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(54) **Title:** INCORPORATION OF DYE INTO GRANULAR LAUNDRY COMPOSITION

(57) **Abstract:** The present invention concerns granular laundry detergent compositions comprising a shading dye containing granule.



WO 2012/172038 A1

INCORPORATION OF DYE INTO GRANULAR LAUNDRY COMPOSITION

Technical Field

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The present invention concerns laundry shading dye compositions.

Background

10 WO 2010/084039 (Unilever) discloses a granular laundry detergent composition comprising:

(a) from 0.00005 to 0.2 wt% of a dye granule, wherein the dye granule comprises:

- 15 (i) 20 to 60 wt% of a shading dye;
- (ii) 40 to 80 wt% of a dispersant selected from: ligninsulphonates; alkali metal salts of the condensation products of naphthalenesulphonic acids and formaldehyde; polyvinylsulphonates; and, ethoxylated novolacs;
- (iii) 0 to 10 of wt% auxiliary agents selected from: anionic surfactants; non-ionic surfactants; acidic polymers; and dust proofing oil;
- 20 (b) from 5 to 50 wt% of a surfactant;
- (c) from 5 to 50 wt% builder selected from: calcium sequestrant materials; precipitating materials; and, calcium ion-exchange materials; and,
- (d) 0.05 to 50 wt% a water soluble carrier salt; and,
- (e) 0 to 20 wt% other ingredients.

25

WO 2009/141173 (Unilever) discloses preferably spray dried cationic phenazine or acid azine dye powder which contain 20 to 100 wt% of the dye. Preferably, the dye powder has an average particle size, APS, from 0.1 to 300 microns, preferably 10 to 100 microns. The spray dried dye powder is mixed with a

30 Na₂SO₄ or NaCl or pre-prepared granular base or full detergent formulation to

- 2 -

give a 0.1 to 5 dye wt% mixture. This dry mix is then mixed into the granular formulation.

Summary of Invention

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We have found that by lowering level of shading dye in a specific granule composition better benefits are obtained.

10 In one aspect the present invention provides a granular laundry detergent composition comprising:

- (a) from 0.0005 to 0.5 wt%, preferably 0.001 to 0.1wt% of a dye granule, wherein the dye granule comprises:
 - (i) 1 to 18 wt%, preferably 10 to 16wt%, of a shading dye;
 - (ii) 62 to 99 wt% of a dispersant selected from: ligninsulphonates; alkali metal salts of the condensation products of naphthalenesulphonic acids and formaldehyde; polyvinylsulphonates; and, ethoxylated novolacs;
 - (iii) 0 to 20 of wt% auxillary agents, preferably selected from: anionic surfactants; non-ionic surfactants; polymers; and, dust proofing oil;
- (b) from 5 to 50 wt% of a surfactant;
- (c) from 5 to 50 wt% builder selected from: calcium sequestrant materials; precipitating materials; and, calcium ion-exchange materials; and,
- (d) 0.05 to 50 wt% a water soluble carrier salt; and,
- (e) the remainder to 100 wt% other ingredients.

25 Preferably the alkali metal salt of the condensation products of naphthalenesulphonic acids and formaldehyde is sodium.

The shading dye preferably has a calculated logP (octanol-water partition coefficient) of between 0.5 and 3 more preferably between 1.0 and 2.5. Log P values are atom based and calculated using Molecular Modeling Pro (version 30 5.2.2, © Norgwyn Montgomery Softwear limited).

Detailed Description of the Invention

Dye Granules

5 The granules are preferably formed by drying a liquid slurry or solution of the materials, for example by vacuum drying, freeze drying, drying in drum dryers, Spin Flash® (Anhydro), but most preferably by spray drying. Most preferably the liquid is water and the shading dye and dispersant are ground before or during the making of the slurry. This grinding is preferably accomplished in mills, such as for
10 example ball, swing, bead or sand mills, or in kneaders. The average particle size of undissolved shading dye in the slurry is preferably less than 1 micron, more preferably less than 0.5 microns, most preferably less than 0.2 microns.

The production of such granules is discussed in WO2006/131530. Such granules
15 are suitably made immediately after synthesis of the dye.

