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(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, NG, 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).

(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, KM, 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, SM, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only)*: **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

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

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BATCHELOR, Stephen, Norman** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **BIRD, Jayne, Michelle** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB).

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

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(54) Title: LAUNDRY TREATMENT COMPOSITIONS

(57) Abstract: The present invention provides a treatment composition comprising a hydrophobic dye.

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LAUNDRY TREATMENT COMPOSITIONS

TECHNICAL FIELD

The present invention relates to laundry treatment compositions that comprise a dye.

BACKGROUND OF THE INVENTION

Garments comprising polyester fibres are ubiquitous. Many garments are white but over the lifetime of these garments the whiteness is dulled reducing the aesthetic value of the garment. There is a need to maintain the white appearance of such garments such that the aesthetic value is retained as long as possible.

Bleach, fluorescers and shading agents are used in modern wash processes to maintain whiteness. The fluorescers and shading agents that are currently available, do not deposit on polyester fibres of garments to a significant degree. All fibres may be subjected to a bleaching process but over time such treatment can lead to the garment taking a yellow hue.

There is a need to provide technology that maintains and enhances the white appearance of polyester comprising garments.

SUMMARY OF THE INVENTION

Dyes disclosed herein are known to be used to dye textiles in industrial processes conducted at high temperatures together with high concentrations of dyes and dispersion agents. Surprisingly the dyes can be used to shade at low levels of dye and surfactant and at routine laundry

temperatures. We have found that hydrophobic dyes are substantive to polyester fibres under normal domestic wash conditions. At low levels of dye a shading whiteness benefit is provided.

In one aspect the present invention provides a laundry treatment composition comprising between 0.0001 to 0.1 wt % of a hydrophobic dye selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, napthoquinone and mono-azo or di-azo dyes, and between 2 to 60 wt % of a surfactant. It is preferred that the dye is a mono-azo dye.

In another aspect the present invention provides a method of treating a textile, the method comprising the steps of: (i) treating a textile with an aqueous solution of the hydrophobic dye, the aqueous solution comprising from 1 ppb to 6 ppm of the hydrophobic dye and from 0.2 g/L to 3 g/L of a surfactant; and, (ii) rinsing and drying the textile. It is preferred that the aqueous solution has an ionic strength from 0.001 to 0.5. It is preferred that the hydrophobic dye is present in the range 10 ppb to 200 ppb. In another aspect it is preferred that the aqueous solution also comprises from 1 ppb to 5 ppm one or more other dyes selected from cotton substantive shading dyes of group consisting of: hydrolysed reactive dye; acid dye; and direct dye.

A "unit dose" as used herein is a particular amount of the laundry treatment composition used for a type of wash, conditioning or requisite treatment step. The unit dose may be in the form of a defined volume of powder, granules or tablet or unit dose detergent liquid.

DETAILED DESCRIPTION OF THE INVENTION

Typical dye suppliers may be found in the colour index, and include Clariant, Dystar, Ciba & BASF.

Hydrophobic dyes are defined as organic compounds with a maximum extinction coefficient greater than 1000 L/mol/cm in the wavelength range of 400 to 750 nm and that are uncharged in aqueous solution at a pH in the range from 7 to 11. The hydrophobic dyes are devoid of polar solubilizing groups. In particular the hydrophobic dye does not contain any sulphonic acid, carboxylic acid, or quaternary ammonium groups. The dye chromophore is preferably selected from the group comprising: azo; methine, pyrazole napthoquinone, phthalocyanine; and, triphenylmethane chromophores. Most preferred are azo dye chromophores.

Many examples of hydrophobic dyes are found in the classes of solvent and disperse dyes.

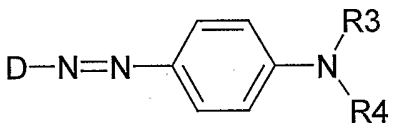
Shading of white garments may be done with any colour depending on consumer preference. Blue and Violet are particularly preferred shades and consequently preferred dyes or mixtures of dyes are ones that give a blue or violet shade on white polyester.

It is preferred that the dye(s) have a peak absorption wavelength of from 550nm to 650nm, preferably from 570nm to 630nm. A combination of dyes may be used which together have the visual effect on the human eye as a single dye having a peak absorption wavelength on polyester of from 550nm to 650nm, preferably from 570nm to 630nm. This may be provide

for example by mixing a red and green-blue dye to yield a blue or violet shade.

