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Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **GRIGOLON, Lisanne, Beatriz** [BR/BR]; Unilever Brazil - HPC La Head Office Anastacio, Av. Manoel Domingos Pinto 481, 05120-000 Sao Paulo (BR). **SORZE, Andrea, Dias** [BR/BR]; Unilever Brazil - HPC La Head Office Anastacio, Av. Manoel Domingos Pinto 481, 05120-000 Sao Paulo (BR). **WILLIAMS, Jacqueline** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB).

(74) Agents: **ELLIOTT, Peter, William** et al.; Unilever Intellectual Property Group, Colworth House, Sharnbrook, Bedford, MK44 1LQ (GB).

(71) Applicant (for AE, AG, AU, BB, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NA, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London Greater London EC4P 4BQ (GB).

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(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

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(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

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(72) Inventors; and
(75) Inventors/Applicants (for US only): **BARBIZAN, Danielle, Santinho** [BR/BR]; Unilever Brazil - HPC La Head Office Anastacio, Av. Manoel Domingos Pinto 481, 05120-000 Sao Paulo (BR). **BATCHELOR, Stephen, Norman** [GB/GB]; Unilever R & D Port Sunlight,

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(54) Title: LAUNDRY TREATMENT COMPOSITIONS

(57) Abstract: A laundry treatment composition which comprises a photostable dye which is substantive to cotton, wherein during multiple treatments applied to a substantially white cotton fabric initially free of the dye, the treatments comprising applying the treatment composition to the cotton fabric in an aqueous environment and the fabric being subsequently dried, the loading of dye on the fabric does not increase in proportion to the number of washes and after 10 treatments applied to a substantially white cotton fabric initially free of the dye, the loading of the dye on the fabric approaches a substantially constant value.

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LAUNDRY TREATMENT COMPOSITIONS**TECHNICAL FIELD**

The present invention relates to laundry treatment compositions which comprise dye which is substantive to cotton but does not build-up over multiple washes.

BACKGROUND AND PRIOR ART

Dyes have been included in laundry treatment products for many years. Perhaps the oldest use of dyes is to add a substantive coloured dye to coloured clothes which require rejuvenation of colour for example a substantive blue dye for rejuvenation of denim. These compositions usually contain a relatively high concentration of substantive dye. More recently non-substantive dyes have also been used to colour otherwise white laundry detergent compositions. In the case of particulate detergents this has been in the form of so-called speckles to add colour to an otherwise white powder, however laundry detergent powders which are completely blue are also known. When dyes have been included in laundry treatment products in this way it was regarded as essential that non-substantive dyes were used to prevent undesired staining of washed fabrics.

It is also known that a small amount of blue or violet dye impregnated into an otherwise 'white' fabric can appear to have enhanced whiteness as described in Industrial Dyes (K.Hunger ed Wiley-VCH 2003). Modern white fabrics are sold with some dye in their material in order to enhance the

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whiteness at the point of sale of the garment. This dye is often blue or violet though other colours are used. However once these garments are worn and subsequently washed with a detergent composition the dye is rapidly removed from the fabric due to dissolution by the surfactant solution. Dye is also lost by reaction with bleach in the wash and fading due to light. This results in a gradual loss of whiteness in addition to any other negative effects such as soiling. In many cases this leads to the appearance of a yellow colour on the cloth.

The present inventors have surprisingly found that if certain substantive dyes are applied to fabrics during an aqueous treatment process then the concentration of dye in the fibres of the fabric does not continuously increase after each treatment process but instead approaches a constant value.

Accordingly, the present invention provides a laundry treatment composition which comprises a dye which is substantive to cotton, wherein during multiple treatments applied to a substantially white cotton fabric initially free of the dye, the treatments comprising applying the treatment composition to the cotton fabric in an aqueous environment and the fabric being subsequently dried, the loading of dye on the fabric does not increase in proportion to the number of washes and after 10 treatments applied to a substantially white cotton fabric initially free of the dye, the loading of the dye on the fabric approaches a substantially constant value.

DETAILED DESCRIPTION OF INVENTION

Unless otherwise stated, all percentages or parts are on a weight basis.

Laundry treatment compositions

The present invention relates to compositions which are used to treat laundry items such as clothes. Such compositions are preferably laundry detergent compositions used for washing (especially particulate detergents, liquid detergents, laundry bars, pastes, gels or tablets), laundry fabric conditioners used for softening fabrics, pre-treatment products, post-treatment products, tumble dryer products, ironing products etc. Preferably they are laundry treatment products which are applied in an aqueous environment.

The dyes may be incorporated into the treatment products in a wide variety of ways. For example dyes which are not sensitive to heat may be included in the slurry which is to be spray dried when the treatment product is a particulate detergent composition. Another way of incorporating dyes into particulate detergent products is to add them to granules which are post-added to the main detergent powder. In this case there may be a concentration of dye in the granules which could present the danger of spotting and dye damage on the clothes to be treated. This can be avoided if the concentration of dye in the granules is less than 0.1%. For liquid products the dyes are simply added to the liquid and blended in substantially homogeneously.

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Because the dyes are substantive, only a small amount is required to provide the enhanced whiteness effect hence preferably the treatment composition comprises from 0.0001 to 0.1 wt%, preferably from 0.0005 to 0.05 wt% of the dye, more preferably from 0.001 to 0.01 wt%, most preferably from 0.002 to 0.008 wt%.

