4%, and in other examples, from about 0.1% to about 2%, by weight of the detergent composition, of additional amines. Non-limiting examples of additional amines may include, but
25 are not limited to, polyetheramines, polyamines, oligoamines, triamines, diamines, pentamines, tetraamines, or combinations thereof. Specific examples of suitable additional amines include tetraethylenepentamine, triethylenetetraamine, diethylenetriamine, or a mixture thereof.

Bleaching Agents – The detergent compositions of the present invention may comprise one or more bleaching agents. Suitable bleaching agents other than bleaching catalysts include
30 photobleaches, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, pre-formed peracids and mixtures thereof. In general, when a bleaching agent is used, the detergent

compositions of the present invention may comprise from about 0.1% to about 50% or even from about 0.1% to about 25% bleaching agent by weight of the detergent composition.

Bleach Catalysts - The detergent compositions of the present invention may also include one or more bleach catalysts capable of accepting an oxygen atom from a peroxyacid and/or salt thereof, and transferring the oxygen atom to an oxidizable substrate. Suitable bleach catalysts include, but are not limited to: iminium cations and polyions; iminium zwitterions; modified amines; modified amine oxides; N-sulphonyl imines; N-phosphonyl imines; N-acyl imines; thiadiazole dioxides; perfluoroimines; cyclic sugar ketones and mixtures thereof.

Encapsulates

The compositions may comprise an encapsulate. The encapsulate may comprise a core, a shell having an inner and outer surface, where the shell encapsulates the core.

The encapsulate may comprise a core and a shell, where the core comprises a material selected from perfumes; brighteners; dyes; insect repellants; silicones; waxes; flavors; vitamins; fabric softening agents; skin care agents, e.g., paraffins; enzymes; anti-bacterial agents; bleaches; sensates; or mixtures thereof; and where the shell comprises a material selected from polyethylenes; polyamides; polyvinylalcohols, optionally containing other co-monomers; polystyrenes; polyisoprenes; polycarbonates; polyesters; polyacrylates; polyolefins; polysaccharides, e.g., alginate and/or chitosan; gelatin; shellac; epoxy resins; vinyl polymers; water insoluble inorganics; silicone; aminoplasts, or mixtures thereof. When the shell comprises an aminoplast, the aminoplast may comprise polyurea, polyurethane, and/or polyureaurethane. The polyurea may comprise polyoxymethyleneurea and/or melamine formaldehyde.

The encapsulate may comprise a core, and the core may comprise a perfume. The encapsulate may comprise a shell, and the shell may comprise melamine formaldehyde and/or cross linked melamine formaldehyde. The encapsulate may comprise a core comprising a perfume and a shell comprising melamine formaldehyde and/or cross linked melamine formaldehyde

Suitable encapsulates may comprise a core material and a shell, where the shell at least partially surrounds the core material. The core of the encapsulate comprises a material selected from a perfume raw material and/or optionally another material, e.g., vegetable oil, esters of vegetable oils, esters, straight or branched chain hydrocarbons, partially hydrogenated terphenyls, dialkyl phthalates, alkyl biphenyls, alkylated naphthalene, petroleum spirits, aromatic solvents, silicone oils, or mixtures thereof.

The wall of the encapsulate may comprise a suitable resin, such as the reaction product of an aldehyde and an amine. Suitable aldehydes include formaldehyde. Suitable amines include melamine, urea, benzoguanamine, glycoluril, or mixtures thereof. Suitable melamines include methylol melamine, methylated methylol melamine, imino melamine and mixtures thereof.

5 Suitable ureas include, dimethylol urea, methylated dimethylol urea, urea-resorcinol, or mixtures thereof.

Suitable formaldehyde scavengers may be employed with the encapsulates, for example, in a capsule slurry and/or added to a composition before, during, or after the encapsulates are added to such composition.

10 Suitable capsules can be purchased from Appleton Papers Inc. of Appleton, Wisconsin USA.

Perfumes

Perfumes and perfumery ingredients may be used in the detergent compositions described herein. Non-limiting examples of perfume and perfumery ingredients include, but are not limited to, aldehydes, ketones, esters, and the like. Other examples include various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes may be included at a concentration ranging from about 0.01% to about 2% by weight of the detergent composition.

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Dye Transfer Inhibiting Agents

Fabric detergent compositions may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents may include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents may be used at a concentration of about 0.0001% to about 10%, by weight of the composition, in some examples, from about 0.01% to about 5%, by weight of the composition, and in other examples, from about 0.05% to about 2% by weight of the composition.