A wide range of suitable solvent and disperse dyes are available. However detailed toxicological studies have shown that a number of such dyes are possible carcinogens, such dyes are not preferred.

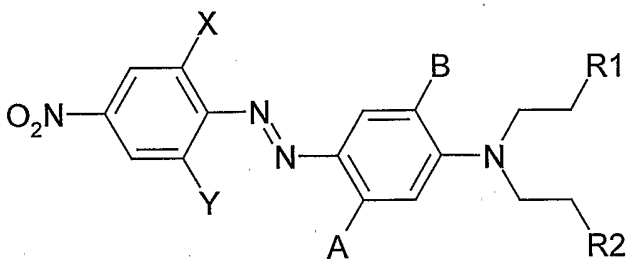
Preferred mono-azo dyes are of the form:



wherein R3 and R4 are optionally substituted C2 to C12 alkyl chains having optionally therein ether (-O-) or ester links, the chain being optionally substituted with -Cl, -Br, -CN, -NO_2, and -SO_2CH_3; and, D denotes an aromatic or hetroaromatic group. Preferably D is selected from the group consisting of: azothiophenes, azobenzothiazoles and azopyridones.

It is preferred that R3 is -CH2CH2R5 and R4 and is -CH2CH2R6 and R5 and R6 are independently selected from the group consisting of: H, -CN, -OH, -C6H5, -OCOR7 and -COOR7, and that R7 is independently selected from: aryl and alkyl. Preferred aryl are -C6H5 and C10H7.

The following is an example of a preferred class of mono-azo dyes:



where X and Y are independently selected from the group consisting of: -H, -Cl, -Br, -CN, $-NO_2$, and $-SO_2CH_3$;

A is selected -H, $-CH_3$, -Cl, and -NHCOR;

B is selected -H, $-OCH_3$, $-OC_2H_5$, and -Cl;

R^1 and R^2 are independently selected from the group consisting of: -H, -CN, -OH, -OCOR, -COOR, -aryl; and

R is C1-C8-alkyl.

The following are preferred azo dyes: 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, 205, 206, 207, 209, 210, 211, 212, 219, 220, 222, 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, 303, 304, 305, 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, 13, 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, 103, 104, 106 or 107, Dianix violet cc, and dyes with CAS-No's

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.

The following are preferred non-azo dyes: Disperse Blue 250, 354, 364, 366, Solvent Violet 8, solvent blue 43,solvent blue 57, Lumogen F Blau 650, and Lumogen F Violet 570.

It is preferred that the dye is fluorescent.

The composition may also comprise between 0.0001 to 0.1 wt % of one or more other dyes selected from cotton substantive shading dyes of group consisting of: hydrolysed reactive dye; acid dye; and direct dye.

BALANCE CARRIERS AND ADJUNCT INGREDIENTS

The laundry treatment composition in addition to the dye comprises the balance carriers and adjunct ingredients to 100 wt % of the composition.

These may be, for example, surfactants, builders, foam agents, anti-foam agents, solvents, fluorescers, bleaching agents, and enzymes. The use and amounts of these components are such that the composition performs depending upon economics, environmental factors and use of the composition.

The composition may comprise a surfactant and optionally other conventional detergent ingredients. The composition may also comprise an enzymatic detergent composition which comprises from 0.1 to 50 wt %, based on the total detergent composition, of one or more surfactants. This surfactant system may in turn comprise 0 to 95 wt % of one or more

anionic surfactants and 5 to 100 wt % of one or more nonionic surfactants. The surfactant system may additionally contain amphoteric or zwitterionic detergent compounds, but this in not normally desired owing to their relatively high cost. The enzymatic detergent composition according to the invention will generally be used as a dilution in water of about 0.05 to 2 wt%.

It is preferred that the composition comprises between 2 to 60 wt % of a surfactant, most preferably 10 to 30 wt %. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C_6 to C_{22} alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C_{11} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C_{16} to C_{18} primary alcohol sulphate together with a C_{12} to C_{15} primary alcohol 3 to 7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt % of the surfactant

system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40 wt % of the surfactant system.