Preferably, the dye granules have an average particle size, APS, from 0.1 to 300 microns, preferably 10 to 100 microns, most preferably 25 to 75 microns. Preferably this is as measured by a laser diffraction particle size analyser,
20 preferably a Malvern HP with 100mm lens.

The dye granules are preferably post-dosed into the powder in a 0.1 to 2 wt% dry mix with an alkali metal salt, preferably Na₂SO₄ or NaCl.

25 Shading Dye

Shading dyes deposit to fabric during the wash or rinse step of the washing process providing a visible hue to the fabric.

30 The shading dyes used in the present invention are blue or violet. In this regard the dye gives a blue or violet colour to a white cloth with a hue angle of 240 to

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345, more preferably 260 to 320, most preferably 270 to 300. The white cloth used is bleached non-mercerised woven cotton sheeting.

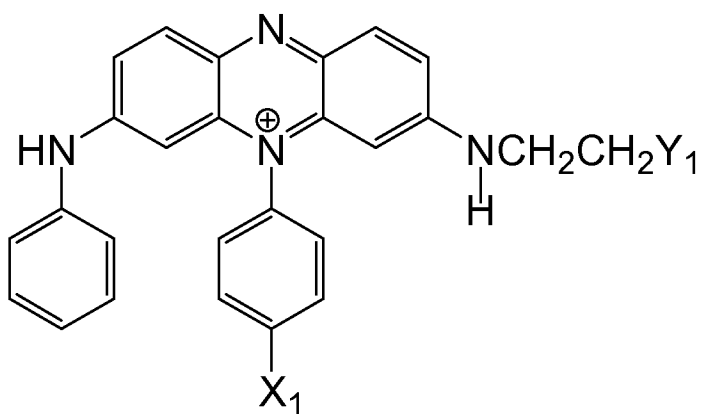
The shading dye preferably has a calculated logP (octanol-water partition coefficient) of between 0.5 and 3 more preferably between 1.0 and 2.5. Log P values are atom based and calculated using Molecular Modeling Pro (Chem SW
5 ®, version 5.2.2, © Norgwyn Montgomery Software limited). Most preferably the dye is uncharged at pH=7.

- 10 The dye chromophore is preferably selected from the group comprising: mono-azo, triphenylmethane, naphtholactam, azine and anthraquinone. Most preferably mono-azo, azine and anthraquinone.

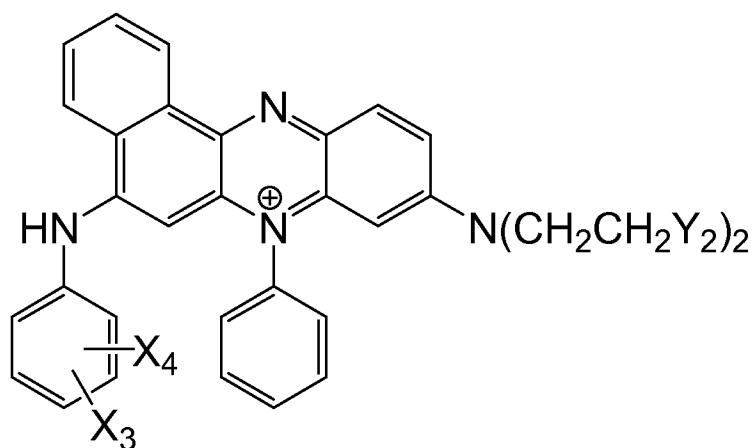
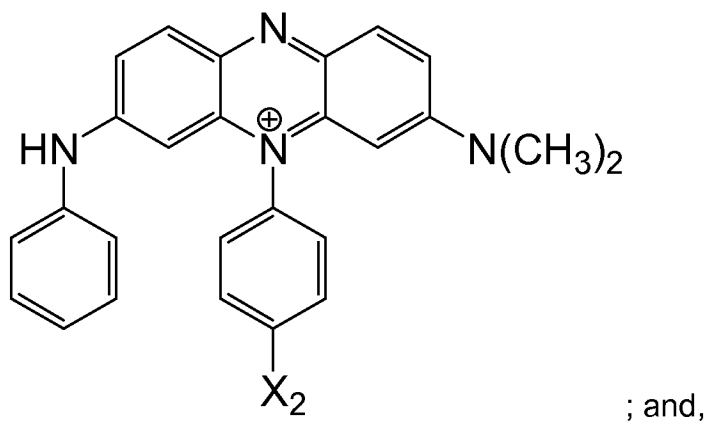
- 15 Many examples of shading dyes are found in the classes of basic, solvent, acid, direct and disperse dyes.