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Chelating Agents

The detergent compositions described herein may also contain one or more metal ion chelating agents. Suitable molecules include copper, iron and/or manganese chelating agents and mixtures thereof. Such chelating agents can be selected from the group consisting of

phosphonates, amino carboxylates, amino phosphonates, succinates, polyfunctionally-substituted aromatic chelating agents, 2-pyridinol-N-oxide compounds, hydroxamic acids, carboxymethyl inulins and mixtures thereof. Chelating agents can be present in the acid or salt form including alkali metal, ammonium, and substituted ammonium salts thereof, and mixtures thereof. Other
5 suitable chelating agents for use herein are the commercial DEQUEST series, and chelants from Monsanto, Akzo-Nobel, DuPont, Dow, the Trilon® series from BASF and Nalco.

The chelant may be present in the detergent compositions disclosed herein at from about 0.005% to about 15% by weight, about 0.01% to about 5% by weight, about 0.1% to about 3.0% by weight, or from about 0.2% to about 0.7% by weight, or from about 0.3% to about 0.6% by
10 weight of the detergent compositions disclosed herein.

Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the detergent compositions described herein. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" and in front-loading style washing machines.
15 The detergent compositions herein may comprise from 0.1% to about 10%, by weight of the composition, of suds suppressor.

Examples 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),
20 N-alkylated amino triazines, waxy hydrocarbons having a melting point below about 100 °C, silicone suds suppressors, and secondary alcohols.

Additional suitable antifoams are those derived from phenylpropylmethyl substituted polysiloxanes.

The detergent composition may comprise a suds suppressor selected from
25 organomodified silicone polymers with aryl or alkylaryl substituents combined with silicone resin and a primary filler, which is modified silica. The detergent compositions may comprise from about 0.001% to about 4.0%, by weight of the composition, of such a suds suppressor.

The detergent composition comprises a suds suppressor selected from: a) mixtures of from about 80 to about 92% ethylmethyl, methyl(2-phenylpropyl) siloxane; from about 5 to
30 about 14% MQ resin in octyl stearate; and from about 3 to about 7% modified silica; b) mixtures of from about 78 to about 92% ethylmethyl, methyl(2-phenylpropyl) siloxane; from about 3 to about 10% MQ resin in octyl stearate; from about 4 to about 12% modified silica; or c) mixtures thereof, where the percentages are by weight of the anti-foam.

Suds Boosters

If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides may be incorporated into the detergent compositions at a concentration ranging from about 1% to about 10% by weight of the detergent composition. Some examples include the C₁₀-C₁₄ monoethanol
5 and diethanol amides. If desired, water-soluble magnesium and/or calcium salts such as MgCl₂, MgSO₄, CaCl₂, CaSO₄, and the like, may be added at levels of about 0.1% to about 2% by weight of the detergent composition, to provide additional suds and to enhance grease removal performance.

Conditioning Agents

10 The composition of the present invention may include a high melting point fatty compound. The high melting point fatty compound useful herein has a melting point of 25°C or higher, and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. Such compounds of low melting point are not intended to be included in this section. The high melting point fatty compound is included
15 in the composition at a level of from about 0.1% to about 40%, or from about 1% to about 30%, or from about 1.5% to about 16% by weight of the composition, from about 1.5% to about 8%.

The composition of the present invention may include a nonionic polymer as a conditioning agent.

Suitable conditioning agents for use in the composition include those conditioning agents
20 characterized generally as silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicones, and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof, or those conditioning agents which otherwise form liquid, dispersed particles in the aqueous surfactant matrix herein. The concentration of the silicone conditioning agent typically ranges from about 0.01% to about 10%.

25 The compositions of the present invention may also comprise from about 0.05% to about 3% of at least one organic conditioning oil as the conditioning agent, either alone or in combination with other conditioning agents, such as the silicones (described herein). Suitable conditioning oils include hydrocarbon oils, polyolefins, and fatty esters.

Fabric Enhancement Polymers

30 Suitable fabric enhancement polymers are typically cationically charged and/or have a high molecular weight. Suitable concentrations of this component are in the range from 0.01% to 50%, or from 0.1% to 15%, or from 0.2% to 5.0%, or from 0.5% to 3.0% by weight of the composition. The fabric enhancement polymers may be a homopolymer or be formed from two

or more types of monomers. The monomer weight of the polymer will generally be between 5,000 and 10,000,000, typically at least 10,000 or in the range 100,000 to 2,000,000. Suitable fabric enhancement polymers will have cationic charge densities of at least 0.2 meq/gm, or at least 0.25 meq/gm, or at least 0.3 meq/gm, but also less than 5 meq/gm, or less than 3 meq/gm, or less than 2 meq/gm at the pH of intended use of the composition, which pH will generally range from pH 3 to pH 9, or between pH 4 and pH 8. The fabric enhancement polymers may be of natural or synthetic origin.