The dyes

The dyes of the present invention are unusual in that they are substantive to cotton. The treatment compositions of the present invention comprises a dye which is substantive to cotton, wherein during multiple treatments applied to a substantially white cotton fabric initially free of the dye, the treatments comprising applying the treatment composition to the cotton fabric in an aqueous environment and the fabric being subsequently dried, the loading of dye on the fabric does not increase in proportion to the number of washes.

The dyes are substantive to a degree such that after 10 treatments, preferably after 5 treatments, applied to a substantially white cotton fabric initially free of the dye, the concentration of the dye in the fabric approaches a substantially constant value.

It is preferred that the dye has a substantivity to cotton in a standard test of greater than 7%, preferably from 8 to 80%, more preferably from 10 to 60%, most preferably from 15 to 40%, wherein the standard test is with a dye loading such that the solution has an optical density of approximately 1

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(5 cm pathlength) at the maximum absorption of the dye in the visible wavelengths (400-700nm), a surfactant concentration of 0.3 g/L and under wash conditions of a liquor to cloth ratio of 45:1, temperature of 20°C, soak times of 45 minutes, agitation time of 10 minutes.

In addition to being substantive, the dyes of the present invention do not show any significant build-up over repeated treatment/wear cycles. In this way a substantially constant amount of dye can be maintained on the clothes even though they are being treated (e.g. washed) and subsequently worn, even over very many such cycles. Many substantive dyes do not show this property and merely build-up on the fabric, increasing their loading in an almost linear manner with each treatment. Eventually these dyes will have the effect of making whites appear coloured and pastel shades will lose their subtle shade. Hence it is essential that the dyes of the present invention do not show this behaviour.

The ratio of the dye loading on white cotton after 5 washes to the dye loading after 1 wash is less than 4, preferably less than 3, more preferably less than 2, most preferably less than 1.5.

Hence the dyes according to the present invention can be said to have an intermediate degree of substantivity, in that during aqueous treatment of the fabrics some of the dye is lost from the fabric to the aqueous solution and some of the dye is deposited onto the fabric.

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The dyes of the present invention are photostable. A photostable dye is a dye which does not quickly photodegrade in the presence of natural summer sunlight. A photostable dye in the current context may be defined as a dye which, when on cotton, does not degrade by more than 10% when subjected to 1 hour of irradiation by simulated Florida sunlight (42 W/m^2 in UV and 343 W/m^2 in visible).

It is preferable that the dyes have a blue and/or violet shade. This can mean that the peak absorption frequency of the dye absorbed on the cloth lies within the range of from 540nm to 650nm, preferably from 570nm to 630nm. It is also possible that the same effect can be achieved by a combination of dyes, each of which not necessarily having a peak absorption within these preferred ranges but together produce an effect on the human eye which is equivalent to a single dye with a peak absorption within one of the preferred ranges.

Organic dyes are described in Industrial Dyes (K.Hunger ed Wiley-VCH 2003). A compilation of available dyes is the Colour Index published by Society of Dyer and Colourists and American Association of Textile Chemists and Colorists 2002 (see <http://www.colour-index.org>). Suitable dyes for the current application may be taken from any of the chromophore types, e.g. azo, anthraquinone, triarylmethane, methine quinophthalone, azine, oxazine thiazine. It is preferred that the dye does not contain a reactive group such as found in procion and remazol dyes. Due to the wider range available azo, anthraquinone and triarylmethane dyes are preferred. Azo dyes are especially preferred.

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Dyes are conventionally defined as being reactive, disperse, direct, vat, sulphur, cationic, acid or solvent dyes. For the purposes of the present invention, acid and/or direct dyes are preferred. Acid dyes are most preferred.

For use in products which contain predominately anionic surfactants, dyes containing acid groups are preferred. For use in products which contain predominantly cationic surfactants, dyes containing basic groups are preferred. This is to prevent precipitation between the dye and surfactant.

Suitable dyes for use in products containing predominately anionic surfactants include those listed in the Colour Index as Direct Violet Dyes (e.g. Direct Violet 1-108), Direct Blue dyes, Acid Blue and Acid Violet dyes.

Suitable dyes for use in products containing predominately cationic surfactants include those listed in the Colour Index as Basic Blue and Basic Violet Dyes.

To avoid shade changes caused by pick or loss of a proton it is preferred that the dye does not have a pKa or pKb at or near the pH of the product. Most preferably no pKa or pKb in the pH range of from 7 to 11.

It is preferred that the dye has a high extinction coefficient, so that a small amount of dye gives a large amount of colour. Preferably the extinction coefficient at the maximum absorption of the dye is greater than 1000 mol^{-1}

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L cm^{-1} , preferably greater than $10,000 \text{ mol}^{-1} \text{ L cm}^{-1}$, more preferably greater than $50,000 \text{ mol}^{-1} \text{ L cm}^{-1}$.

Suitable dyes can be obtained from any major supplier such as Clariant, Ciba Speciality Chemicals, Dystar, Avecia or Bayer.