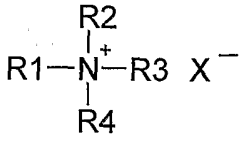
CATIONIC COMPOUND

When the present invention is used as a fabric conditioner it needs to contain a cationic compound.

Most preferred are quaternary ammonium compounds.

It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C_{12} to C_{22} alkyl chain.

It is preferred if the quaternary ammonium compound has the following formula:



in which R^1 is a C_{12} to C_{22} alkyl or alkenyl chain; R^2, R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl quaternary ammonium bromide.

A second class of materials for use with the present invention are the quaternary ammonium of the above structure in which R^1 and R^2 are independently selected from C_{12} to C_{22} alkyl or alkenyl chain; R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion.

A detergent composition according to claim 1 in which the ratio of (ii) cationic material to (iv) anionic surfactant is at least 2:1.

Other suitable quaternary ammonium compounds are disclosed in EP 0 239 910 (Procter and Gamble).

It is preferred if the ratio of cationic to nonionic surfactant is from 1:100 to 50:50, more preferably 1:50 to 20:50.

The cationic compound may be present from 0.02 wt % to 20 wt % of the total weight of the composition.

Preferably the cationic compound may be present from 0.05 wt % to 15 wt %, a more preferred composition range is from 0.2 wt % to 5 wt %, and most preferably the composition range is from 0.4 wt % to 2.5 wt % of the total weight of the composition.

If the product is a liquid it is preferred if the level of cationic surfactant is from 0.05 wt % to 10 wt % of the total weight of the composition. Preferably the cationic compound may be present from 0.2 wt % to 5 wt %, and most preferably from 0.4 wt % to 2.5 wt % of the total weight of the composition.

If the product is a solid it is preferred if the level of cationic surfactant is 0.05 wt % to 15 wt % of the total weight of the composition. A more preferred composition range is from 0.2 wt % to 10 wt %, and the most preferred

composition range is from 0.9 wt % to 3.0 wt % of the total weight of the composition.

BLEACHING SPECIES

The laundry treatment composition may comprise bleaching species. The bleaching species, for example, may selected from perborate and percarbonate. These peroxyl species may be further enhanced by the use of an activator, for example, TAED or SNOBS. Alternatively or in addition to, a transition metal catalyst may used with the peroxyl species. A transition metal catalyst may also be used in the absence of peroxyl species where the bleaching is termed to be via atmospheric oxygen, see, for example WO02/48301. Photobleaches, including singlet oxygen photobleaches, may be used with the laundry treatment composition. A preferred photobleach is vitamin K3.

FLUORESCENT AGENT

The laundry treatment composition most preferably comprises a fluorescent agent(optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in laundry treatment composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred

fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]trazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

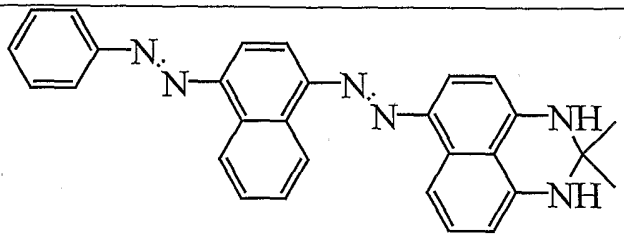
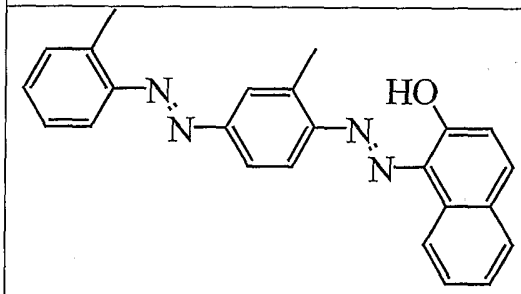
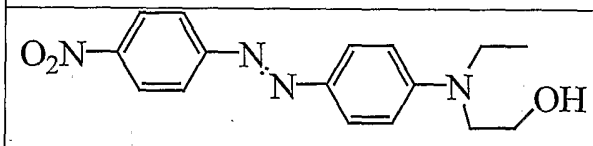
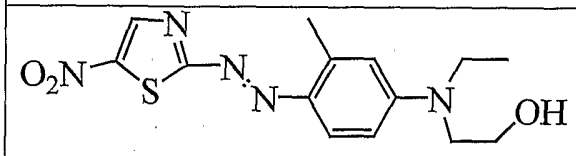
EXAMPLES

Example 1

Approximately 1000 ppm solutions of the dyes listed in the table below, were made in ethanol.