Pearlescent Agent

The laundry detergent compositions of the invention may comprise a pearlescent agent. Non-limiting examples of pearlescent agents include: mica; titanium dioxide coated mica; bismuth oxychloride; fish scales; mono and diesters of alkylene glycol. The pearlescent agent may be ethyleneglycoldistearate (EGDS).

Hygiene and malodour

The compositions of the present invention may also comprise one or more of zinc ricinoleate, thymol, quaternary ammonium salts such as Bardac®, polyethylenimines (such as Lupasol® from BASF) and zinc complexes thereof, silver and silver compounds, especially those designed to slowly release Ag⁺ or nano-silver dispersions.

Buffer System

The detergent compositions described herein may be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 7.0 and about 12, and in some examples, between about 7.0 and about 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, lactic acid or lactate, monoethanol amine or other amines, boric acid or borates, and other pH-adjusting compounds well known in the art.

The detergent compositions herein may comprise dynamic in-wash pH profiles. Such detergent compositions may use wax-covered citric acid particles in conjunction with other pH control agents such that (i) about 3 minutes after contact with water, the pH of the wash liquor is greater than 10; (ii) about 10 minutes after contact with water, the pH of the wash liquor is less than 9.5; (iii) about 20 minutes after contact with water, the pH of the wash liquor is less than 9.0; and (iv) optionally, wherein, the equilibrium pH of the wash liquor is in the range of from about 7.0 to about 8.5.

Catalytic Metal Complexes

The detergent compositions may include 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 copper, iron, 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.

Water-Soluble Film

The compositions of the present invention may also be encapsulated within a water-soluble film. Preferred film materials are preferably polymeric materials. The film material can, for example, be obtained by casting, blow-moulding, extrusion or blown extrusion of the polymeric material, as known in the art.

Preferred polymers, copolymers or derivatives thereof suitable for use as pouch material are selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), and combinations thereof. Preferably, the level of polymer in the pouch material, for example a PVA polymer, is at least 60%. The polymer can have any weight average molecular weight, preferably from about 1000 to 1,000,000, more preferably from about 10,000 to 300,000 yet more preferably from about 20,000 to 150,000. Mixtures of polymers can also be used as the pouch material.

Naturally, different film material and/or films of different thickness may be employed in making the compartments of the present invention. A benefit in selecting different films is that the resulting compartments may exhibit different solubility or release characteristics.

Suitable film materials are PVA films known under the MonoSol trade reference M8630, M8900, H8779 and PVA films of corresponding solubility and deformability characteristics.

The film material herein can also comprise one or more additive ingredients. For example, it can be beneficial to add plasticisers, for example glycerol, ethylene glycol, diethyleneglycol, propylene glycol, sorbitol and mixtures thereof. Other additives include functional detergent additives to be delivered to the wash water, for example organic polymeric dispersants, etc.

The film is soluble or dispersible in water, and preferably has a water-solubility of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out here after using a glass-filter with a maximum pore size of 20 microns: 50 grams $\pm$ 0.1 gram of film material is added in a pre-weighed 400 ml beaker and 245ml * 1ml of distilled water is added. This is stirred vigorously on a magnetic stirrer set at 600 rpm, for 30 minutes. Then, the mixture is filtered through a folded qualitative sintered-glass filter with a pore size as defined above (max. 20 micron). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining material is determined (which is the dissolved or dispersed fraction). Then, the percentage solubility or dispersability can be calculated.

The film may comprise an aversive agent, for example a bittering agent. Suitable bittering agents include, but are not limited to, naringin, sucrose octaacetate, quinine hydrochloride, denatonium benzoate, or mixtures thereof. Any suitable level of aversive agent may be used in the film. Suitable levels include, but are not limited to, 1 to 5000ppm, or even 100 to 2500ppm, or even 250 to 2000rpm.

The film may comprise an area of print. The area of print may cover the entire film or part thereof. The area of print may comprise a single colour or maybe comprise multiple colours, even three colours. The area of print may comprise white, black and red colours. The area of print may comprise pigments, dyes, blueing agents or mixtures thereof. The print may be present as a layer on the surface of the film or may at least partially penetrate into the film.