Preferred shading dyes are:

- (1) acid azine dyes as described in WO 2008/017570, preferably acid blue 59, acid blue 98 and acid violet 50.
- 20 (2) a cationic azine dye, preferably of the following form blue or violet cationic phenazine dye which is not covalently bound to a negatively charged substituent, the phenazine dye selected from:



- 5 -



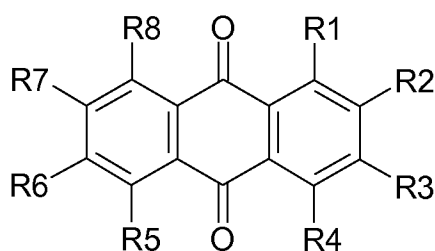
wherein:

- 5 X_1 is selected from: $-F$; $-N(CH_3)_2$; $-N(CH_2CH_3)_2$; $-N(H)COCH_3$; and, $-N(H)COCH_2CH_3$;
- X_2 is selected from: $-F$; $-N(CH_3)_2$; $-N(CH_2CH_3)_2$; $-N(H)COCH_3$; and, $-N(H)COCH_2CH_3$;
- X_3 is selected from: $-H$; $-F$; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, $-OC_2H_5$;
- 10 X_4 is selected from: $-H$; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, $-OC_2H_5$;
- Y_1 is selected from: $-OH$; $-OCH_2CH_2OH$; $-CH(OH)CH_2OH$; and,
- Y_2 is selected from: $-OH$; $-OCH_2CH_2OH$; $-CH(OH)CH_2OH$; $-OC(O)CH_3$; and, $C(O)OCH_3$.
- 15 (3) cationic azo dyes, preferably cationic mono-azo dyes. The cationic azo dye preferably bear the cationic groups on a chain. The dye may also a bear an anionic group.

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(4) hydrophobic dyes as follows:

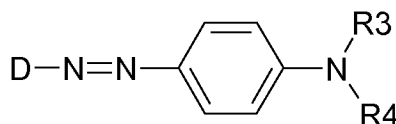
(4a) solvent violet 13 and disperse violet 27 and an anthraquinone structure of the following anthraquinone structure (I):



(I),

wherein R1, R4, R5, and R8 are independently selected from the groups consisting of -H, -OH, -NH₂, NHCOCH₃ and -NO₂, such that a maximum of only one -NO₂ group and a maximum of two -H are present as R1, R4, R5, and R8 substituents; and R2, R3, R6, and R7 is selected from -H, F, Br, Cl or -NO₂, and -

(4b) mono-azo dye selected from a compound of the following formula:

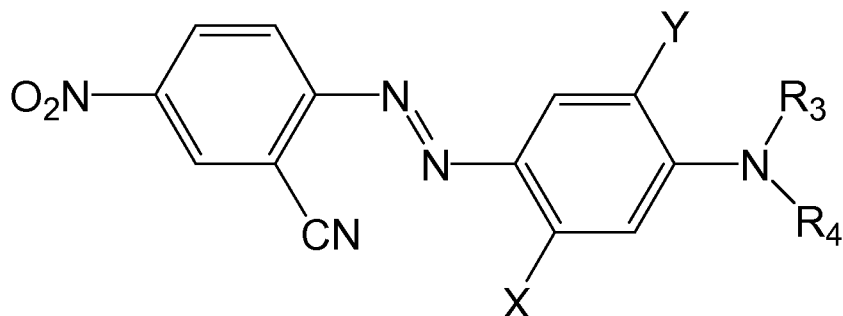


wherein R₃ and R₄ are optionally substituted C2 to C12 alkyl chains having optionally therein ether (-O-) or ester links, the chain being optionally substituted with -Cl, -Br, -CN, -NO₂, and -SO₂CH₃; and, D denotes an aromatic or hetroaromatic group.