A stock solution of 1.8g/L of a base washing powder in water was created. The washing powder contained 18% NaLAS, 73% salts (silicate, sodium tri-poly-phosphate, sulphate, carbonate), 3% minors including perborate, fluorescer and enzymes, remainder impurities and water. The solution was divided into 100ml aliquots and the solvent dyes added from the ethanol solutions to give 5.8 ppm solutions. 1 g of pure woven polyester fabric was added to each of the wash solutions and the solution then shaken for 30 minutes, rinsed and dried. From the colour of the fabric it was clear that dye had deposited to the fabric. To quantify this the colour was measured using a reflectance spectrometer and expresses as the deltaE value compared to a polyester washed analogously but without dye present.

The results are given below

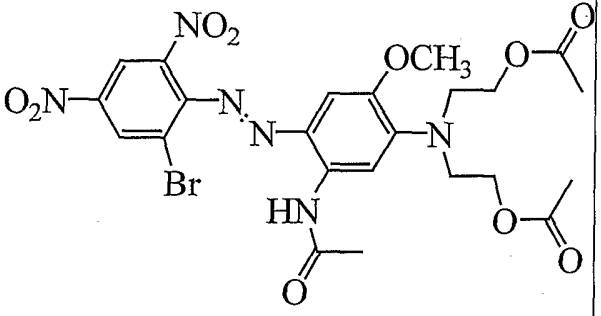
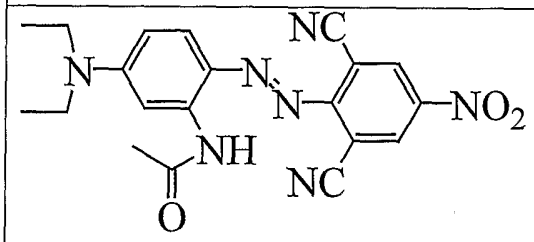
Dye	Dye - ppm in solution	deltaE
No dye (to indicate error level)	0	0.2
 solvent black 3	5.7	5.0
 solvent red 24	5.8	10.6
 disperse red 1	5.8	10.9
 disperse blue 106	5.8	4.8

Example 2

50 ppm solutions of the dyes listed in the table below, were made in ethanol. Concentration refers to dyes as received from the supplier. In general solvent dyes are pure (>90%) and disperse dyes have purities in the range 20-50%.

A stock solution of 1.8g/L of a base washing powder in water was created. The washing powder contained 18% NaLAS, 73% salts (silicate, sodium tri-poly-phosphate, sulphate, carbonate), 3% minors including perborate, fluorescer and enzymes, remainder impurities and water. The solution was divided into 100ml aliquots and the dyes added from the ethanol solutions with rapid stirring to give 200ppb solutions. 1 g of pure knitted polyester fabric was added to each of the wash solutions and the solution then shaken for 30 minutes, rinsed and dried. From the colour of the fabric it was clear that dye had deposited to the fabric. To quantify this the colour was measured using a reflectance spectrometer and expresses as the delta E value compared to a polyester washed analogously but without dye present. Following the washes the Ganz whiteness of the cloth was also measured (see "assessment of Whiteness and Tint of Fluorescent Substrates with Good Instrument Correlation" *Colour Research and Application* 19, 1994).
The experiments were repeated using knitted nylon as a fabric type.

The results are displayed in the table below.

Dye Maximum visible absorption wavelength in ethanol given.	OD 10cm	Ganz	ΔE polyester	ΔE nylon	CT
Control	0	81	0.1	0.4	-
 Disperse Blue 79:1 (576nm) LogP = 4.5	0.048	113	4.7	1.7	96
 Disperse Blue 165 (611nm) LogP =3.5	0.014	129	7.5	5.0	107
Disperse Blue 367 (610nm)	0.0067	91	1.4	1.1	250
Solvent blue 43 Triphenylmethane (602nm)	0.33	88	0.9	0.4	2.1
Lumogen F Blau 650 (ex BASF)	-	88	0.3	0.6	-
Lumogen F Violett 570 (ex BASF)	-	87	0.1	0.2	-