Laundry detergent compositions

Detergent-active compounds (surfactants) may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds. The total amount of surfactant present is suitably within the range of from 5 to 60 wt%, preferably from 5 to 40 wt%.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅; primary and secondary alkylsulphates, particularly C₈-C₂₀ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

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Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkanolamides, alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are long or short hydrocarbyl chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising anion (for example, compounds in which R₁ is a C₈-C₂₂ alkyl group, preferably a C₈-C₁₀ or C₁₂-C₁₄ alkyl group, R₂ is a methyl group, and R₃ and R₄, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

Amphoteric and zwitterionic surfactants that may be used include alkyl amine oxides, betaines and sulphobetaines. In accordance with the present invention, the detergent surfactant (a) most preferably comprises an anionic sulphonate or sulphate surfactant optionally in admixture with one or more cosurfactants selected from ethoxylated nonionic surfactants, non-ethoxylated nonionic surfactants, ethoxylated sulphate anionic surfactants, cationic

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surfactants, amine oxides, alkanolamides and combinations thereof.

Surfactants are preferably present in a total amount of from 5 to 60 wt%, more preferably from 10 to 40 wt%.

Laundry detergent compositions of the present invention preferably contain a detergency builder, although it is conceivable that formulations without any builder are possible.

Laundry detergent compositions of the invention suitably contain from 10 to 80%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

Preferably the builder is selected from zeolite, sodium tripolyphosphate, sodium carbonate, sodium citrate, layered silicate, and combinations of these.

The zeolite used as a builder may be the commercially available zeolite A (zeolite 4A) now widely used in laundry detergent powders. Alternatively, the zeolite may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070B (Unilever), and commercially available as Doucil (Trade Mark) A24 from Ineos Silicas Ltd, UK.

Zeolite MAP is defined as an alkali metal aluminosilicate of zeolite P type having a silicon to aluminium ratio not

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exceeding 1.33, preferably within the range of from 0.90 to 1.33, preferably within the range of from 0.90 to 1.20. Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The particle size of the zeolite is not critical. Zeolite A or zeolite MAP of any suitable particle size may be used.

Also preferred according to the present invention are phosphate builders, especially sodium tripolyphosphate. This may be used in combination with sodium orthophosphate, and/or sodium pyrophosphate.

Other inorganic builders that may be present additionally or alternatively include sodium carbonate, layered silicate, amorphous aluminosilicates.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates and acrylic/maleic copolymers; polyaspartates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyl-iminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

Organic builders may be used in minor amounts as supplements to inorganic builders such as phosphates and zeolites. Especially preferred supplementary organic builders are citrates, suitably used in amounts of from 5 to 30 wt %, preferably from 10 to 25 wt %; and acrylic polymers, more

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especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt %, preferably from 1 to 10 wt%. Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

As well as the surfactants and builders discussed above, the compositions may optionally contain bleaching components and other active ingredients to enhance performance and properties.

These optional ingredients may include, but are not limited to, any one or more of the following: soap, peroxyacid and persalt bleaches, bleach activators, sequestrants, cellulose ethers and esters, other antiredeposition agents, sodium sulphate, sodium silicate, sodium chloride, calcium chloride, sodium bicarbonate, other inorganic salts, proteases, lipases, cellulases, amylases, other detergent enzymes, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam controllers, foam boosters, acrylic and acrylic/maleic polymers, citric acid, soil release polymers, fabric conditioning compounds, coloured speckles, and perfume.

Detergent compositions according to the invention may suitably contain a bleach system. The bleach system is preferably based on peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates

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and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%.

Preferred bleach precursors are peroxy-carboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxy-carbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED). Also of interest are peroxybenzoic acid precursors, in particular, N,N,N-trimethylammonium toluoyloxy benzene sulphonate.

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (Trade Mark), EDTMP.

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Although, as previously indicated, in one preferred embodiment of the invention enzymes are preferably absent, in other embodiments detergent enzymes may be present. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

In particulate detergent compositions, detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used in any effective amount.

Antiredeposition agents, for example cellulose esters and ethers, for example sodium carboxymethyl cellulose, may also be present.

The compositions may also contain soil release polymers, for example sulphonated and unsulphonated PET/POET polymers, both end-capped and non-end-capped, and polyethylene glycol/polyvinyl alcohol graft copolymers such as Sokolan (Trade Mark) HP22. Especially preferred soil release polymers are the sulphonated non-end-capped polyesters described and claimed in WO 95 32997A (Rhodia Chimie).

Powder detergent composition of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally postdosing (dry-mixing) further ingredients.

"Concentrated" or "compact" powders may be prepared by mixing and granulating processes, for example, using a high-speed mixer/granulator, or other non-tower processes.

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Tablets may be prepared by compacting powders, especially "concentrated" powders.

Fabric conditioners

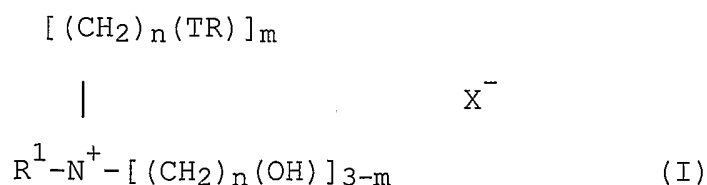
Cationic softening material is preferably a quaternary ammonium fabric softening material.

The quaternary ammonium fabric softening material compound has two C12-28 alkyl or alkenyl groups connected to the nitrogen head group, preferably via at least one ester link. It is more preferred if the quaternary ammonium material has two ester links present.

Preferably, the average chain length of the alkyl or alkenyl group is at least C₁₄, more preferably at least C₁₆. Most preferably at least half of the chains have a length of C₁₈.