Other Adjunct Ingredients

A wide variety of other ingredients may be used in the detergent compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, and solid or other liquid fillers, erythrosine, colloidal silica, waxes, probiotics, surfactin, aminocellulosic polymers, Zinc Ricinoleate, perfume microcapsules, rhamnolipids, sophorolipids, glycopeptides, methyl ester sulfonates, methyl ester ethoxylates, sulfonated estolides, cleavable surfactants, biopolymers, silicones, modified silicones, aminosilicones, deposition aids, locust bean gum, cationic hydroxyethylcellulose polymers, cationic guar, hydrotropes (especially cumenesulfonate salts, toluenesulfonate salts, xylenesulfonate salts, and naphthalene salts), antioxidants, BHT, 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, hydroxyethylcellulose polymers, hydrophobically modified cellulose polymers or hydroxyethylcellulose polymers, starch perfume encapsulates, emulsified oils, bisphenol
5 antioxidants, microfibrinous cellulose structurants, properfumes, styrene/acrylate polymers, triazines, soaps, superoxide dismutase, benzophenone protease inhibitors, functionalized TiO₂, dibutyl phosphate, silica perfume capsules, and other adjunct ingredients, silicate salts (e.g., sodium silicate, potassium silicate), choline oxidase, pectate lyase, mica, titanium dioxide coated mica, bismuth oxychloride, and other actives.

10 The detergent 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, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, perfumes, preservatives, chelants,
15 proteins, skin active agents, sunscreens, UV absorbers, vitamins, niacinamide, caffeine, and minoxidil.

The detergent 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,
20 botanical, and natural colors, including water soluble components such as those having C.I. Names. The detergent compositions of the present invention may also contain antimicrobial agents.

Method of Making Cleaning compositions

The cleaning compositions of the present disclosure may be prepared by conventional
25 methods known to one skilled in the art, such as by a batch process or by a continuous loop process. The cleaning compositions of the present invention can be formulated into any suitable form and prepared by any process chosen by the formulator.

Methods of Use

The present disclosure includes methods for cleaning soiled material. As will be
30 appreciated by one skilled in the art, the detergent compositions of the present invention 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 soiled material and then optionally rinsing the soiled material. The soiled material may be subjected to a washing step prior to the optional rinsing step.

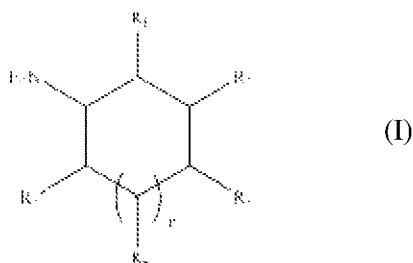
5 For use in laundry pretreatment applications, the method may include contacting the detergent compositions described herein with soiled fabric. Following pretreatment, the soiled fabric may be laundered in a washing machine or otherwise rinsed.

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 detergent composition in accord with the invention. An “effective amount” of the detergent composition means from about 20g 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 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, top-loading, vertical-axis Japanese-type automatic washing machine).

The detergent compositions herein may be used for laundering of fabrics at reduced wash 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.

25 The present disclosure includes a method of treating a textile, the method comprising the steps of: (a) treating the textile with an aqueous solution of from about 0.1 g/L to about 3 g/L of a surfactant; from about 1 ppb to about 5 ppm of a fabric shading dye suitable for providing a blue or violet shade to white cotton or polyester; and from about 0.1ppm to about 500 ppm, or about 0.1ppm to about 100 ppm, of a cyclic amine of

30 Formula (I):



where the radicals R₁, R₂, R₃, R₄ and R₅ are independently selected from NH₂, -H, linear or branched alkyl or alkenyl having from about 1 to about 10 carbon atoms and n is from about 0 to about 3 and where at least one of the radicals is NH₂; and (b) rinsing and drying the textile,
5 where the fabric shading dye is selected from azine, anthraquinone, mono-azo, and dis-azo dyes, optionally substituted with polyalkyleneoxy groups.

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,
10 caliper (thickness), absorbency, and strength characteristics. Non-limiting examples of suitable commercially available nonwoven substrates include those marketed under the tradenames SONTARA® by DuPont and POLYWEB® by James River Corp.

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

15 Packaging for the Compositions

The detergent compositions described herein can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials, and any suitable laminates.

Multi-Compartment Pouch Additive

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

EXAMPLES

In the following examples, the individual ingredients within the cleaning compositions are expressed as percentages by weight of the cleaning compositions unless indicated otherwise.