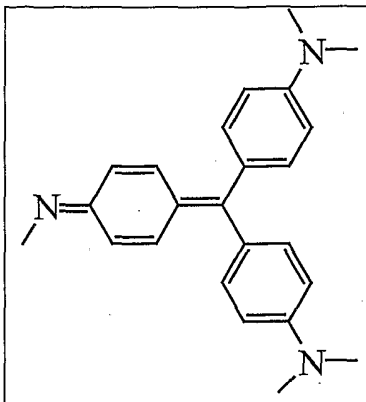
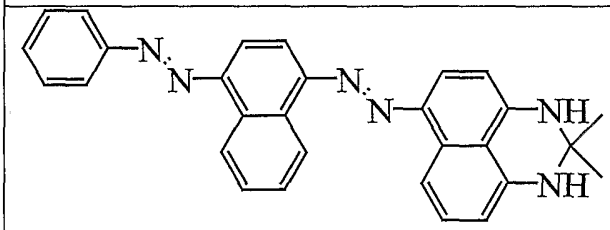
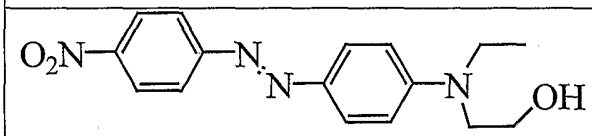
 Solvent Violet 8 (Methyl Violet B Base) (580nm) LogP = 4.5	0.26	89	1.1	0.6	3.5
 solvent black 3 (604nm) logP = 8.5	0.11	74	1.5	0.6	6.4
Dianix Violet CC (550nm) (ex Dystar)	0.013	132	8.0	7.5	623
 Disperse red 1 (482nm) LogP = 4.0	0.023	71	3.4	11.8	150

Table - notes

The ganz whiteness values are accurate to +/-5 units.

All deltaE measurements are UV excluded.

Only where known is the structure of the dye given.

The optical density, OD, is that of a 200ppb solution in water at 10cm. The value was obtained by extrapolated from

from measurement in ethanol solutions at higher levels for accuracy.

CT is a measure of the Colour Transferred from the wash solution to the polyester and is defined as:

$$CT = deltaE/OD$$

From the deltaE results in the table all the dyes coloured the polyester.
From the Ganz results, dyes which are blue or violet increase the whiteness. The Black and red dyes decrease the whiteness.
The lumogen dyes add fluorescence to the polyester, as observed by eye in a light box with UV-irradiation.

Example 3

The experiment of example 2 was repeated, but using 40 ppb of the dyes listed below. The L:C was changed to 30:1 and consisted by weight of 43% woven polyester and 57% non-mercerised cotton sheeting. The Ganz whiteness of the polyester was 89 for disperse blue 79:1. Whiteness benefits were also observed on the cotton. Repetition of the experiment using nylon, also gave benefits.

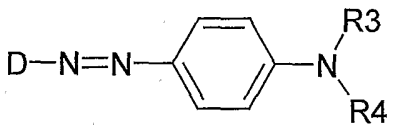
We claim:

1. A laundry treatment composition comprising between 0.0001 to 0.1 wt % of a hydrophobic dye selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, napthoquinone and mono-azo or di-azo dyes, and between 2 to 60 wt % of a surfactant.

2. A laundry treatment composition according to claim 1, wherein the hydrophobic dye is a disperse or solvent dye.

3. A laundry treatment composition according to claim 1 or 2, wherein the dye is a mono-azo dye.

4. A laundry treatment composition according to claim 3, wherein the mono-azo dye is selected from a compound of the following formula:



wherein R3 and R4 are optionally substituted C2 to C12 alkyl chains having optionally therein ether (-O-) or ester links, the chain being optionally substituted with -Cl, -Br, -CN, $-NO_2$, and $-SO_2CH_3$; and, D denotes an aromatic or hetroaromatic group.

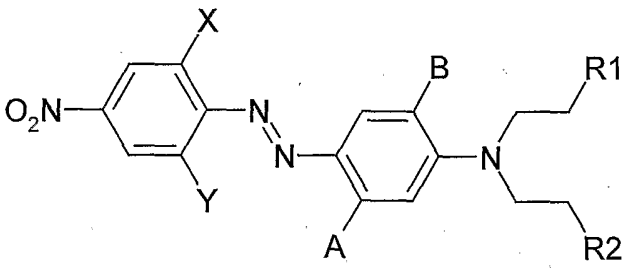
5. A laundry treatment composition according to claim 4, wherein R3 is -CH2CH2R5 and R4 and is -CH2CH2R6 and R5

and R6 are independently selected from the group consisting of: H, -CN, -OH, -C6H5, -OCOR7 and -COOR7, wherein R7 is independently selected from: aryl and alkyl.