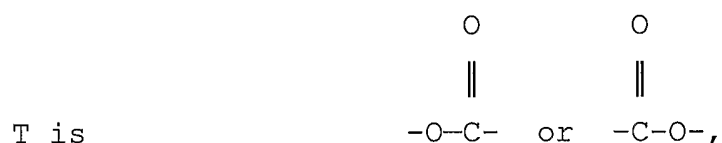
It is generally preferred if the alkyl or alkenyl chains are predominantly linear.

The first group of cationic fabric softening compounds for use in the invention is represented by formula (I):



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wherein each R is independently selected from a C₅₋₃₅ alkyl or alkenyl group, R¹ represents a C₁₋₄ alkyl, C₂₋₄ alkenyl or a C₁₋₄ hydroxyalkyl group,

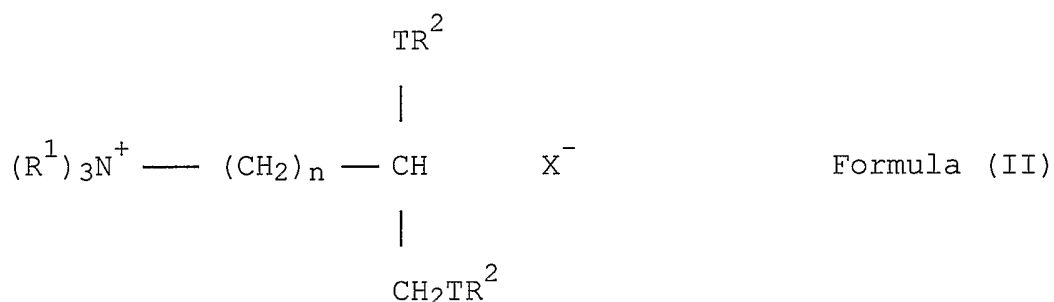


n is 0 or a number selected from 1 to 4, m is 1, 2 or 3 and denotes the number of moieties to which it relates that pend directly from the N atom, and X⁻ is an anionic group, such as halides or alkyl sulphates, e.g. chloride, methyl sulphate or ethyl sulphate.

Especially preferred materials within this formula are di-alkenyl esters of triethanol ammonium methyl sulphate. Commercial examples include Tetranyl AHT-1 (di-hardened oleic ester of triethanol ammonium methyl sulphate 80% active), AT-1 (di-oleic ester of triethanol ammonium methyl sulphate 90% active), L5/90 (palm ester of triethanol ammonium methyl sulphate 90% active), all ex Kao. Other unsaturated quaternary ammonium materials include Rewoquat WE15 (C₁₀-C₂₀ and C₁₆-C₁₈ unsaturated fatty acid reaction products with triethanolamine dimethyl sulphate quaternised 90 % active), ex Witco Corporation.

The second group of cationic fabric softening compounds for use in the invention is represented by formula (II):

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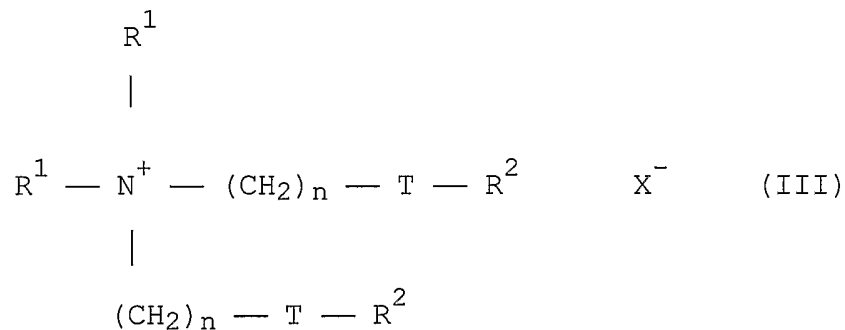


wherein each R^1 group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; n is 0 or an integer from 1 to 5 and T and X^- are as defined above.

Preferred materials of this class such as 1,2 bis[tallowoyloxy]-3-trimethylammonium propane chloride and 1,2-bis[oleyloxy]-3-trimethylammonium propane chloride and their method of preparation are, for example, described in US 4137180 (Lever Brothers), the contents of which are incorporated herein. Preferably these materials also comprise small amounts of the corresponding monoester, as described in US 4137180.

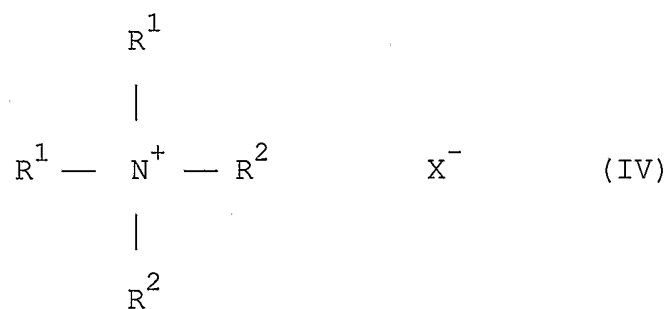
A third group of cationic fabric softening compounds for use in the invention is represented by formula (III):

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wherein each R^1 group is independently selected from C_{1-4} alkyl, or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; n is 0 or an integer from 1 to 5 and T and X^- are as defined above.

