(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 775 121 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
17.11.2021 Bulletin 2021/46

(21) Application number: **19709506.0**

(22) Date of filing: **13.03.2019**

(51) Int Cl.:
C11D 1/06 *(2006.01)* ***C11D 3/10*** *(2006.01)*
C11D 3/12 *(2006.01)* ***C11D 3/37*** *(2006.01)*
C11D 3/40 *(2006.01)* ***C11D 11/00*** *(2006.01)*
C11D 17/06 *(2006.01)*

(86) International application number:
PCT/EP2019/056233

(87) International publication number:
WO 2019/192813 (10.10.2019 Gazette 2019/41)

(54) **DYE GRANULE**

FARBSTOFFGRANULAT

GRANULÉ DE COLORANT

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **03.04.2018 EP 18165379**

(43) Date of publication of application:
17.02.2021 Bulletin 2021/07

(73) Proprietors:
- **Unilever Global IP Limited**
  Wirral, CH62 AZD (GB)
  Designated Contracting States:
  CY DE GB IE IT MT
- **Unilever IP Holdings B.V.**
  3013 AL Rotterdam (NL)
  Designated Contracting States:
  AL AT BE BG CH CZ DK EE ES FI FR GR HR HU IS LI LT LU LV MC MK NL NO PL PT RO RS SE SI SK SM TR

(72) Inventors:
- **BATCHELOR, Stephen, Norman**
  Wirral, Merseyside CH63 3JW (GB)
- **BIRD, Jayne, Michelle**
  Ellesmere Port, Cheshire CH66 2HT (GB)

(74) Representative: **Brooijmans, Rob Josephina Wilhelmus**
Unilever N.V.
Unilever Patent Group
Bronland 14
6708 WH Wageningen (NL)

(56) References cited:
EP-A1- 3 081 625
WO-A1-2007/006357
WO-A1-2009/132870

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 3 775 121 B1

Description

Field of the invention

[0001] This invention relates to dye granules, a laundry composition comprising dye granules and a method for preparing said granules and said composition.

Background of the invention

[0002] 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.

[0003] WO 2005/003274 describes a laundry treatment composition which comprises a surfactant and from 0.0001 to 0.1 wt % of a combination of dyes which together have a visual effect on the human eye as a single dye having a peak absorption wavelength on cotton of from 540 nm to 650 nm, preferably from 570 nm to 630 nm, the combination comprising a photostable dye which is substantive to cotton. Such a dye or combination of dyes may be referred to as a shading dye.

[0004] WO 2005/003275 teaches that such a shading dye may be incorporated into a treatment composition in a variety of ways. For example, dyes that are not sensitive to heat may be included in a slurry and spray dried. Alternatively, the dye may be incorporated into granules that are post-dosed to a detergent powder. However, it has been found at higher concentrations of shading dye in the granules of this type that there could be a danger of spotting and dye damage on the clothes. WO 2005/003275 suggests that these problems may be avoided if the concentration of dye in the granules is less than 0.1 wt %.

[0005] EP 1814974 discloses dye granules comprising non-ionic surfactant and a solid carrier, wherein the non-ionic surfactant has 0.0001 to 5 wt % dye dissolved therein.

[0006] EP3081625A1 discloses a solid free-flowing particulate laundry detergent composition comprising: (a) from 0.1wt% to 5wt% hueing agent particle comprising: (i) from 2wt% to 10wt% hueing agent, wherein the hueing agent is an azothiophene dye polymer of a specific structure; and (ii) from 60wt% to 98wt% clay; (b) from 35wt% to 80wt% spray-dried particle comprising: (a) from 8wt% to 24wt% alkyl benzene sulphonate anionic detersive surfactant; (b) from 5wt% to 18wt% silicate salt; (c) from 0wt% to 10wt% sodium carbonate; and (d) from 0wt% to 5wt% carboxylate polymer.

[0007] When (non-ionic) surfactants, which are solid at 293K are used, poor delivery of the dye to solution or fabric can result when washing at low temperatures, such as below 40 °C.

[0008] There is a need for detergent shading dye granules which provide improved dye delivery when used during washing at low temperatures.

Summary of the invention

[0009] It has been found that a detergent granule comprising a blue or violet shading dye and an alkyl ether carboxylate provides enhanced dye deposition.

[0010] In addition to providing enhanced dye deposition, it has been found that the combination of AEC and binder reduces direct contact staining (spotting); that is staining that occurs when the granule is in direct contact with damp fabric.

[0011] Accordingly, the present invention relates to a detergent dye granule comprising:

(i) from 0.005 to 5 wt % of a blue or violet shading dye;
(ii) from 5 to 60 wt % of alkyl ether carboxylate surfactant, wherein the alkyl ether carboxylate surfactant is of the following structure:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

wherein R^1 is selected from saturated and mono-unsaturated C_{10} to C_{18} linear or branched alkyl chains, wherein n is from 5 to 40 and wherein the alkyl ether carboxylate surfactant is a solid at 293 degrees Kelvin at 1 bar pressure;
(iii) from 20 to 90 wt % of a solid carrier;
(iv) from 1 to 10 wt % of a binder.

[0012] In a second aspect, the present invention relates to a process to provide a granular laundry detergent composition comprising the step of mixing dye granules comprising

(i) from 0.005 to 5 wt % of a blue or violet shading dye;

(ii) from 5 to 60 wt % of alkyl ether carboxylate surfactant, wherein the alkyl ether carboxylate surfactant is of the following structure:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

wherein R^1 is selected from saturated and mono-unsaturated C_{10} to C_{18} linear or branched alkyl chains, wherein n is from 5 to 40 and
wherein the alkyl ether carboxylate surfactant is a solid at 293 degrees Kelvin at 1 bar pressure;

(iii) from 20 to 90 wt % of a solid carrier;

with other detergent granules to provide a granular laundry detergent composition.

[0013] In a further aspect, the present invention relates to a granular laundry detergent composition comprising:

a) dye granules as defined herein in an amount such as to provide 0.0005 to 0.5wt % of dye as based on the total weight of the granular laundry detergent composition,
b) 2 to 70 wt % surfactant, based on total weight of the granular laundry detergent composition,
c) 5 to 50 wt % builder, based on total weight of the granular laundry detergent composition,
d) 0.05 to 50 wt % water-soluble solid carrier based on total weight of the granular laundry detergent composition,

wherein the sum of ingredients a), b), c) and d) is at least 80 wt.%, based on the total weight of the composition.

[0014] In a further aspect, the present invention relates to a method of treating a textile, the method comprising the steps of:

(i) treating a textile with an aqueous solution of the granular laundry detergent composition as defined herein, the aqueous solution comprising from 1 ppb to 5 ppm of shading dye and from 0.2 g/L to 3 g/L of surfactant; and
(ii) rinsing and drying the textile.