	Liquid Detergent	Compact Liquid Detergent	Liquid Detergent	Liquid Detergent	Compact Liquid Detergent
		2X			2X

	A (wt%)	B (wt%)	C (wt%)	D (wt%)	E (wt%)
AES C ₁₂₋₁₅ alkyl ethoxy (1.8) sulfate	15.8	----	7.4	13.0	----
AES C ₁₄₋₁₅ alkyl ethoxy (1.8) sulfate	----	21.6	----	----	21.6
Alkyl benzene sulfonate ¹	9.6	12.7	4.2	7.8	12.7
Sodium formate	----	----	----	0.1	----
Calcium formate	0.2	0.2	----	0.1	0.1
Monoethanolamine (MEA)	2.7	2.9	----	2.5	2.9
Diethylene glycol (DEG)	2.7	2.3	1.3	2.0	2.3
Amine Oxide	0.9	----	----	0.8	----
Sodium Tetraborate	1.3	1.0	1.6	1.5	1.0
Diethylenetriamine Pentaacetic acid ²	----	----	0.58	----	----
NI 24-9 ³	----	----	7.42	----	----
Cyclic Amine ⁴	1.0	1.0	1.0	0.5	1.0
Chelant ⁵	0.6	0.7	0.1	0.5	0.7
Citric Acid	2.8	1.6	2.7	2.5	1.6
C ₁₂₋₁₈ Fatty Acid	1.2	1.4	1.1	1.1	1.3
Cationic Co-polymer ⁶	----	----	0.2	----	----
Ethanol	2.1	3.9	0.9	1.7	3.9
Ethoxylated Polyethyleneimine ⁷	2.7	2.6	2.5	----	2.6
Ethoxylated Sulfonated Acrylate Dispersant ⁸	----	----	----	2.8	----

Amphiphilic alkoxyated grease cleaning polymer ⁹	1.87	2.0	1.7	2.0	2.0
A compound having the following general structure: bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃)-N ⁺ -C _x H _{2x} -N ⁺ -(CH ₃)-bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	----	----	1.45	----	----
1,2-Propanediol	4.2	6.5	2.0	2.5	2.0
Protease: V42 Preferenz® ¹⁰	0.066	0.066	0.06	0.06	0.066
Mannanase: Mannaway® ¹¹	0.001	0.001	----	----	0.001
Xyloglucanase: Whitezyme® ¹²	0.002	0.002	0.002	0.002	0.002
Amalays: V445 Everest 200L® ¹³	0.009	0.009	0.015	0.009	0.009
Cyclic amine ¹⁴					
Fabric Shading Dye ¹⁵	0.05	0.05	0.05	0.05	0.05
Brightener 15	2.1	2.7	0.23	0.21	2.7
Brightener 49	----	1.2	----	---	1.2
Hydrogenated Castor Oil	----	----	0.20	----	0.20
Sodium Cumene Sulfonate	0.71	----	1.50	0.6	----
Silicone	----	----	2.0	----	1.0
Industrial Grade Salt	0.032	0.033	----	----	----
pH	7.0 - 8.2	6.0 - 8.0	7.0 – 8.0	7.0-8.3	6.0 - 8.0
Water, perfume, dyes & other components	100% To balance				

	Liquid Detergent	Liquid Detergent	Liquid Detergent	Liquid Detergent
	F	G	H	I
	(wt%)	(wt%)	(wt%)	(wt%)
AES C ₁₂₋₁₄ alkyl ethoxy (3.0) sulfate	1.2	1.2	1.2	1.2
AES C ₁₄₋₁₅ alkyl ethoxy (1.8) sulfate	----	----	----	----
Alkyl benzene sulfonate ¹	10.0	10.0	10.0	10.0
Sodium formate	0.23	0.23	0.23	0.23
Calcium Chloride	0.01	0.3	0.3	0.3
Monoethanolamine (MEA)	0.2	0.2	0.2	0.2
Diethylene glycol (DEG)	----	----	----	----
Amine Oxide	----	----	----	0.7
Sodium Tetraborate	----	----	----	----
Diethylenetriamine Pentaacetic acid ²	----	----	----	----
NI 24-7 ³	0.4	0.4	0.4	0.4
Cyclic Amine ⁴	1.0	1.0	1.0	1.0
Chelant ⁵	0.4	0.4	0.4	0.4
Citric Acid	3.1	3.1	3.1	3.1
Fatty Acid	2.6	2.6	2.6	2.6
Cationic Co-polymer ⁶	----	----	----	----