6. A laundry treatment composition according to claim 5, wherein the aryl is -C6H5 or C10H7.

7. A laundry treatment composition according to anyone of claims 4 to 6, wherein D is selected from the group consisting of: azothiophenes, azobenzothiazoles and azopyridones.

8. A laundry treatment composition according to claim 3, wherein the mono-azo is of the form:



where X and Y are independently selected from the group consisting of: -H, -Cl, -Br, -CN, $-NO_2$, and $-SO_2CH_3$;
A is selected -H, $-CH_3$, -Cl, and -NHCOR;
B is selected -H, $-OCH_3$, $-OC_2H_5$, and -Cl;
R^1 and R^2 are independently selected from the group consisting of: -H, -CN, -OH, -OCOR, -COOR, -aryl; and,
R is C1-C8-alkyl.

9. A laundry treatment composition according to claim 1, wherein the dye is selected from the group consisting of (azo): 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, 205, 206, 207, 209, 210, 211, 212, 219, 220, 222, 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, 303, 304, 305, 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, 13, 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, 103, 104, 106 or 107, Dianix violet cc, and dyes with CAS-No's 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.

10. A laundry treatment composition according to claim 1, wherein the dye is selected from the group consisting of (non-azo): Disperse Blue 250, 354, 364, 366, Solvent Violet 8, solvent blue 43,solvent blue 57, Lumogen F Blau 650, and Lumogen F Violet 570.

11. A laundry treatment composition according any one of claims 1 to 3, wherein the dye is selected is fluorescent.

12. A laundry treatment composition according to any preceding claim, wherein the laundry treatment composition comprises from 0.005 to 2 wt % of a fluorescer other than the dye per se.

13. A laundry treatment composition according to any preceding claim, wherein the dye give a blue or violet shade when deposited on white polyester.

14. A laundry treatment composition according to any preceding claim, wherein the composition comprises between 0.0001 to 0.1 wt % of one or more other dyes selected from cotton substantive shading dyes of group consisting of: hydrolysed reactive dye; acid dye; and direct dye.

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

(i) treating a textile with an aqueous solution of a hydrophobic dye as defined in any one of claims 1 to 10, the aqueous solution comprising from 1 ppb to 5 ppm of the hydrophobic dye and from 0.2 g/L to 3 g/L of a surfactant; and,

(ii) rinsing and drying the textile.

16. A method of treating a textile according to claim 15, wherein the hydrophobic dye is present in the range 10 ppb to 200 ppb.

17. A method of treating a textile according to claim 15 or 16, wherein the aqueous solution has an ionic strength from 0.001 to 0.5.

18. A method of treating a textile according to any one of claims 15 to 17, wherein the aqueous solution comprises from 1 ppb to 6 ppm one or more other dyes selected from cotton substantive shading dyes of group consisting of: hydrolysed reactive dye; acid dye; and direct dye.

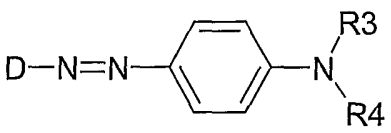
We claim:

1. A domestic method of treating a textile garment, the method comprising the steps of:
(i) treating a textile with an aqueous solution of a hydrophobic dye, the aqueous solution comprising from 1 ppb to 5 ppm of the hydrophobic dye and from 0.2 g/L to 3 g/L of a surfactant; and,
(ii) rinsing and drying the textile, wherein the hydrophobic dye is selected from: benzodifuranes; methine; triphenylmethanes; napthalimides; pyrazole; napthoquinone; mono-azo and di-azo dyes, and between 2 to 60 wt % of a surfactant.

2. A domestic method of treating a textile according to claim 1, wherein the hydrophobic dye is a disperse or solvent dye.