Detailed description of the invention

[0015] In a first aspect, the present invention relates to a detergent dye granule comprising:

(i) from 0.005 to 5 wt % of a blue or violet shading dye;
(ii) from 5 to 60 wt % of alkyl ether carboxylate surfactant, wherein the alkyl ether carboxylate surfactant is of the following structure:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

wherein R^1 is selected from saturated and mono-unsaturated C_{10} to C_{18} linear or branched alkyl chains, wherein n is from 5 to 40 and
wherein the alkyl ether carboxylate surfactant is a solid at 293 degrees Kelvin and at 1 bar pressure;

(iii) from 20 to 90 wt % of a solid carrier;
(iv) from 0.5 to 10 wt % of a binder, wherein the binder may be a polymer.

[0016] The word 'comprising' as used herein is intended to mean 'including' but not necessarily 'consisting of' or 'composed of'. In other words, the listed steps or options need not be exhaustive.

[0017] Unless specified otherwise, numerical ranges expressed in the format 'from x to y' or 'x-y' are understood to include x and y. When for a specific feature multiple preferred ranges are described in the format 'from x to y' or 'x-y', it is understood that all ranges combining the different endpoints are also contemplated. For the purpose of the invention, ambient temperature is defined as a temperature of about 20 °C.

[0018] Unless indicated otherwise, weight percentages (wt %) are based on the total weight of the formulation.

[0019] As used herein "granule" means a particle having a size from 50 to 1800 microns. The granule size is as determined by passing through a mesh sieve. Preferably the size is in the range 100 to 800 microns.

[0020] As used herein "shading dye" means a blue or violet anionic dye that deposits onto polyester, cotton or polycotton fabrics under domestic wash conditions.

[0021] As use herein, "solid carrier" means any solid material (at 293 degrees Kelvin at 1 bar pressure) in particulate form suitable for admixing into a laundry detergent formulation.

[0022] The term "particulate" as used herein in relation to a material, refers to a material that consists of discrete particles, preferably the discrete particles having a weight average particle size in the range of 5-200 μm.

[0023] As used herein, "binder" means a material used to bind together two or more other materials in the dye granule.

Alkyl ether carboxylate

[0024] The alkyl ether carboxylate according to the present invention are of the form R^1-$(OCH_2CH_2)_n$-OCH_2-COOH.

[0025] The alkyl chain, R^1, is selected from saturated and mono-unsaturated C_{10} to C_{18} linear or branched alkyl chains preferably selected from: C_{12}; C_{14}; C_{16}; and, C_{18} linear alkyl chain. The alkyl chain is most preferably selected from $CH_3(CH_2)_{15}$, $CH_3(CH_2)_{17}$, and mixtures thereof.

[0026] The alkyl ether carboxylic acid has n selected from 5 to 40, preferably 7 to 35, more preferably 8 to 30, even more preferably from 10 to 25. Preferably the value of n is selected so that the protonate form of the alkyl ether carboxylate is a solid at 293K/1bar.

[0027] Weights of alkyl ether carboxylic acid are calculated as the protonated form, R^1-$(OCH_2CH_2)_n$-OCH_2-COOH. They may be used as salt version for example sodium salt, or amine salt.

[0028] Alkyl ether carboxylic acid are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®).

[0029] Alkyl ether carboxylic acids synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996).

[0030] They may be synthesised via the reaction of the corresponding alcohol ethoxylate with chloroacetic acid or monochloro sodium acetate in the presence of NaOH: R^1-$(OCH_2CH_2)_n$-OH +NaOH + $ClCH_2COONa \rightarrow$ R^1-$(OCH_2CH_2)_n$-OCH_2COOH + NaCl + H_2O

[0031] In this synthesis residual R^1-$(OCH_2CH_2)_n$-OH may be present, preferably levels of R^1-$(OCH_2CH_2)_n$-OH are from 0 to 10 wt% in the alkyl ether carboxylic acid. Low levels of diglycolic acid and glycolic acid may be present as biproducts.

[0032] NaCl from the synthesis may be present in the aqueous liquid laundry detergent composition. Additional NaCl may be added to the composition.

[0033] They alkyl ether carboxylic acid may also be synthesised via an oxidation reaction:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2CH_2OH \rightarrow R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2COOH.$$

[0034] The oxidation is typically conducted using oxygen as the oxidant under basic conditions in the presence of metal catalyst such as Pd/Pt, as described in DE3135946; DE2816127 and EP0304763.

Shading dye

[0035] Depending on the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on class and particular efficacy within any particular class.

[0036] Dyes are discussed in K.Hunger (ed). Industrial Dyes: Chemistry, Properties, Applications (Weinheim: Wiley-VCH 2003). Organic dyes are listed in the colour index (Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists)

[0037] Shading dyes for use in laundry detergents preferably have an extinction coefficient at the maximum absorption in the visible range (400 to 700 nm) of greater than 5000 L $mol^{-1}cm^{-1}$, preferably greater than 10000 L $mol^{-1}cm^{-1}$. The shading dyes are blue or violet in colour.

[0038] Preferred shading dye chromophores are azo, azine, anthraquinone, phthalocyanine and triphenylmethane.

[0039] Azo, anthraquinone, phthalocyanine and triphenylmethane dyes preferably carry a net anionic charged or are uncharged. Azine dyes preferably carry a net anionic or cationic charge.

[0040] Shading dyes deposit to fabric during the wash or rinse step of the washing process providing a visible hue to the fabric. In this regard the dye gives a blue or violet colour to a white cloth with a hue angle of 240 to 345, more preferably 260 to 320, most preferably 270 to 300. The white cloth used in this test is bleached non-mercerised woven cotton sheeting.

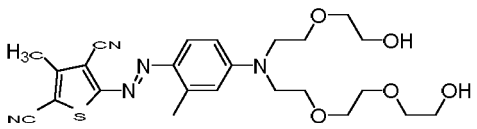
[0041] Shading dyes are discussed in WO2005/003274, WO2006/032327(Unilever), WO2006/032397(Unilever), WO2006/045275(Unilever), WO 2006/027086(Unilever), WO2008/017570(Unilever), WO 2008/141880(Unilever), WO2009/132870(Unilever), WO 2009/141 173 (Unilever), WO 2010/099997(Unilever), WO 2010/102861 (Unilever), WO 2010/148624(Unilever), WO2008/087497 (P&G), WO201 1/01 1799 (P&G), WO2012/054820 (P&G), WO2013/142495 (P&G) and WO2013/151970 (P&G).

[0042] The shading dye chromophore is most preferably selected from mono-azo, bis-azo, anthraquinone, and azine.

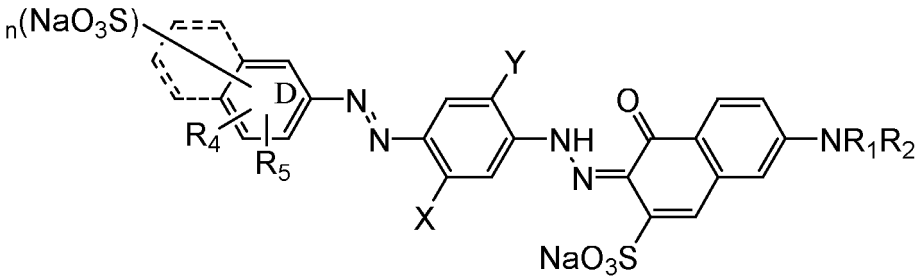
[0043] In an embodiment, a mixture of the shading dyes may be used. Preferably, at least two, at least three or at least four shading dyes are used in combination.