Ethanol	0.99	0.99	0.99	0.99
Grease Cleaning Polymer ¹⁷	1.1	1.1	----	1.1
Particulate Dispersant ⁸	---	----	0.6	-----
Amphiphilic alkoxyated grease cleaning polymer ⁹	----	----	1.1	-----
A compound having the following general structure: bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃)- N ⁺ -C _x H _{2x} -N ⁺ -(CH ₃)- bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	0.6	0.6	----	0.6
1,2-Propanediol	1.5	1.5	1.5	1.5
Protease: Preferenz® ¹⁰	0.021	0.021	0.021	0.021
Mannanase: Mannaway® ¹¹	0.003	0.003	0.003	0.003
Xyloglucanase: Whitezyme® ¹²	0.003	0.003	0.003	0.003
Amalays: V445 Everest 200L® ¹³	0.004	0.004	0.004	0.004
Fabric Shading Dye ¹⁴	0.05	0.05	0.05	0.05
Brightener 15	----	----	-----	----
Brightener 49	0.08	0.08	0.08	0.08
Hydrogenated Castor Oil	0.25	0.25	0.25	0.25
Sodium Cumene Sulfonate	0.46	0.46	0.46	0.46
Silicone	----	----	-----	----
Industrial Grade Salt	----	----	-----	----

NI 45-7 ¹⁶	9.6	5.8	5.8	5.8
pH	7.0-8.3	7.0-8.3	7.0-8.3	7.0-8.3
Water, perfume, dyes & other components	100% To balance			

	Soluble Unit Dose	Soluble Unit Dose	Soluble Unit Dose
	J	K	L
	(wt%)	(wt%)	(wt%)
AES C ₁₂₋₁₄ alkyl ethoxy (3.0) sulfate	8.8	15.1	13.9
AES C ₁₄₋₁₅ alkyl ethoxy (1.8) sulfate	----	----	----
Alkyl benzene sulfonate ¹	18.5	22.1	20.6
Sodium formate	----	----	----
Magnesium Chloride	0.3	0.3	0.3
Monoethanolamine (MEA)	8.4	10.4	10.1
Diethylene glycol (DEG)	----	----	----
Dipropylene Glycol	0.1	4.0	4.0
Amine Oxide	----	----	----
Sodium Tetraborate	----	----	----
Diethylenetriamine Pentaacetic acid ²	----	----	----

NI 24-7 ³	14.4	4.0	4.0
Cyclic Amine ⁴	1.0	1.0	1.0
Chelant ⁵	2.0	2.0	2.4
Citric Acid	0.65	0.6	0.7
Fatty Acid	6.1	4.5	6.6
Cationic Co-polymer ⁶	----	----	----
Ethanol	----	----	----
Grease Cleaning Polymer ¹⁷	1.4	4.0	2.2
Ethoxylated Polyethyleneimine ⁷	5.3	1.6	3.5
Particulate Dispersant ⁸	----	----	----
Amphiphilic alkoxyated grease cleaning polymer ⁹	----	----	----
A compound having the following general structure: bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃)-N ⁺ -C _x H _{2x} -N ⁺ -(CH ₃)-bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	----	----	----
1,2-Propanediol	15.1	11.2	11.5
Protease: Preferenz® ¹⁰	0.05	0.05	0.06
Mannanase: Mannaway® ¹¹	0.003	0.003	0.003
Xyloglucanase: Whitezyme® ¹²	0.006	0.006	0.006
Termamyl Ultra	0.002	0.002	0.002

Amalaysse: V445 Everest 200L® ¹³	0.003	0.003	0.003
Lipase capsule slurry	----	----	----
Fabric Shading Dye ¹⁴	0.04	0.05	0.05
Brightener 15	----	----	----
Brightener 49	0.31	0.32	0.3
TexCare 300 A ¹⁷	----	----	0.5
Hydrogenated Castor Oil	0.1	0.2	0.2
Sodium Cumene Sulfonate	----	----	----
Silicone	----	----	----
Industrial Grade Salt	----	----	----
NI 45-7 ¹⁹	----	----	----
Acusol OP305	0.13	0.15	0.1

1. Linear alkylbenzenesulfonate having an average aliphatic carbon chain length C₁₁-C₁₂ supplied by Stepan, Northfield, Illinois, USA

2. Available for Sigma Aldrich

5 3. AE9 is C₁₂₋₁₃ alcohol ethoxylate, with an average degree of ethoxylation of 9, supplied by Huntsman, Salt Lake City, Utah, USA.