A fourth group of cationic fabric softening compounds for use in the invention is represented by formula (IV):



wherein each R^1 group is independently selected from C_{1-4} alkyl, or C_{2-4} alkenyl groups; and wherein each R^2 group is

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independently selected from C₈₋₂₈ alkyl or alkenyl groups;
and X⁻ is as defined above.

The iodine value of the parent fatty acyl compound or acid from which the cationic softening material is formed is from 0 to 140, preferably from 0 to 100, more preferably from 0 to 60.

It is especially preferred that the iodine value of the parent compound is from 0 to 20, e.g. 0 to 4. Where the iodine value is 4 or less, the softening material provides excellent softening results and has improved resistance to oxidation and associated odour problems upon storage.

When unsaturated hydrocarbyl chains are present, it is preferred that the cis:trans weight ratio of the material is 50:50 or more, more preferably 60:40 or more, most preferably 70:30 or more, e.g. 85:15 or more.

The iodine value of the parent fatty acid or acyl compound is measured according to the method set out in respect of parent fatty acids in WO-A1-01/46513.

The softening material is preferably present in an amount of from 1 to 60% by weight of the total composition, more preferably from 2 to 40%, most preferably from 3 to 30% by weight.

The composition optionally comprises a silicone. Typical silicones for use in the compositions of the present

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invention are siloxanes which have the general formula $R_aSiO_{(4-a)/2}$ wherein each R is the same or different and is selected from hydrocarbon and hydroxyl groups, 'a' being from 0 to 3. In the bulk material, 'a' typically has an average value of from 1.85-2.2.

The silicone can have a linear or cyclic structure. It is particularly preferred that the silicone is cyclic as it is believed that cyclic silicones deliver excellent faster drying characteristics to fabrics.

Preferably, the silicone is a polydi-C₁₋₆alkyl siloxane.

Particularly preferred is polydimethyl siloxane. The siloxane is preferably end-terminated, if linear, either by a tri-C₁₋₆ alkylsilyl group (e.g. trimethylsilyl) or a hydroxy-di-C₁₋₆ alkylsilyl group (e.g. hydroxy-dimethylsilyl) groups, or by both.

More preferably the silicone is a cyclic polydimethyl siloxane.

Suitable commercially available silicones include DC245 (polydimethylcyclopentasiloxane also known as D5), DC246 (polydimethylcyclohexasiloxane also known as D6), DC1184 (a pre-emulsified polydimethylpentasiloxane also known as L5) and DC347 (a pre-emulsified 100cSt PDMS fluid) all ex Dow Corning.

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The silicone may be received and incorporated into the composition either directly as an oil or pre-emulsified.

Pre-emulsification is typically required when the silicone is of a more viscous nature.

Suitable emulsifiers include cationic emulsifiers, nonionic emulsifiers or mixtures thereof.

The reference to the viscosity of the silicone denotes either the viscosity before emulsification when the silicone is provided as an emulsion for incorporation into the fabric conditioning composition or the viscosity of the silicone itself when provided as an oil for incorporation into the fabric conditioning composition.

The silicone preferably has a viscosity (as measured on a Brookfield RV4 viscometer at 25°C using spindle No.4 at 100 rpm) of from 1cSt to less than 10,000 centi-Stokes (cSt), preferably from 1cSt to 5,000cSt, more preferably from 2cSt to 1,000cSt and most preferably 2cSt to 100cSt.

It has been found that drying time can be reduced using silicones having a viscosity of from 1 to 500,000 cSt. However, it is most preferred that the viscosity is from 1 to less than 10,000cSt.

The silicone active ingredient is preferably present at a level of from 0.5 to 20%, more preferably from 1 to 12%, most preferably from 2 to 8% by weight, based on the total weight of the composition.

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Optionally and advantageously, one or more un-alkoxylated fatty alcohols are present in fabric conditioners of the present invention.

Preferred alcohols have a hydrocarbyl chain length of from 10 to 22 carbon atoms, more preferably 11 to 20 carbon atoms, most preferably 15 to 19 carbon atoms.

The fatty alcohol may be saturated or unsaturated, though saturated fatty alcohols are preferred as these have been found to deliver greater benefits in terms of stability, especially low temperature stability.

Suitable commercially available fatty alcohols include tallow alcohol (available as Hydrenol S3, ex Sidobre Sinnova, and Laurex CS, ex Clariant).

The fatty alcohol content in the compositions is from 0 to 10% by weight, more preferably from 0.005 to 5% by weight, most preferably from 0.01 to 3% by weight, based on the total weight of the composition.

It is particularly preferred that a fatty alcohol is present if the composition is concentrated, that is if more than 8% by weight of the cationic softening agent is present in the composition.

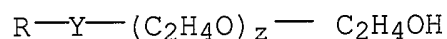
It is preferred that the compositions further comprise a nonionic surfactant. Typically these can be included for the purpose of stabilising the compositions.

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Suitable nonionic surfactants include addition products of ethylene oxide and/or propylene oxide with fatty alcohols, fatty acids and fatty amines.

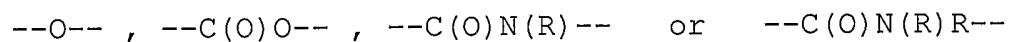
Any of the alkoxyated materials of the particular type described hereinafter can be used as the nonionic surfactant.