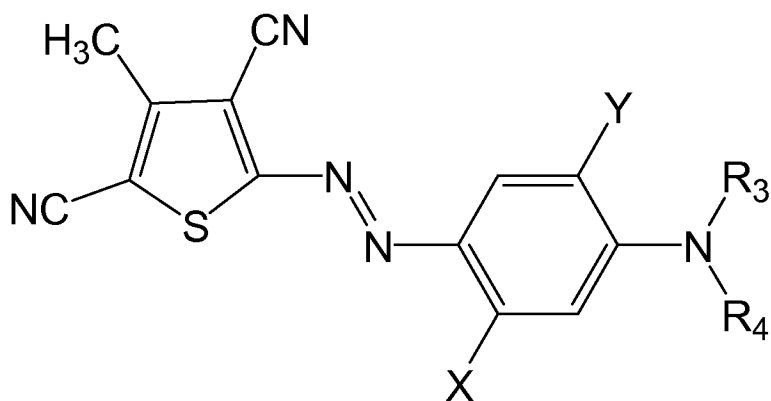
The aromatic rings may be further substituted by preferably -Cl, -Br, -CN, CH₃, C₂H₅, -NO₂, -SO₂CH₃ and -NHCOR and R is selected from CH₃, C₂H₅, and CH₂Cl.

Most preferred azo dyes are of the form:

- 7 -



And



5

Where X and Y are selected from H, CH₃, C₂H₅, -Cl, -Br, -CN, -NO₂, -SO₂CH₃ and -NHCOR and R is selected from CH₃, C₂H₅, and CH₂Cl. Preferably X is NHCOCH₃ or NHCOCH₂Cl.

10

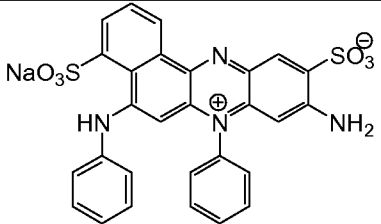
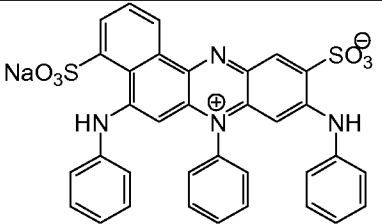
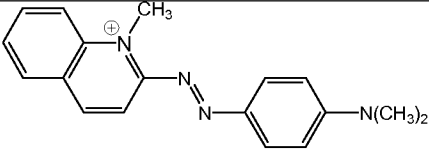
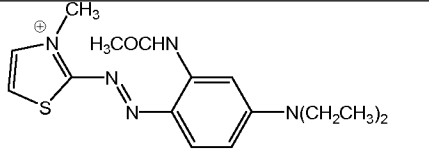
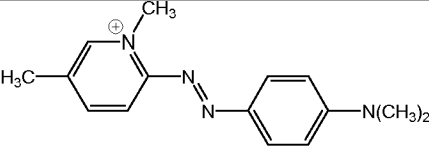
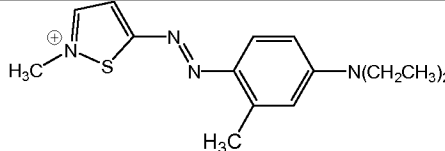
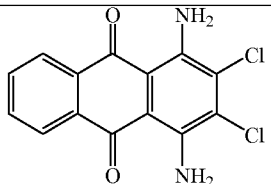
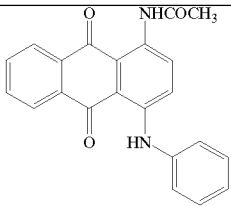
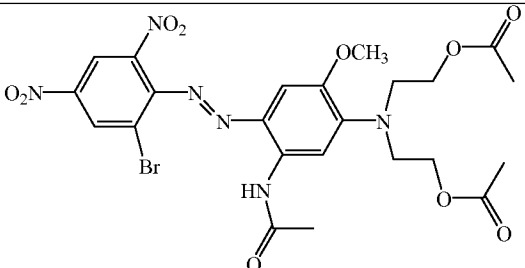
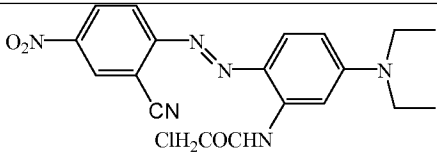
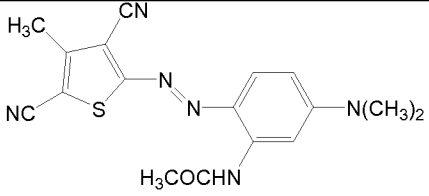
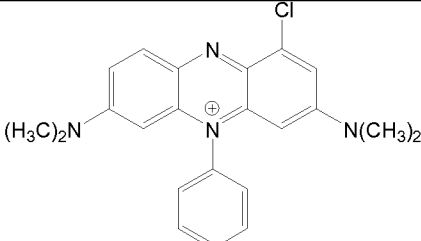
Shading of white garments may be done with any colour depending on consumer preference. Blue and Violet are particularly preferred shades and consequently preferred dyes or mixtures of dyes are ones that give a blue or violet shade on white fabrics.