4. Baxxodur® ECX210 supplied by BASF

5. Suitable chelants are, for example, diethylenetetraamine pentaacetic acid (DTPA) supplied by Dow Chemical, Midland, Michigan, USA or Hydroxyethane di phosphonate (HEDP) supplied by Solutia, St
10 Louis, Missouri, USA Bagsvaerd, Denmark

6. Cationic co-polymer of a mole ratio of 16% acrylamide and 84% diallyldimethylammonium chloride with an average molecular weight of 38 kDa available from BASF, Ludwigshafen

7. Polyethyleneimine (MW = 600) with 20 ethoxylate groups per -NH.

8. Dispersant polymer Sulfonated Ethoxylated Acrylate supplied by Nippon Shokobai

9. Amphiphilic alkoxyated grease cleaning polymer is a polyethyleneimine (MW = 600) with 24 ethoxylate groups per –NH and 16 propoxylate groups per –NH 5.

10. Proteases may be supplied by Genencor International, Palo Alto, California, USA (e.g. Purafect Prime®) or by Novozymes, Bagsvaerd, Denmark (e.g. Liquanase®, Coronase®) or by Dupont, USA (e.g. 5 Preferenz®)

11, Mannaway® are all products of Novozymes, Bagsvaerd, Denmark .Suitable Brighteners are for example, Tinopal® AMS, Tinopal® CBS-X, Sulphonated zinc phthalocyanine Ciba Specialty Chemicals, Basel, Switzerland

12. Whitezyme® is a product of Novozymes, Bagsvaerd, Denmark

10 13. Suitable analyses are Everest 200L® is a product of Dupont, USA, Natalase® is a products of Novozymes, Bagsvaerd, Denmark.

14. Baxxodur® ECX210 (methylcyclohexane 1,3-diamine).

15 15. Fabric shading Dye is Direct Violet 9 or Direct Violet 66, Direct Violet 99, supplied by BASF, Ludwigshafen, Germany. Acid Violet 50, Disperse Violet 28, Solvent Violet 13, or ethoxylated mono-azo and bis azo dyes such as Liquitint Violet DD, or Liquitint Violet ION, supplied by Milliken, Spartanburg, South Carolina.

16. NI 45-7 is C₁₄₋₁₅ alcohol ethoxylate, with an average degree of ethoxylation of 7.

17. TexCare 300A is an anionic soil release polymer supplied by Clariant.

20 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.”

25 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 30 invention. Further, to the extent that any meaning or definition of a term in this document

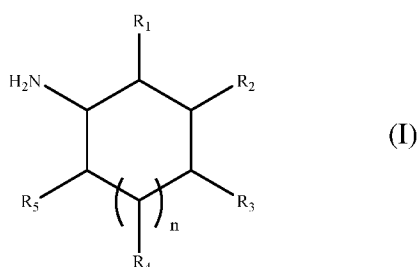
conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

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
5 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

What is claimed is:

1. A cleaning composition comprising:
from about 1% to about 70%, by weight of the composition, of a surfactant; from 0.0001% to 0.05%, by weight of the composition, of a fabric shading dye, a brightener, or a mixture thereof; and from about 0.1% to about 10%, by weight of the composition, of a cyclic amine of Formula (I):



wherein the radicals R_1 , R_2 , R_3 , R_4 and R_5 are independently selected from NH_2 , $-H$, linear or branched alkyl or alkenyl having from about 1 to about 10 carbon atoms and n is from about 0 to about 3 and wherein at least one of the radicals is NH_2 .

2. The cleaning composition of claim 1 wherein said cyclic amine is a diamine.
3. The cleaning composition according to any one of the preceding claims wherein n is about 1.
4. The cleaning composition according to any one of the preceding claims wherein R_2 is NH_2 .
5. The cleaning composition according to any one of the preceding claims wherein at least one of R_1 , R_3 , R_4 and R_5 is CH_3 and preferably the remaining radicals are H .
6. The cleaning composition according to any one of the preceding claims, wherein said cyclic amine of Formula (I) has a molecular weight of from about 100 to about 1,000 grams/mole.