Suitable surfactants are substantially water soluble surfactants of the general formula:



where R is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkenyl hydrocarbyl groups; and primary, secondary and branched chain alkenyl-substituted phenolic hydrocarbyl groups; the hydrocarbyl groups having a chain length of from 8 to about 25, preferably 10 to 20, e.g. 14 to 18 carbon atoms.

In the general formula for the alkoxyated nonionic surfactant, Y is typically:



in which R has the meaning given above or can be hydrogen; and Z is preferably from 8 to 40, more preferably from 10 to 30, most preferably from 11 to 25, e.g. 12 to 22.

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The level of alkoxylation, Z , denotes the average number of alkoxy groups per molecule.

Preferably the nonionic surfactant has an HLB of from about 7 to about 20, more preferably from 10 to 18, e.g. 12 to 16. Examples of nonionic surfactants follow. In the examples, the integer defines the number of ethoxy (EO) groups in the molecule.

The deca-, undeca-, dodeca-, tetradeca-, and pentadecaethoxylates of n-hexadecanol, and n-octadecanol having an HLB within the range recited herein are useful viscosity/dispersibility modifiers in the context of this invention. Exemplary ethoxylated primary alcohols useful herein as the viscosity/dispersibility modifiers of the compositions are C₁₈ EO(10); and C₁₈ EO(11). The ethoxylates of mixed natural or synthetic alcohols in the "tallow" chain length range are also useful herein. Specific examples of such materials include tallow alcohol-EO(11), tallow alcohol-EO(18), and tallow alcohol-EO (25), coco alcohol-EO(10), coco alcohol-EO(15), coco alcohol-EO(20) and coco alcohol-EO(25).

The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-, and nonadeca-ethoxylates of 3-hexadecanol, 2-octadecanol, 4-eicosanol, and 5-eicosanol having an HLB within the range recited herein are useful viscosity and/or dispersibility modifiers in the context of this invention. Exemplary ethoxylated secondary alcohols useful herein as

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the viscosity and/or dispersibility modifiers of the compositions are: C₁₆ EO(11); C₂₀ EO(11); and C₁₆ EO(14).

As in the case of the alcohol alkoxyates, the hexa- to octadeca-ethoxyates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the range recited herein are useful as the viscosity and/or dispersibility modifiers of the instant compositions. The hexa- to octadeca-ethoxyates of p-tri-decylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful as the viscosity and/or dispersibility modifiers of the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18).

As used herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

The alkenyl alcohols, both primary and secondary, and alkenyl phenols corresponding to those disclosed immediately hereinabove can be ethoxylated to an HLB within the range recited herein and used as the viscosity and/or dispersibility modifiers of the instant compositions.

Branched chain primary and secondary alcohols which are available from the well-known "OXO" process can be

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ethoxylated and employed as the viscosity and/or dispersibility modifiers of compositions herein.

Suitable polyol based surfactants include sucrose esters such sucrose monooleates, alkyl polyglucosides such as stearyl monoglucosides and stearyl triglucoside and alkyl polyglycerols.

The above nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

The nonionic surfactant is present in an amount from 0.01 to 10%, more preferably 0.1 to 5%, most preferably 0.35 to 3.5%, e.g. 0.5 to 2% by weight, based on the total weight of the composition.

The fabric conditioner compositions of the invention preferably comprise one or more perfumes.

It is well known that perfume is provided as a mixture of various components. Suitable components for use in the perfume include those described in "Perfume and Flavor Chemicals (Aroma Chemicals) by Steffen Arctander, published by the author 1969 Montclair, N.J. (US), reprinted 1st April 1982 library of Congress Catalog Number 75-91398.

The perfume is preferably present in an amount from 0.01 to 10% by weight, more preferably 0.05 to 5% by weight, most

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preferably 0.5 to 4.0% by weight, based on the total weight of the composition.

The liquid carrier employed in the instant compositions is at least partly water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is more than about 50%, preferably more than about 80%, more preferably more than about 85%, by weight of the carrier. The level of liquid carrier is greater than about 50%, preferably greater than about 65%, more preferably greater than about 70%. Mixtures of water and a low molecular weight, e.g. <100, organic solvent, e.g. a lower alcohol such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols including monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and polyhydric (polyols) alcohols are also suitable carriers for use in the compositions of the present invention.

Co-active softeners for the cationic surfactant may also be incorporated in an amount from 0.01 to 20% by weight, more preferably 0.05 to 10%, based on the total weight of the composition. Preferred co-active softeners include fatty esters, and fatty N-oxides.

Preferred fatty esters include fatty monoesters, such as glycerol monostearate (hereinafter referred to as "GMS"). If GMS is present, then it is preferred that the level of GMS in the composition is from 0.01 to 10% by weight, based on the total weight of the composition.

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The co-active softener may also comprise an oily sugar derivative. Suitable oily sugar derivatives, their methods of manufacture and their preferred amounts are described in WO-A1-01/46361 on page 5 line 16 to page 11 line 20, the disclosure of which is incorporated herein.

It is useful, though not essential, if the compositions comprise one or more polymeric viscosity control agents. Suitable polymeric viscosity control agents include nonionic and cationic polymers, such as hydrophobically modified cellulose ethers (e.g. Natrosol Plus, ex Hercules), cationically modified starches (e.g. Softgel BDA and Softgel BD, both ex Avebe). A particularly preferred viscosity control agent is a copolymer of methacrylate and cationic acrylamide available under the tradename Flosoft 200 (ex SNF Floerger).