3. A domestic method of treating a textile according to claim 1 or 2, wherein the dye is a mono-azo dye.

4. A domestic method of treating a textile according to claim 3, wherein the mono-azo dye is selected from a compound of the following formula:



wherein R3 and R4 are optionally substituted C2 to C12 alkyl chains having optionally therein ether (-O-) or

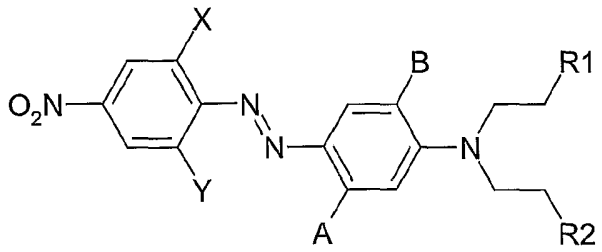
ester links, the chain being optionally substituted with -Cl, -Br, -CN, $-NO_2$, and $-SO_2CH_3$; and, D denotes an aromatic or hetroaromatic group.

5. A domestic method of treating a textile according to claim 4, wherein R3 is -CH2CH2R5 and R4 and is -CH2CH2R6 and R5 and R6 are independently selected from the group consisting of: H, -CN, -OH, -C6H5, -OCOR7 and -COOR7, wherein R7 is independently selected from: aryl and alkyl.

6. A domestic method of treating a textile according to claim 5, wherein the aryl is -C6H5 or C10H7.

7. A domestic method of treating a textile according to anyone of claims 4 to 6, wherein D is selected from the group consisting of: azothiophenes, azobenzothiazoles and azopyridones.

8. A domestic method of treating a textile to claim 3, wherein the mono-azo is of the form:



where X and Y are independently selected from the group consisting of: -H, -Cl, -Br, -CN, $-NO_2$, and $-SO_2CH_3$;
A is selected -H, $-CH_3$, -Cl, and -NHCOR;

B is selected -H, $-OCH_3$, $-OC_2H_5$, and -Cl;
R^1 and R^2 are independently selected from the group consisting of: -H, -CN, -OH, -OCOR, -COOR, -aryl; and,
R is C1-C8-alkyl.

9. A domestic method of treating a textile according to claim 1, wherein the dye is selected from the group consisting of: 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, 205, 206, 207, 209, 210, 211, 212, 219, 220, 222, 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, 303, 304, 305, 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, 13, 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, 103, 104, 106 or 107, Dianix violet cc, and dyes with CAS-No's 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.

10. A domestic method of treating a textile according to claim 1, wherein the dye is selected from the group

consisting of: Disperse Blue 250, 354, 364, 366, Solvent Violet 8, solvent blue 43,solvent blue 57, Lumogen F Blau 650, and Lumogen F Violet 570.

11. A domestic method of treating a textile according any one of claims 1 to 3, wherein the dye is selected is fluorescent.

12. A domestic method of treating a textile according to any preceding claim, wherein the laundry treatment composition comprises a fluorescer other than the dye per se.

13. A domestic method of treating a textile according to any preceding claim, wherein the dye gives a blue or violet shade when deposited on white polyester.

14. A domestic method of treating a textile according to any preceding claim, wherein the hydrophobic dye is present in the range 10 ppb to 200 ppb.

15. A domestic method of treating a textile according to claim 13 or 15, wherein the aqueous solution has an ionic strength from 0.001 to 0.5.

16. A domestic method of treating a textile according to any preceding claim, wherein the aqueous solution comprises from 1 ppb to 6 ppm one or more other dyes selected from cotton substantive shading dyes of group consisting of: hydrolysed reactive dye; acid dye; and direct dye.

STATEMENT UNDER ARTICLE 19 (1)

Dear Sirs

Re: International Application No. PCT/EP2005/009846
Unilever Case C4441 (C)

We enclose a new set of claims 1 to 16, under Article 19 PCT, to replace claims 1 to 18 presently on file for PCT/EP2005/009846. We also enclose a track changes document which shows the changes made to the claims. We also enclose a copy of US 2005/0235429 which we refer to as **D3a** in this response.

The only independent claim, claim 1, in the amended claims is now limited to a domestic method of treating a textile garment The limitation for the domestic was finds support in the paragraph bridging pages 1 an 2. The limitations of claim 15 have also been incorporated into claim 1.

Whilst there is no equivalent of Article 69 EPC under the PCT it is respectfully submitted that the Examiner should keep this in mind when assessing the scope of the claims as amended.

The prior art cited in the written opinion of the international searching authority dated 30 December 2005 is now discussed with respect to the amended claims.