15

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, for example disperse blue 1. Such dyes are not preferred.

20 The following table illustrates calculated logP values for various dyes.

- 8 -

 logP=0.82	 logP=2.86
 logP=1.81	 logP=1.47
 logP=1.65	 logP=1.45
 logP=1.93	 logP=2.56
 logP=3.76	 logP=5.45
 logP=3.71	 logP=1.41

Most preferably the dye used in the invention is disperse violet 28.

Builder

5

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

- 10 Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

- 15 Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate. Preferably, the laundry treatment composition comprises sodium carbonate in the range from 5 to 50 wt%, most preferably 10 to 35 wt%. In the method, when used with granular laundry treatment composition, the aqueous wash solution preferably comprises 0.1 to 4 g/L of sodium carbonate.

- 20 Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

25

The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below.

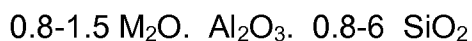
Many builders are also bleach-stabilising agents by virtue of their ability to

- 30 complex metal ions.

- 10 -

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate) are preferred builders.

5 The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15%w. Aluminosilicates are materials having the general formula:



10

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

15

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

20

25 Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt% of phosphate.

Enzymes

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The composition may comprise one or more enzymes, which provide cleaning performance, fabric care and/or sanitation benefits.

- 11 -

Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectases, lyases, and mannanases, or mixtures thereof.

- 5 Most suitable lipases are disclosed in WO 2007/087257.

Fluorescent Agent

The composition preferably comprises a fluorescent agent (optical brightener).

- 10 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 the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred classes of
- 15 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-naphthol[1,2-
- 20 triazin-2-yl]]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl.

Perfume

- 25 Preferably the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, most preferably 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA
- 30 Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

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It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

5

In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]).

Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

10

Perfume and top note may be used to cue the whiteness benefit of the invention.

It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

15

Experimental

Example

Spray dried shading dye granules were made of the following wt% composition:-

20

Ingredient	Granule number					
	1	2	3	4	5	6 (ref.)
Disperse Violet 28	5	15	15	15	15	30
Lignin sulphonate	95	85	80	80	80	70
SCMC	-	-	5	-	-	-
CP5	-	-	-	5	-	-
Alkaline silicate	-	-	-	-	5	-

SCMC = sodium carboxymethylcellulose (a polymer).

CP5 = Sokalan® CP5 ex BASF, the sodium salt of an Acrylic acid / Maleic acid co-polymer.

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The granules were sieved to give a size fraction from 25 to 75 microns.

The granules were mixed into a detergent powder 18 wt% Linear alkyl benzene sulphonate, 23wt% sodium sulphate, 35wt% light soda ash, 9wt% zeolite, 2wt% sodium tripolyphosphate, 2wt% soap, remainder moisture and minors, so that the detergent powder contained 0.0015wt% of disperse violet 28. The washing powders were then used to wash cloths in a top loading automatic washing machine (1.5g/L powder doseage, 24° French Hard water Liquor to cloth ratio 30:1). After 5 repeat washes the cloth were removed and the colour of the cloth measured using a reflectometer and expressed as the CIE L*a*b* value. The results are given in the table below.

Granule number	b*	
	Woven cotton	Woven polyester
1	-2.7	-3.2
2	-3.7	-4.2
3	-3.4	-3.8
4	-3.4	-3.9
5	-3.6	-3.9
6 (reference)	-1.7	-2.1

CIE b* measure the yellow (+ve) to blue (-ve) colour axis

15 The product with best performance give the largest negative b* value.

The level of Disperse Violet 28 in all products was the same.