Nonionic and/or cationic polymers are preferably present in an amount of 0.01 to 5wt%, more preferably 0.02 to 4wt%, based on the total weight of the composition.

Other optional nonionic softeners, bactericides, soil-releases agents may also be incorporated in fabric conditioners of the invention.

The compositions may also contain one or more optional ingredients conventionally included in fabric conditioning compositions such as pH buffering agents, perfume carriers, fluorescers, colourants, hydrotropes, antifoaming agents, antiredeposition agents, polyelectrolytes, enzymes, optical brightening agents, pearlescers, anti-shrinking agents,

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anti-wrinkle agents, anti-spotting agents, antioxidants, sunscreens, anti-corrosion agents, drape imparting agents, preservatives, anti-static agents, ironing aids and other dyes.

The product may be a liquid or solid. Preferably the product is a liquid which, in its undiluted state at ambient temperature, comprises an aqueous liquid, preferably an aqueous dispersion of the cationic softening material.

When the product is an aqueous liquid, it preferably has a pH of greater than 1.5 and less than 5, more preferably greater than 2 and less than 4.5.

The fabric conditioner composition is preferably used in the rinse cycle of a home textile laundering operation, where, it may be added directly in an undiluted state to a washing machine, e.g. through a dispenser drawer or, for a top-loading washing machine, directly into the drum. Alternatively, it can be diluted prior to use. The compositions may also be used in a domestic hand-washing laundry operation.

EXAMPLES

Example 1

To determine the substantivity of a range of dyes the following experiment was performed. A stock solution of 1.5g/L of a base washing powder in water was created. The washing powder contained 18% NaLAS, 73% salts (silicate,

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sodium tri-poly-phosphate, sulphate, carbonate), 3% minors including perborate, fluorescer and enzymes, remainder impurities and water. The solution was divided into 60ml aliquots and dye added to this to give a solution of optical density of approximately 1 (5 cm pathlength) at the maximum absorption of the dye in the visible lengths, 400-700nm. The optical density was measured using a UV-visible spectrometer. 1 piece of bleached, non-mercerised, non-fluorescent woven cotton cloth (ex Phoenic Calico) weighing 1.3g was placed in the solution at room temperature (20°C). This cloth represents a slightly yellow cotton. The cloth was left to soak for 45 minutes then the solution agitated for 10 mins, rinsed and dried. Following this the optical density of the solution was re-measured and the amount of dye absorbed by the cloth calculated. This experiment was repeated for each dye and 4 replicates were done per dye.

The dyes used and the % deposition is given in table 1. Table 2 gives the maximum extinction coefficient, ϵ_{max} , in the wash solution and the peak absorption wavelength in solution and on cotton. All values are reported to 2 significant figures.

Table 1

<u>Dye</u>	<u>% Deposition</u>
Acid Black 1	23
Food Black 1	0.50
Direct Blue 1	48
Direct Violet 51	69
Direct Blue 71	34
Acid Violet 9	2.1
Acid Blue 80	6.8
Acid Violet 17	18
Acid Red 88	47
Acid Red 150	33

Table 2

<u>Dye</u>	<u>Type</u>	$\epsilon_{,ax}$ [mol ⁻¹ L cm ⁻¹]	λ_{max} [nm] in solution, on cotton
Acid Black 1	Azo	51000	620, 630
Food Black 1	Azo	41000	570, 590
Direct Blue 1	Azo	120000	600, 640
Direct Violet 51	Azo	65000	550, 570
Direct Blue 71	Azo	120000	590, 600
Acid Violet 9	Triaryl	46000	540
Acid Blue 80	Anthraquinone	27000	630, 630
Acid Violet 17	Triaryl	53000	520, 590
Acid Red 88	Azo	14400	510, 520
Acid Red 150	Azo	23600	520, 530

Example 2

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The experiment of example 1 was repeated except the dye level in the wash solution was decreased to 1/10th, so that the optical density was 0.1 (5 cm path length). Following the washes the Ganz whiteness of the cloth was measured (see "assessment of Whiteness and Tint of Fluorescent Substrates with Good Interinstrument Correlation" *Colour Research and Application* 19, 1994). The results are displayed in table 3, the ganz whiteness values are accurate to +/-5 units. Large increase in the measured Ganz whiteness are found for the substantive blue and violet dyes with λ_{max} on cotton in the range 570 to 640.

Table 3

Dye	Ganz whiteness
control	150
Acid Black 1	171
Food Black 1	155
Direct Blue 1	190
Direct Violet 51	208
Direct Blue 71	205
Acid Violet 9	153
Acid Blue 80	152
Acid Violet 17	170

Acid black 1, direct blue 1, direct violet 51, direct blue 71 and acid violet 17 gave the greatest increase in Ganz whiteness.

Example 3

The clothes of experiment 2 were dried and then rewashed twice using the same method (drying in between washes). The build up of dye on the cloth was measured using a

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reflectometer and expressed as the K/S at the absorption maximum of the dye. K/S is the remission value and calculated using the Kubelka-Munk equation:

$$K/S = (1-R)^2 / 2R$$

K/S is proportional to the loading of the dye on the cloth and therefore provides a convenient measure of the dye build up. R is the reflectance at the maximum absorbance of the dye.

The results are shown in table 3.