The Examiner appears to be considering industrial and domestic disclosures to be equivalent. Industrial dying/shading is different to a domestic process.
There is great control in industrial processes in concentration, temperature and reproducibility. The industrial process is conducted at high temp see **D3** (WO 03/093565) page 20, line 42 to page 21, line 29; the temperatures are not domestic. The applicant has primarily working from US 2005/0235429 (**D3a**) which as far as the applicant can determine an English equivalent of **D3**. The process as referred to above is disclosed in paragraphs [0113] to [0117] of **D3a**. Reference is made to the examples of **D3a**; the Exhaust process is run at 130 °C and the Thermasol process is run at a minimum of 128 °C (see table 2). Both the Thermasol and the Exhaust processes disclosed in **D3a**

require pressure apparatus because water boils at 100 °C. An industrial applied to a textile materials is a one off process and not of multiple applications. In contrast to industrial processes, a domestic process has to work under a variety of conditions. The temperature of domestic processes is variable; the process needs to be viable at ambient temperatures. The duration of washing is not standard. There is no reason to extrapolate from an industrial dying or shading process.

D1 US 4,886,517
D1 (US 4,886,517) discloses a hair dye and not a domestic method of treating a textile garment.

D2 (WO 04/072217)
D2 (WO 04/072217) does not disclose a shading dye. **D2** is concerned with photobleaches. Dyes are photostable and reference is made to page 4, line 21 to page 5 of **D2**: "As one skilled in the art will appreciate not only an amine substituent would serve to quench the excited state of the quinone; examples of other such substituents to be avoided which are three atoms remote from a carbonyl of the quinone are: -OH, NR2, -NHR, wherein R is alkyl or aromatic." Napthaquinone as described in **D2** is not a dye, as it molar extinction coefficients above 400nm are all below 1000.

D3 (WO 03/093565)
D3 (WO 03/093565) discloses an industrial process and not a domestic laundry process for shading a textile. **D3** requires large amounts of optical brightner (fluorescer). **D3** generically discloses solvent violet 13 but not explicitly. Use of solvent violet 13 is not within the scope of the amended claims.

Regarding the Examiners point 4.3, the Examiner needs to consider the Ganz values. The benefits are best measured by the Ganz values which give 88 and 87 over a control of 81. This difference shows that Lumogen F Blau 650 and Lumogen F Violet 570 provide a significant benefit.

Regarding the Examiners point 5, azo has been removed as found in parenthesis. Dianix violet CC is readily available from Dystar as indicated in the application.

Regarding the Examiners point 5, all the dyes found in claims 9 and 10 are within the definition of the dyes of claim 1 and are commercially readily available as indicated on the top of page 3.

Regarding the Examiners point 5.2, Lumogen F Blau 650, Disperse blue 366, Solvent Blue 57, and Lumogen F Violet 570 and widely recognised tradenames and are hence internationally recognised; we are not aware of other names for these dyes.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/009846

A. CLASSIFICATION OF SUBJECT MATTER
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)
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 4 886 517 A (BUGAUT ET AL) 12 December 1989 (1989-12-12) column 1, lines 7-11 column 4, lines 54-57 examples 2,5 -----	1-14
X	WO 2004/072217 A (UNILEVER) 26 August 2004 (2004-08-26) page 1, line 23 - page 2, line 9 page 3, lines 6-14 example 1 -----	1,11-18

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[X] Further documents are listed in the continuation of box C.

[X] 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	Date of mailing of the international search report
16 December 2005	28/12/2005

Name and mailing address of the ISA	Authorized officer
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	Bertran Nadal, J

Form PCT/ISA/210 (second sheet) (January 2004)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/093565 A (BASF AG) 13 November 2003 (2003-11-13) page 1, line 6 - page 2, line 15 page 12, lines 10-19 page 14, line 35 - page 20, line 10; compounds B1-B7, C1-C4 page 20, lines 37-41 page 21, lines 31-38 claims 1,9,11	1-18
A	US 4 494 957 A (NIWA ET AL) 22 January 1985 (1985-01-22) column 4, lines 21-39 claims	1-18
A	US 3 958 928 A (LALA ET AL) 25 May 1976 (1976-05-25) column 1, line 51 - column 3, line 25 claim 1	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2005/009846

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