The products with granules containing 5 and 15wt% Disperse Violet 28 perform significantly better than the product with 30wt% Disperse Violet 28.

CLAIMS

1. A granular laundry detergent composition comprising:
 - (a) from 0.0005 to 0.5 wt% of a dye granule, wherein the dye granule
5 comprises:
 - (i) 1 to 18 wt% of a shading dye;
 - (ii) 62 to 99 wt% of a dispersant selected from: ligninsulphonates;
alkali metal salts of the condensation products of
naphthalenesulphonic acids and formaldehyde;
10 polyvinylsulphonates; and, ethoxylated novolacs;
 - (iii) 0 to 20 of wt% auxillary agents;
 - (b) from 5 to 50 wt% of a surfactant;
 - (c) from 5 to 50 wt% builder selected from: calcium sequestrant materials;
precipitating materials; and, calcium ion-exchange materials; and,
 - 15 (d) 0.05 to 50 wt% a water soluble carrier salt; and,
 - (e) the remainder to 100 wt% other ingredients.
2. A granular laundry detergent composition according to claim 1, wherein the
20 shading dye has a calculated logP (octanol-water partition coefficient) of
between 0.5 and 3.
3. A granular laundry detergent composition according to claim 1 or 2, wherein
the dispersant is a ligninsulphonate and/or the condensation products of
naphthalenesulphonic acids and formaldehyde.
25
4. A granular laundry detergent composition according to any one of the
preceding claims, wherein the builder is selected from: carbonates; zeolites;
silicates and sodium tripolyphosphate.
- 30 5. A granular laundry detergent composition according to any one of the
preceding claims, wherein the shading dye is disperse violet 28.

- 15 -

6. A granular laundry detergent composition according to any preceding claim, wherein the composition comprises a fluorescer selected from the group consisting of: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole,
5 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-sulfostyryl)biphenyl.

10

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061406

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C11D3/34	C11D3/37	C11D3/40 C11D3/42 C11D17/06
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/084039 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]) 29 July 2010 (2010-07-29) cited in the application page 2, lines 3-23 claims; examples	1-6
A	WO 2006/131530 A1 (CLARIANT INT LTD [CH]) 14 December 2006 (2006-12-14) cited in the application page 13, line 10 - page 14, line 18 page 29; example M1	1-6
A	US 4 762 636 A (BALLIELLO PAOLO [DE] ET AL) 9 August 1988 (1988-08-09) column 1, line 28 - column 2, line 44 ----- -/--	1-6
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 September 2012		Date of mailing of the international search report 26/09/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Bertran Nadal, Josep

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/061406

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 2006/032397 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 30 March 2006 (2006-03-30) claims; examples -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/061406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010084039	A1	29-07-2010	AR 075154 A1 16-03-2011
		CN 102292426 A 21-12-2011	
		EP 2382299 A1 02-11-2011	
		US 2011275551 A1 10-11-2011	
		WO 2010084039 A1 29-07-2010	
WO 2006131530	A1	14-12-2006	BR PI0611916 A2 05-10-2010
		JP 2008542514 A 27-11-2008	
		KR 20080011317 A 01-02-2008	
		US 2009123711 A1 14-05-2009	
		WO 2006131530 A1 14-12-2006	
US 4762636	A	09-08-1988	AU 594434 B2 08-03-1990
		AU 6952687 A 03-09-1987	
		BR 8700957 A 22-12-1987	
		EP 0236270 A2 09-09-1987	
		JP 62207400 A 11-09-1987	
		PT 84359 A 01-03-1987	
		US 4762636 A 09-08-1988	
WO 2006032397	A1	30-03-2006	AR 051102 A1 20-12-2006
		AT 435271 T 15-07-2009	
		BR PI0515028 A 01-07-2008	
		CA 2575592 A1 30-03-2006	
		CN 101023158 A 22-08-2007	
		EP 1794275 A1 13-06-2007	
		EP 2009088 A2 31-12-2008	
		EP 2133409 A2 16-12-2009	
		ES 2326901 T3 21-10-2009	
		US 2008034511 A1 14-02-2008	
		WO 2006032397 A1 30-03-2006	