7. The cleaning composition according to any one of the preceding claims, wherein said cyclic amine of Formula (I) has a molecular weight of from about 100 to about 450 grams/mole.
8. The cleaning composition according to any one of the preceding claims, wherein said cyclic amine of Formula (I) has a molecular weight of from about 100 to about 150 grams/mole.
9. The cleaning composition according to any one of the preceding claims, wherein said cleaning composition comprises from about 0.2% to about 5%, by weight of the composition, of the cyclic amine of Formula (I).
10. The cleaning composition according to any one of the preceding claims further comprising from about 0.001% to about 1% by weight of an enzyme.
11. The cleaning composition according to any one of the preceding claims, wherein said enzyme is selected from the group consisting of lipase, amylase, protease, mannanase, and combinations thereof.
12. The cleaning composition according to any one of the preceding claims, wherein said surfactant comprises one or more surfactants selected from the group consisting of anionic surfactants, cationic surfactants, nonionic surfactants, and amphoteric surfactants.
13. The cleaning composition according to any one of the preceding claims wherein the anionic surfactant is selected from the group consisting of alkyl sulfate, alkyl alkoxy sulfate, alkyl benzene sulfonate, and mixtures thereof.
14. The cleaning composition according to any one of the preceding claims further comprising from about 0.1% to about 10% by weight of an additional amine selected from polyetheramines, oligoamines, triamines, diamines, or a combination thereof.
15. The cleaning composition according to any one of the preceding claims wherein the fabric shading dye is selected from the group consisting of azine, anthraquinone, mono-

azo, and dis-azo dyes, optionally substituted with polyalkyleneoxy groups, preferably polyethyleneoxy groups.

16. The cleaning composition according to any one of the preceding claims, wherein said surfactant comprises an anionic surfactant selected from the group consisting of alkyl sulfate, alkyl alkoxy sulfate, alkyl benzene sulfonate, and mixtures thereof and an amine oxide.

17. The cleaning composition according to any one of the preceding claims, wherein said surfactant comprises a nonionic surfactant and an amine oxide.

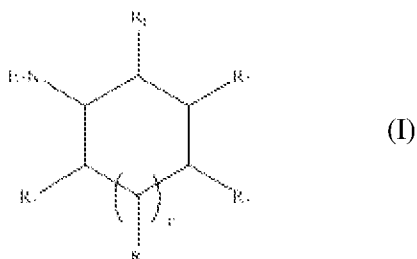
18. The cleaning composition according to any one of the preceding claims, wherein said surfactant comprises from about 1% to about 25%, preferably about 5% to about 25%, more preferably about 10% to about 25%, by weight of the cleaning composition, of a nonionic surfactant and an amine oxide.

19. The cleaning composition according to any one of the preceding claims, wherein said cleaning composition further comprises an adjunct 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, encapsulates, 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, perfumes, and mixtures thereof.

20. The cleaning composition according to any one of the preceding claims, wherein said cleaning composition further comprises an adjunct selected from the group consisting of alkoxyated polyalkylenimines, amphiphilic graft co-polymers, carboxylate polymers, and mixtures thereof.

21. A method of treating a textile, the method comprising the steps of:

(a) treating the textile with an aqueous solution of from about 0.1 g/L to about 3 g/L of a surfactant; from about 1 ppb to about 5 ppm of a fabric shading dye suitable for providing a blue or violet shade to white cotton or polyester; and from about 0.1ppm to about 500 ppm of a cyclic amine of Formula (I):



wherein the radicals R_1 , R_2 , R_3 , R_4 and R_5 are independently selected from NH_2 , $-H$, linear or branched alkyl or alkenyl having from about 1 to about 10 carbon atoms and n is from about 0 to about 3 and wherein at least one of the radicals is NH_2 ; and

(b) rinsing and drying the textile,

wherein the fabric shading dye is selected from azine, anthraquinone, mono-azo, and dis-azo dyes, optionally substituted with polyalkyleneoxy groups.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/042464

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/30 C11D3/40 C11D3/42
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/057976 A1 (THERMPHOS TRADING GMBH) 27 May 2010 (2010-05-27)	1-3, 5-16, 19, 21
A	page 2, lines 21-22, 29-31; claim 19 page 12, lines 14-16 page 12, line 34 - page 13, line 3 page 14, lines 25-33 page 16, lines 6-7 page 12, lines 4-6; claim 10 page 12, lines 27-28 page 13, lines 22-30	17, 18
X	----- WO 03/033636 A1 (PROCTER & GAMBLE) 24 April 2003 (2003-04-24) page 9, paragraph 3; claims 8, 9 claims 15-19; examples II-V, VII, VIII ----- -/-	1-3, 6-21



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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

5 October 2016

Date of mailing of the international search report

12/10/2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/042464

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/63333 A1 (PROCTER & GAMBLE) 26 October 2000 (2000-10-26) pages 22-23; claim 3; examples 1-2 page 4, line 26 - page 5, line 18; claims 1-7,10,11 page 2, lines 11-15 pages 6-8,12 pages 14,19,20	1-14, 16-20
A	----- WO 95/00635 A1 (PROCTER & GAMBLE) 5 January 1995 (1995-01-05) pages 4-5; claims 3,22 -----	10-13, 15-18,21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/042464

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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