[0044] In a preferred embodiment, the shading dye is a mono-azo dye. Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxylated and are preferably uncharged or anionically charged at pH=7. Alkoxylated thiophene dyes are discussed in WO2013/142495 and WO2008/087497.

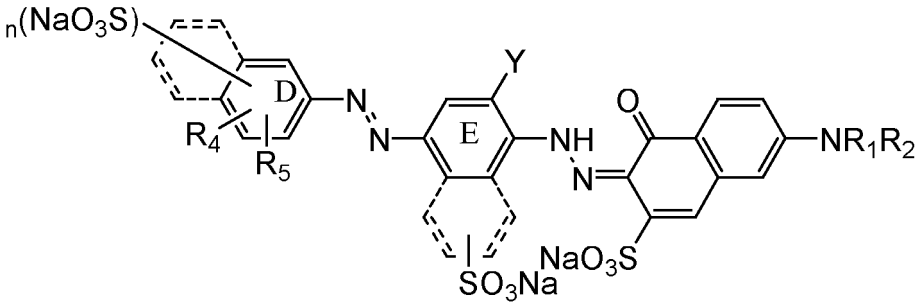
[0045] In a preferred embodiment, the shading dye belongs to the class of thiophene dyes. An example of a thiophene dye has the following structure:



[0046] In another preferred embodiment, the shading dye is a bis-azo dye. Bis azo-dyes are preferably sulphonate bis-azo-dyes. Preferably the shading dye is of the following structures:



or

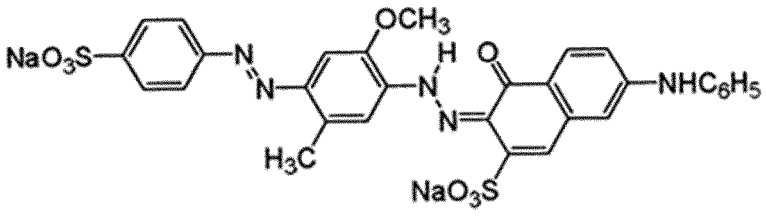


wherein:

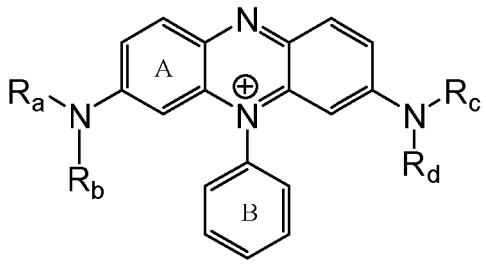
ring D and E may be independently naphthyl or phenyl as shown;
R^1 is selected from: hydrogen and C_1-C_4-alkyl, preferably hydrogen;
R^2 is selected from: hydrogen, C_1-C_4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;
R^3 and R^4 are independently selected from: hydrogen and C_1-C_4-alkyl, preferably hydrogen or methyl;
X and Y are independently selected from: hydrogen, C_1-C_4-alkyl and C_1-C_4-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

[0047] Preferred examples of sulphonated bis-azo compounds are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, direct violet 66, direct violet 99 and alkoxlyated versions thereof. Alkoxylated bis-azo dyes are discussed in WO2012/-54058 and WO2010/151906

[0048] Preferably, the shading dye has the following structure:

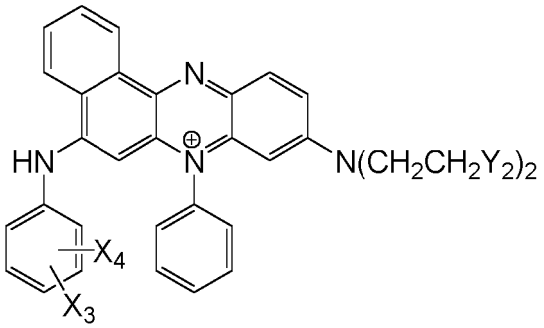


[0049] In yet another preferred embodiment, the shading dye is an azine dye. Azine dyes typically have the following core structure:



wherein R_a, R_b, R_c and R_d are selected from: H, an branched or linear C_1 to C_7-alkyl chain, benzyl a phenyl, and a naphthyl;
the dye is substituted with at least one SO_3^- or —COO^- group;
the B ring does not carry a negatively charged group or salt thereof;
and the A ring may further substituted to form a naphthyl;
the dye is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, Cl, Br, I, F, and NO_2.

[0050] Preferably, the azine dyes have the following general structure:

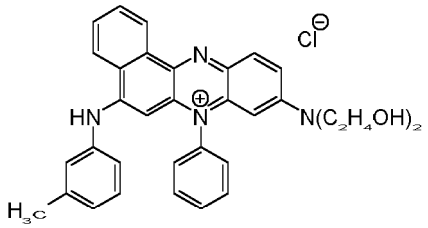


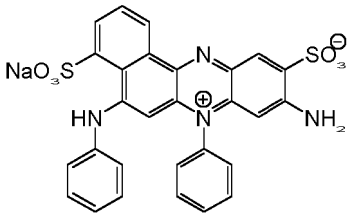
wherein:

X_3 is selected from: -H; -F; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, —OC_2H_5;
X_4 is selected from: -H; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, —OC_2H_5;
Y_2 is selected from: —OH; $-OCH_2CH_2OH$; $-CH(OH)CH_2OH$; $-OC(O)CH_3$; and, $C(O)OCH_3$.

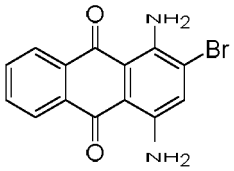
[0051] Azine dyes are preferably selected from sulphonated phenazine dyes and cationic phenazine dyes. Preferred examples are acid blue 98, acid violet 50, dye with CAS-NO 72749-80-5, acid blue 59, and the phenazine dye selected from:

[0052] Preferably, the shading dyes are of the following structure:



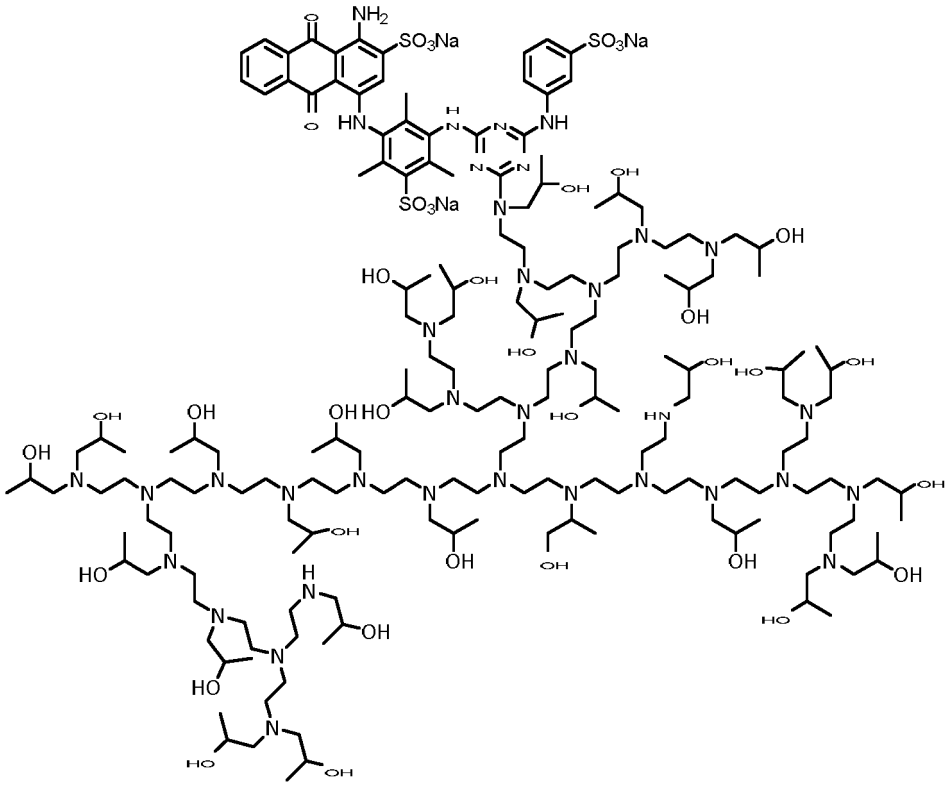


[0053] In another embodiment, the shading dye is a reactive blue anthraquinone dye. An example of an anthraquinone dye has the following structure:



[0054] In a preferred embodiment, the shading dye is a reactive blue anthraquinone dye covalently linked to an alkoxylated polyethyleneimine. The alkoxylation is preferably selected from ethoxylation and propoxylation, most preferably propoxylation. Preferably 80 to 95 mol% of the N-H groups in the polyethylene imine are replaced with iso-propyl alcohol groups by propoxylation. Preferably the polyethylene imine before reaction with the dye and the propoxylation has a molecular weight of 600 to 1800.

[0055] An example structure of a preferred reactive anthraquinone covalently attached to a propoxylated polyethylene imine is the following structure:



Solid carrier

[0056] The solid carrier may be water/surfactant soluble carrier or water/surfactant insoluble. The solid carrier may be a solid material in particulate form, preferably having a weight average particle size in the range 5 to 500 micrometres, preferably 10 to 200 micrometres.

[0057] Preferably, the solid carrier is water/surfactant insoluble. In a preferred embodiment, the solid carrier is a clay or zeolite. Zeolites are water-insoluble crystalline or amorphous aluminosilicates, examples being 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. In a preferred embodiment, the solid carrier is a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

[0058] In another embodiment, the solid carrier is a clay. Typically, the clay is a phyllosilicate clay with a 2:1 layer structure, which definition includes pyrophyllite clays, smectite or montmorillonite clays, saponites, vermiculites and micas Preferably, the clay is of bentonitic origin, bentonites being primarily montmorillonite type clays together with various impurities, the level and nature of which depends on the source of the clay material. In a preferred embodiment, the solid carrier is a montmorillonite clay, preferably bentonite.

[0059] In yet another embodiment the solid carrier is water/surfactant soluble. In a preferred embodiment, the solid carrier is a carbonate salt, a sulphate salt, a chloride sale or a citrate salt.

[0060] Preferably, the solid carrier is a carbonate salt. A preferred carbonate salt is sodium carbonate and/or sodium bicarbonate. Alternatively, the carbonate material may be potassium carbonate and/or potassium bicarbonate. A highly preferred carbonate material is sodium carbonate.

[0061] The carbonate salt may also be a double salt, such as burkeite. Burkeite is a congruent double salt with the chemical formula, $Na_6(SO_4)_2(CO_3)$, and sodium complex salts from aqueous salt solution. Alternatively, the carbonate salt may be a sequicarbonate or a crystal growth modified carbonate such as habit modified carbonate or crystal growth modified burkeite.

[0062] In a preferred embodiment, the carbonate salt is selected from the group of sodium carbonate, sodium sulphate, sodium chloride, and sodium citrate.

[0063] The carbonate salt is, at least part thereof, typically in particulate form, typically having a weight average particle size in the range of from 80 to 500 micrometres. However, it may be preferred for the carbonate material, or at least part thereof, to be in micronized particulate form, typically having a weight average particle size in the range of from 4 to 40 micrometres.

[0064] In a preferred embodiment, the solid carrier comprises one or more of sodium carbonate, clays and zeolites, more preferably comprises sodium carbonate and even more preferably comprises at least 50 wt % of sodium carbonate,

based on the total weight of the solid carrier as comprised by the dye granule.

[0065] Preferably, the solid carrier comprises at least 60 wt %, more preferably at least 70 wt %, even more preferably at least 80 wt.% sodium carbonate, based on the total weight of the solid carrier.

Binder

[0066] The dye granule comprises a binder. A binder is a material used to bind together two or more other materials the dye granule. Its two principal properties are adhesion and cohesion. The binder may be other than a non-ionic surfactant.

[0067] The dye granule comprises, based on the total weight of the dye granule, 0.5 to 10 wt % binder, preferably 0.75 to 8 wt %, even more preferably 1 to 7 wt.%, and most preferably 1.5 to 5 wt % binder.

[0068] The binder may be a polymeric material. Preferably, the binder has a melting point above 30 °C.

[0069] Suitable polymers for use herein are water-soluble. By water-soluble, it is meant herein that the polymers have a solubility greater than 5 g/L at 20 °C in demineralised water. The binder is preferably an acidic polymer. By an acidic polymer, it is meant herein that a 1% solution of said polymer has a pH of less than 7, preferably less than 5.5.

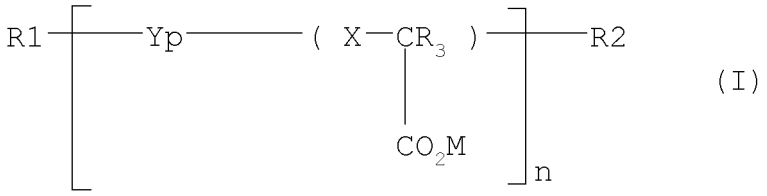
[0070] Preferably the binder is selected from the group consisting of a polyacrylate, polyethylene glycol, polyacrylate/maleate copolymer and combination thereof.

[0071] In a preferred embodiment, the binder is a copolymer, preferably comprising acrylic acid moieties and more preferably is copolymer of maleic acid and acrylic acid.

[0072] The average molar mass, Mw, is preferably from 2000 to 100000. Preferably, the polymer is an acrylic/maleic with a ratio of acrylic to maleic segments of from about 30:1 to about 1:1.

[0073] Suitable polymers for use herein have a molecular weight in the range of from 1000 to 280,000, preferably from 1500 to 150,000. Typically, the binder has an average molecular mass (M_w) from 2000 to 100000 Dalton, more preferably from 5000 to 80000 Dalton, even more preferably from 10000 to 50000 Dalton.