Table 3

dye	% deposition in 1 st wash	K/S		
		Wash 1	Wash 3	Wash 5
control	-	0.0076	0.0083	0.0097
Acid Black 1	23	0.0421	0.0757	0.0835
Food Black 1	0.50	0.0141	0.0234	0.0265
Direct Blue 1	48	0.0552	0.1705	0.2737
Direct Violet 51	69	0.0609	0.1720	0.2706
Direct Blue 71	34	0.0544	0.1445	0.2079
Acid Violet 9	2.1	0.0093	0.0105	0.0115
Acid Blue 80	6.8	0.0073	0.0085	0.0095
Acid Violet 17	18	0.0180	0.0143	0.0162

The results show that dyes with substantivity below 30% show much lower/no build up over multiple washes and that dyes with substantivity below 7% are not effective at providing a benefit. Hence Dyes with substantivities between 7 and 30% have the property of being substantive enough to deliver a

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benefit but not so substantitive as to build up over multiple treatments.

CLAIMS

1. A laundry treatment composition which comprises a photostable dye which is substantive to cotton, wherein during multiple treatments applied to a substantially white cotton fabric initially free of the dye, the treatments comprising applying the treatment composition to the cotton fabric in an aqueous environment and the fabric being subsequently dried, the loading of dye on the fabric does not increase in proportion to the number of washes and after 10 treatments applied to a substantially white cotton fabric initially free of the dye, the loading of the dye on the fabric approaches a substantially constant value.
2. A laundry treatment composition as claimed in claim 1, wherein the ratio of the dye loading on white cotton after 5 washes to the dye loading after 1 wash is less than 4, preferably less than 3, more preferably less than 2, most preferably less than 1.5.
3. A composition as claimed in any preceding claim, which is a laundry detergent composition, preferably a particulate laundry detergent composition.
4. A composition as claimed in claim 1 or claim 2, which is a laundry fabric conditioner.
5. A composition as claimed in any preceding claim, which comprises surfactant.

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6. A composition as claimed in claim 5, wherein the surfactant is a non-soap surfactant.
7. A composition as claimed in claim 5 or claim 6, wherein the surfactant is an anionic or cationic surfactant.
8. A composition as claimed in claim 7, wherein the surfactant is C₈-C₁₅ linear alkyl benzene sulphonate.
9. A composition as claimed in any one of claims 5 to 8, which comprises from 5 to 60 wt% of surfactant.
10. A composition as claimed in any preceding claim, which comprises fluorescer.
11. A composition as claimed in any preceding claim wherein the dye has a peak absorption wavelength of from 540nm to 650nm, preferably from 570nm to 630nm.
12. A composition as claimed in any preceding claim, wherein the dye comprises a combination of dyes which together have the visual effect on the human eye as a single dye having a peak absorption wavelength on cotton of from 540nm to 650nm, preferably from 570nm to 630nm.
13. A composition as claimed in any preceding claim, wherein the dye has a substantivity to cotton in a standard test of greater than 7%, preferably from 8 to 80%, more preferably from 10 to 60%, most preferably from 15 to 40%, wherein the standard test is with a dye

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concentration such that the solution has an optical density of approximately 1 (5 cm pathlength) at the maximum absorption of the dye in the visible wavelengths (400-700nm), a surfactant concentration of 0.3 g/L and under wash conditions of a liquor to cloth ratio of 45:1, temperature of 20°C, soak times of 45 minutes, agitation time of 10 minutes.

14. A composition as claimed in any preceding claim, which comprises from 0.0001 to 0.1 wt%, preferably from 0.0005 to 0.05 wt% of the dye, more preferably from 0.001 to 0.01 wt%, most preferably from 0.002 to 0.008 wt%.
15. A composition as claimed in claim 14, wherein the dye is an azo, anthraquinone or triarylmethane dye, preferably azo.
16. A composition as claimed in claim 15, wherein the dye is selected from the group of acid and direct dyes.
17. A composition as claimed in claim 16, wherein the dye is selected from acid black 1 and acid violet 17.

INTERNATIONAL SEARCH REPORT

International Application No
 PCT/EP2004/006091

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D3/40

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)
 IPC 7 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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 893 818 A (MILLSAPS WILLIAM A ET AL) 7 July 1959 (1959-07-07) column 1, lines 15-25 column 3, line 66 - column 4, line 4 claim 1	1-17
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Further documents are listed in the continuation of box C.

Patent family members are listed in 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 document 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

10 September 2004

Date of mailing of the international search report

24/09/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Bertran Nadal, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/006091

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 6 521 581 B1 (LEE KWANG H ET AL) 18 February 2003 (2003-02-18) column 13, lines 1-34 claims 1,6; examples 1,2 -----	1-16
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X	US 3 931 037 A (HALL RANDALL BRIAN) 6 January 1976 (1976-01-06) column 2, lines 5-14,43-50; claims 1-3 -----	1-16
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2004/006091

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 1-14 (partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

Continuation of Box II.2

Claims Nos.: 1-14 (partially)

Present claim 1 relates to a composition defined by reference to a desirable characteristic or property, namely the loading of dye on the fabric, which does not increase in proportion to the number of washes and after 10 treatments applied to a substantially white cotton fabric initially free of the dye, the loading of the dye on the fabric approaches a substantially constant value.

The claims cover all compositions having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such compositions. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the composition by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the compositions comprising a dye as defined in claim 15.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/006091

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/006091

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