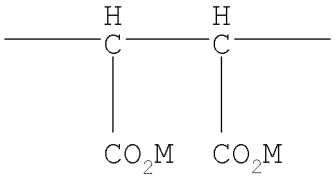
[0074] Suitable binders that are therefore particularly useful in the present invention, include those having the following empirical formula I:



(I)

wherein X is 0 or CH_2; Y is a comonomer or comonomer mixture; R_1 and R_2 are bleach-stable polymer-end groups; R^3 is H, OH or C_{1-4} alkyl; M is H, and mixtures thereof with alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, and mixtures thereof.

[0075] Preferred polycarboxylate polymers fall into several categories. A first category belongs to the class of copolymeric polycarboxylate polymers which, formally at least, are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid and mesaconic acid as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an alpha -C1-C4 alkyl acrylic acid as second monomer. Referring to formula I, therefore, preferred polycarboxylate polymers of this type are those in which X is CHO, R^3 is H or C_{1-4} alkyl, especially methyl, p is from about 0.1 to about 1.9, preferably from about 0.2 to about 1.5, n averages from about 10 to about 1500, preferably from about 50 to about 1000, more preferably from 100 to 800, especially from 120 to 400 and Y comprises monomer units of formula II



(II)

[0076] Such polymers are available from BASF under the trade name Sokalan® CP5 (neutralised form) and Sokalan® CP45 (acidic form).

[0077] Binder materials are commercially readily available. The water-soluble polymers of the Sokalan® type sold by BASF® are preferred.

[0078] The following is a list of such suitable products: Sokalan CP 10; Sokalan CP 10 S; Sokalan CP 12 S; Sokalan CP 13 S; Sokalan CP 45; Sokalan CP 5; Sokalan CP 7; Sokalan CP 9; Sokalan DCS; Sokalan HP 165; Sokalan HP 22 G; Sokalan HP 25; Sokalan HP 50; Sokalan HP 53; Sokalan HP 53 K; Sokalan HP 56; Sokalan HP 59; Sokalan HP 60; Sokalan HP 66; Sokalan PA 110 S; Sokalan PA 15; Sokalan PA 15 CL; Sokalan PA 20; Sokalan PA 20 PN; Sokalan PA 25 CL; Sokalan PA 30; Sokalan PA 40; Sokalan PM 70; and, Sokalan SR 100.

[0079] Preferred examples of binders are Sokalan CP5, Sokalan CP7, Sokalan CP9, Sokalan CP10S, Sokalan CP10, Sokalan CP12 S, Sokalan CP13 S, available from BASF. Maleic acid-acrylic acid copolymers are most preferred.

Dye granule

[0080] The dye granule preferably has a size of from 180 to 1000 microns as based on the ability to pass through a graded sieve. Preferably, the dye granule has a size of 250-800 microns as based on the ability to pass through a graded sieve.

[0081] The dye 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 an alkyl ether carboxylate surfactant and the shading dye and blended prior to combining with the carrier and binder.

[0082] Preferably, the dye granules have an average particle size, APS, from 0.1 to 300 microns, preferably 10 to 100 microns. Preferably this is as measured by a laser diffraction particle size analyser, preferably a Malvern HP with 100mm lens.

[0083] The dye granules are preferably post-dosed into a laundry detergent powder composition.

Laundry composition

[0084] The laundry composition preferably comprises surfactant selected from anionic and non-ionic surfactants (which includes a mixture of the same) in addition to the alkyl ether carboxylate of the dye granule.

[0085] Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal or amine salts of fatty acids (soaps), 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 alkyl radicals.

[0086] 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.

[0087] The anionic surfactant is preferably selected from: linear alkyl benzene sulphonate; alkyl sulphates; alkyl ether sulphates; soaps; alkyl (preferably methyl) ester sulphonates, and mixtures thereof.

[0088] The most preferred anionic surfactants are selected from: linear alkyl benzene sulphonates; alkyl sulphates; soaps; alkyl ether sulphates and mixtures thereof. Preferably the alkyl ether sulphate is a C_{12}-C_{14} n-alkyl ether sulphate with an average of 1 to 3EO (ethoxylate) units. Sodium lauryl ether sulphate is particularly preferred (SLES). Preferably the linear alkyl benzene sulphonate is a sodium C_{11} to C_{15} alkyl benzene sulphonates (LAS). Preferably the alkyl sulphates is a linear or branched sodium C_{12} to C_{18} alkyl sulphates. Sodium dodecyl sulphate is particularly preferred, (SDS, also known as primary alkyl sulphate). Soaps are preferably C_{12} to C_{18} saturated fatty acids, preferably they are present at levels of less than 3wt% of the formulation.

[0089] The level of anionic surfactant in the laundry composition is from (i) 10 to 40 wt%. It is preferable in the composition that LAS is the dominant anionic surfactant present.

[0090] In carbonate built powder detergent, it is preferably that >90wt% of the anionic surfactant present is LAS.

[0091] Non-ionic surfactant may be present in the surfactant mix.

[0092] Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having an aliphatic hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids or amides, especially ethylene oxide either alone or with propylene oxide. Preferred nonionic detergent compounds are the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide.

[0093] Preferably the non-ionic surfactant is an alkyl ethoxylated non-ionic surfactant and is a C_8 to C_{18} primary alcohol, most preferably a C_{12}-C_{16} primary alcohol, with an average ethoxylation of 7EO to 9EO units.

[0094] Preferably further (non-ionic) surfactants which are solid at 293 degrees Kelvin at 1 bar pressure, are, if present, predominantly formulated not in the dye granule of the invention, but in other parts of the laundry detergent composition.

[0095] Preferably, of the total weight amount of further (non-ionic) surfactants present in the granular laundry detergent composition as a whole, at most 50 wt. %, 40 wt. %, 35 wt.%, 30 wt. %, 25 wt. %, 20 wt. %, 15 wt. %, 10 wt. %, 5 wt. % is comprised by the dye granule according to the invention.

[0096] Preferably, the dye granule according to the invention comprises at most 50 wt.% of further (non-ionic) surfactants which are solid at 293 degrees Kelvin at 1 bar pressure, preferably at most 30 wt. %, more preferably at most 25 wt. %, even more preferably at most 10 wt. %, most preferably at most 1 wt. %.

[0097] Preferably the dye granule according to the invention comprises less than 10 wt.% further non-ionic surfactants which are solid at 293 degrees Kelvin at 1 bar pressure, preferably less than 5 wt.%, more preferably less than 1 wt. %.

Builders or Complexing Agents

[0098] Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0099] Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

[0100] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0101] 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.

[0102] The composition may also contain 0-65 wt % 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 complex metal ions.

[0103] Zeolite and carbonate (including bicarbonate and sesquicarbonate) are preferred builders for powder detergents.

[0104] 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 5wt%. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$$

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.

[0105] Alternatively, or additionally to the aluminosilicate builders, other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst) may be present.

[0106] Spray drying of the powder detergent is preferred.

Polymers

[0107] The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Enzymes

[0108] One or more enzymes are preferred present in a laundry composition of the invention and when practicing a method of the invention.

[0109] Preferably the level of each further enzyme in the laundry composition of the invention is from 0.0001 wt% to 0.1 wt% protein.

[0110] The further enzyme is preferably selected from: amylases, mannanases, lipases; and, cellulases, most preferably amylases and lipases. Suitable lipases include those sold under the tradenames lipex®, Lipoclean® and Lipolex® by Novozymes, Bagsvaerd Denmark.

[0111] Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Perfume

[0112] 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 Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

[0113] 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.

[0114] 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.

[0115] Perfume and top note may be used to cue the cleaning and whiteness benefit of the invention.

Fluorescent Agent

[0116] The composition 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 the 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]triazole, 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.

[0117] It is preferred that the aqueous solution used in the method has a fluorescer present. When a fluorescer is present in the aqueous solution used in the method it is preferably in the range from 0.0001 g/l to 0.1 g/l, preferably 0.001 to 0.02 g/l.

Further dyes

[0118] Preferred non-shading dyes are selected are selected from blue dyes, most preferably anthraquinone dyes bearing sulphonate groups and triphenylmethane dye bearing sulphonate groups. Preferred compounds are acid blue 80, acid blue 1, acid blue 3; acid blue 5, acid blue 7, acid blue 9, acid blue 1 1, acid blue 13, acid blue 15, acid blue 17, acid blue 24, acid blue 34, acid blue 38, acid blue 75, acid blue 83, acid blue 91, acid blue 97, acid blue 93, acid blue 93:1, acid blue 97, acid blue 100, acid blue 103, acid blue 104, acid blue 108, acid blue 109, acid blue 1 10, and acid blue 213. On dissolution granules with non-shading dyes provide an attractive colour to the wash liquor.

[0119] The granular laundry detergent composition comprises:

a) dye granules according to the present invention in an amount such as to provide 0.0005 to 0.5 wt % of dye as based on the total weight of the granular laundry detergent composition,
b) 2 to 70 wt % surfactant, based on total weight of the granular laundry detergent composition,
c) 5 to 50 wt % builder, based on total weight of the granular laundry detergent composition,
d) 0.05 to 50 wt % water-soluble solid carrier based on total weight of the granular laundry detergent composition,

wherein the sum of ingredients a), b), c) and d) is at least 80 wt.%, based on the total weight of the composition.

[0120] Preferably, the dye containing granule is contained in the laundry detergent composition in an amount such that the dye level from the granule in the total detergent composition is between 0.001 to 0.025 wt.%, more preferably between 0.0015 to 0.025 wt.%.

[0121] Preferably, the detergent granules comprise at most 10 wt % of the total amount of dye and at most 25 wt % of the total amount of alkyl ether carboxylate surfactant.

[0122] It is also disclosed a process to prepare a dye granule comprising the step of combining a shading dye with a binder, solid carrier and an alkyl ether carboxylate surfactant alkyl ether carboxylate surfactant, wherein the alkyl ether carboxylate surfactant is of the following structure:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

wherein R^1 is selected from saturated and mono-unsaturated C_{10} to C_{18} linear or branched alkyl chains, wherein n is from 5 to 40.

[0123] The description of the components of the dye granule apply *mutatis mutandis* to the components used in the method for preparing a dye granule as defined herein.

[0124] Preferably, the shading dye is premixed with the alkyl ether carboxylate prior to combining with the binder and solid carrier. Typically, the alkyl ether carboxylate is heated to at least 5 °C, preferably at least 10 °C, more preferably at least 20 °C above its melting point prior to mixing with the shading dye.

[0125] Preferably, the melting point of the alkyl ether carboxylate is in the range of from 313K to 353K.

[0126] In a third aspect, the present invention provides a process to provide a granular laundry detergent composition comprising the step of mixing the dye granules according to the present invention with other detergent granules to provide a granular laundry detergent composition as defined herein. Preferably the dye granules are dry mixed with the other detergent granules.

[0127] The description of the components of the granular laundry detergent composition apply *mutatis mutandis* to the components used in the method for preparing a granular laundry detergent composition as defined herein.

[0128] In a fourth 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 granular laundry detergent composition as defined herein, the aqueous solution comprising from 1 ppb to 5 ppm of shading dye and from 0.2 g/L to 3 g/L of surfactant; and
(ii) rinsing and drying the textile.

[0129] In an embodiment, the maximum temperature of the aqueous solution in step (i) is 50 degrees Celsius, preferably 45 degrees Celsius and more preferably 40 degrees Celsius.

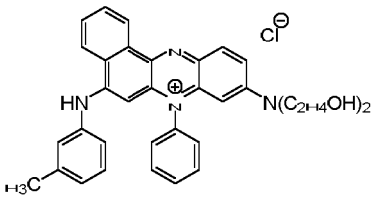
[0130] Preferably, the maximum temperature of the aqueous solution in step (i) is between 15 and 40 degrees Celsius, more preferably between 20 and 35 degrees Celsius.

[0131] In a preferred embodiment, the temperature of the aqueous solution used for rinsing does not exceed the temperature of step (i).

Examples

Example 1 granulation

[0132] Alkyl ether carboxylate (or the Na salt of cetearyl with 20 moles of ethoxylation) was melted at 60°C and 0.3wt% of shading dye mixed into the alkyl ether carboxylate. The shading dye used was a cationic azine dye of the following structure:



[0133] Sodium Carbonate was added to a food processor using the knife blade for mixing. The liquid alkyl ether carboxylate and dye mix was then slowly added till the mixture just started to form a dough. The binder, Sokalan CP5, (Maleic acid-acrylic acid copolymer, sodium salt) was then added and granules resulted. These granules were placed in an oven at 50°C to dry and a sieve fraction of 0.5 to 1.8mm taken and used for further experiments.

[0134] The composition of the alkyl ether carboxylate granule was

	1	A	B
Sodium Carbonate	68 wt%	69.9wt%	68 wt%
alkyl ether carboxylate	23 wt%	-	28 wt%
Sokalan CP5	8.93wt%	7.33wt%	-
T48 shading dye	0.07wt%	0.07wt%	0.07wt%
Non-ionic surfactant: fatty alcohol non-ionic (cetearyl with 20 moles of ethoxylation).	-	22.7wt%	-

[0135] Formulations A and B are not according to the invention.

[0136] The formulation in the absence of binder (Sokalan CP5) did not form granules. A complete match of the levels of the different components is not possible due to the different properties of the fatty alcohol non-ionic and the alkyl ether carboxylate.

Example 2 Dye delivery

[0137] A base laundry detergent powder was created of the following formulation

Ingredient	Weight%
Linear alkyl benzene sulfonate	14.5
Sodium carbonate	20.0
Sodium sulphate	50.0
Sodium silicate	6.0
Zeolite	2.5
Blue and red salt speckles	1.8
Parfum	0.3
Sodium carboxymethylcellulose	0.1
Sokalan CP5	0.1
Minors (inc. moisture)	To 100%

[0138] The granules of example 1 were added to the base laundry powder so that it contained 0.01wt % of the shading dye.

[0139] 4g/L of this detergent powder was then used to wash 3 pieces of 65:35 white woven polycotton at a Liquor to cloth ratio of 30:1 in 26 ° French hard water for 30 minutes at 20 °C. Washes took place in a plastic bottle placed on an orbital shaker at 150rpm. Following the wash the clothes were removed, rinsed, dried, the colour of the cloth measured using a reflectometer and expressed as the CIE Lab values. The degree of dye deposition was measured as Δb, where:

$$\Delta b = b(\text{control powder no shading dye}) - b\ (\text{powder with shading dye})$$

[0140] The results are given in the table below, alongside the 95% confidence limits calculated from the 3 clothes.

Dye granule	Δb	95%
1	1.9	0.1
A	0.0	0.1

[0141] The alkyl ether carboxylate granule effectively delivers the shading dye, as evidenced by a Δb =1.9, the equivalent non-ionic granule does not.

Example 3 Dye Spotting on fabric

[0142] The alkyl ether granules of example 1 were remade but with different levels of the binder CP5. In these granules 0.2wt % of shading dye was mixed with the alkyl ether carboxylate. The granules were added to the base laundry detergent powder to give 0.005wt % dye. 3g of the powder sprinkled onto a 10 by 10cm square of polyester fabric than had been place on wet terry towling. The fabric square and powder was left for 2 hours at 20 °C, rinsed, dried and then number of visible spots counted. The experiment was repeated with cotton, polycotton and nylon-elastane fabrics and the total number of spots across the 4 fabrics calculated as the numerical sum. The granule composition and the spotting results are given in the table below:

Granule	No of spots
9.9 wt% Sokalan CP5 69.3 wt% Sodium Carbonate 20.8 wt% alkyl ether carboxylate/shading dye mix	13
(0.042wt% shading dye in granule)	
9.9 wt% Sokalan CP5 66.5 wt% Sodium Carbonate 23.6 wt% alkyl ether carboxylate/shading dye mix (0.047wt%shading dye in granule)	6
6.2 wt% Sokalan CP5 71.9 wt% Sodium Carbonate 21.9 wt% alkyl ether carboxylate/shading dye mix (0.044wt% shading dye in granule)	12
4.5 wt% Sokalan CP5 64.9 wt% Sodium Carbonate 30.7 wt% alkyl ether carboxylate/shading dye mix (0.061wt% shading dye in granule)	2
1.7 wt% Sokalan CP5 64.5 wt% Sodium Carbonate 33.8 wt% alkyl ether carboxylate/shading dye mix (0.068wt% shading dye in granule)	0

Claims

1. A detergent dye granule comprising:

(i) from 0.005 to 5 wt % of a blue or violet shading dye;
(ii) from 5 to 60 wt % of alkyl ether carboxylate surfactant, wherein the alkyl ether carboxylate surfactant is of the following structure:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

wherein R^1 is selected from saturated and mono-unsaturated C_{10} to C_{18} linear or branched alkyl chains, wherein n is from 5 to 40, and,
wherein the alkyl ether carboxylate surfactant is a solid at 293 degrees Kelvin at 1 bar pressure;

(iii) from 20 to 90 wt % of a solid carrier;
(iv) from 0.5 to 10 wt % of a binder.

2. A dye granule according to claim 1, wherein R^1 is selected from linear, saturated C_{12}, C_{14}, C_{16} and C_{18} alkyl chains and preferably R^1 is selected from C_{16} and C_{18} alkyl chains.

3. A dye granule according to claim 1 or claim 2, wherein the n of the alkyl ether carboxylate surfactant is from 7 to 35, preferably from 10 to 25.

4. A dye granule according to any one of claims 1 to 3, wherein the amount of dye in the dye granule is from 0.01 to 0.1 wt %.

5. A dye granule according to any one of claims 1 to 4, wherein the dye is a shading dye with a chromophore selected from azo, azine, anthraquinone, phthalocyanine, triphenylmethane dyes and combinations thereof, preferably selected from azo, azine dyes and combinations thereof.

6. A dye granule according to any one of claims 1 to 5, wherein the solid carrier comprises one or more of sodium carbonate, clays and zeolites, more preferably comprises sodium carbonate and even more preferably comprises

at least 50 wt % of sodium carbonate based on the total weight of the solid carrier as comprised by the dye granule.

7. A dye granule according to any one of claims 1 to 6, wherein the binder has an average molecular mass (M_w) from 2000 to 100000 Dalton and preferably the dye granule comprises 1 to 5 wt % binder.

8. A dye granule according to any one of claims 1 to 7, wherein the binder is a copolymer, preferably comprising acrylic acid moieties and more preferably is copolymer of maleic acid and acrylic acid.

9. A dye granule according to any one of claims 1 to 8, wherein the dye granule has a size of from 180 to 1000 microns as based on the ability to pass through a graded sieve.

10. A dye granule according to any one of claims 1 to 9, wherein the total amount of alkyl ether carboxylate surfactant is from 10 to 40 wt % and wherein the total amount of dye is from 0.001 to 0.1 wt %.

11. A granular laundry detergent composition comprising:

a) dye granules according to any one of claims 1 to 10 in an amount such as to provide 0.0005 to 0.5 wt % of dye as based on the total weight of the granular laundry detergent composition,
b) 2 to 70 wt % surfactant, based on total weight of the granular laundry detergent composition,
c) 5 to 50 wt % builder, based on total weight of the granular laundry detergent composition,
d) 0.05 to 50 wt % water-soluble solid carrier based on total weight of the granular laundry detergent composition,

wherein the sum of ingredients a), b), c) and d) is at least 80 wt.%, based on the total weight of the composition.

12. A process to provide a granular laundry detergent composition comprising the step of mixing the dye granules according to any one of claims 1 to 10 with detergent granules to provide a granular laundry detergent composition.

13. A process according to claim 12, wherein the detergent granules comprise at most 10 wt % of the total amount of dye and at most 25 wt % of the total amount of alkyl ether carboxylate surfactant.

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

(i) treating a textile with an aqueous solution of the granular laundry detergent composition as claimed in claim 11, the aqueous solution comprising from 1 ppb to 5 ppm of shading dye and from 0.2 g/L to 3 g/L of surfactant; and
(ii) rinsing and drying the textile.

15. A method of treating a textile according to claim 14, wherein the maximum temperature of the aqueous solution at step (i) is 50 degrees Celsius, preferably 45 degrees Celsius and more preferably 40 degrees Celsius.

Patentansprüche

1. Reinigungsmittelfarbstoffgranulat, umfassend:

(i) 0,005 bis 5 Gew.-% eines blauen oder violetten Nunacierfarbstoffs;
(ii) 5 bis 60 Gew.-% Alkylethercarboxylat-Tensid, wobei das Alkylethercarboxylat-Tensid die folgende Struktur aufweist:

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

wobei R^1 ausgewählt ist aus gesättigten und einfach ungesättigten linearen oder verzweigten C_{10}- bis C_{18}-Alkylketten, wobei n 5 bis 40 ist,
und wobei das Alkylethercarboxylat-Tensid bei 293 Grad Kelvin bei 1 bar Druck ein Feststoff ist;

(iii) 20 bis 90 Gew.-% eines festen Trägers;
(iv) 0,5 bis 10 Gew.-% eines Bindemittels.

2. Farbstoffgranulat nach Anspruch 1, wobei R^1 ausgewählt ist aus linearen, gesättigten C_{12}-, C_{14}-, C_{16}- und C_{18}-Alkylketten und wobei R^1 bevorzugt ausgewählt ist aus C_{16}- und C_{18}-Alkylketten.

3. Farbstoffgranulat nach Anspruch 1 oder Anspruch 2, wobei das n des Alkylethercarboxylat-Tensids 7 bis 35, bevorzugt 10 bis 25, beträgt.

4. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 3, wobei die Farbstoffmenge im Farbstoffgranulat 0,01 bis 0,1 Gew.-% beträgt.

5. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 4, wobei der Farbstoff ein Nuancierfarbstoff mit einem Chromophor, ausgewählt aus Azo-, Azin-, Anthrachinon-, Phthalocyanin-, Triphenylmethan-Farbstoffen und Kombinationen davon, bevorzugt ausgewählt aus Azo-, Azin-Farbstoffen und Kombinationen davon.

6. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 5, wobei der feste Träger eines oder mehrere von Natriumcarbonat, Tonen und Zeolithen umfasst, bevorzugter Natriumcarbonat umfasst und noch bevorzugter mindestens 50 Gew.-% Natriumcarbonat, bezogen auf die Gesamtgewicht des festen Trägers, wie vom Farbstoffgranulat umfasst, umfasst.

7. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 6, wobei das Bindemittel eine durchschnittliche Molekularmasse (M_w) von 2000 bis 100000 Dalton aufweist und wobei das Farbstoffgranulat bevorzugt 1 bis 5 Gew.-% Bindemittel umfasst.

8. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 7, wobei das Bindemittel ein Copolymer ist, das bevorzugt Acrylsäure-Einheiten umfasst, und bevorzugter ein Copolymer von Maleinsäure und Acrylsäure ist.

9. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 8, wobei das Farbstoffgranulat eine Größe von 180 bis 1000 Mikron aufweist, bezogen auf die Fähigkeit, ein abgestuftes Sieb zu passieren.

10. Farbstoffgranulat nach irgendeinem der Ansprüche 1 bis 9, wobei die Gesamtmenge an Alkylethercarboxylat-Tensid 10 bis 40 Gew.-% beträgt und wobei die Gesamtmenge an Farbstoff 0,001 bis 0,1 Gew.-% beträgt.

11. Granuläre Waschmittelzusammensetzung, umfassend:

a) Farbstoffgranalien nach irgendeinem der Ansprüche 1 bis 10 in einer solchen Menge, dass 0,0005 bis 0,5 Gew.-% Farbstoff, bezogen auf das Gesamtgewicht der granulären Waschmittelzusammensetzung, bereitgestellt werden,
b) 2 bis 70 Gew.-% Tensid, bezogen auf das Gesamtgewicht der granulären Waschmittelzusammensetzung,
c) 5 bis 50 Gew.-% Builder, bezogen auf das Gesamtgewicht der granulären Waschmittelzusammensetzung,
d) 0,05 bis 50 Gew.-% wasserlöslichen festen Träger, bezogen auf das Gesamtgewicht der granulären Waschmittelzusammensetzung,

wobei die Summe der Inhaltsstoffe a), b), c) und d) mindestens 80 Gew.% beträgt, bezogen auf das Gesamtgewicht der Zusammensetzung.

12. Verfahren zur Bereitstellung einer granulären Waschmittelzusammensetzung, umfassend den Schritt des Mischens der Farbstoffgranalien nach irgendeinem der Ansprüche 1 bis 10 mit Reinigungsmittelgranalien, um eine granuläre Waschmittelzusammensetzung bereitzustellen.

13. Verfahren nach Anspruch 12, wobei die Reinigungsmittelgranalien höchstens 10 Gew.-% der Gesamtmenge Farbstoff und höchstens 25 Gew.-% der Gesamtmenge Alkylethercarboxylat-Tensid umfassen.

14. Verfahren zum Behandeln eines Textils, wobei das Verfahren die folgenden Schritte umfasst:

(i) Behandeln eines Textils mit einer wässrigen Lösung der granulären Waschmittelzusammensetzung wie in Anspruch 11 beansprucht, wobei die wässrige Lösung 1 ppb bis 5 ppm Nuancierfarbstoff und 0,2 g/L bis 3 g/L Tensid umfasst; und
(ii) Spülen und Trocknen des Textils.

15. Verfahren zum Behandeln eines Textils nach Anspruch 14, wobei die maximale Temperatur der wässrigen Lösung in Schritt (i) 50 Grad Celsius, bevorzugt 45 Grad Celsius und bevorzugter 40 Grad Celsius beträgt.

Revendications

1. Granulé de colorant de détergent comprenant :

(i) de 0,005 à 5 % en masse d'un colorant de nuançage bleu ou violet ;
(ii) de 5 à 60 % en masse de tensioactif de carboxylate d'alkyléther, où le tensioactif de carboxylate d'alkyléther est de la structure suivante :

$$R^1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH$$

où R^1 est choisi parmi des chaînes alkyle linéaires ou ramifiées en C_{10} à C_{18} saturées et mono-insaturées, où n est de 5 à 40, et, où le tensioactif de carboxylate d'alkyléther est un solide à 293 degrés Kelvin à une pression de 1 bar ;

(iii) de 20 à 90 % en masse d'un support solide ;
(iv) de 0,5 à 10 % en masse d'un liant.

2. Granulé de colorant selon la revendication 1, où R^1 est choisi parmi des chaînes alkyle en C_{12}, C_{14}, C_{16} et C_{18} saturées, linéaires et R^1 est de préférence choisi parmi des chaînes alkyle en C_{16} et C_{18}.

3. Granulé de colorant selon la revendication 1 ou revendication 2, où le n du tensioactif de carboxylate d'alkyléther est de 7 à 35, de préférence de 10 à 25.

4. Granulé de colorant selon l'une quelconque des revendications 1 à 3, où la quantité de colorant dans le granulé de colorant est de 0,01 à 0,1 % en masse.

5. Granulé de colorant selon l'une quelconque des revendications 1 à 4, où le colorant est un colorant de nuançage avec un chromophore choisi parmi des colorants azo, azine, anthraquinone, phtalocyanine, triphénylméthane et combinaisons de ceux-ci, de préférence choisi parmi des colorants azo, azine et combinaisons de ceux-ci.

6. Granulé de colorant selon l'une quelconque des revendications 1 à 5, où le support solide comprend un ou plusieurs de carbonate de sodium, argiles et zéolites, comprend encore mieux du carbonate de sodium et comprend bien mieux encore au moins 50 % en masse de carbonate de sodium sur la base de la masse totale du support solide comme compris par le granulé de colorant.

7. Granulé de colorant selon l'une quelconque des revendications 1 à 6, où le liant présente une masse moléculaire moyenne (M_w) de 2 000 à 100 000 Dalton et le granulé de colorant comprend de préférence de 1 à 5 % en masse de liant.

8. Granulé de colorant selon l'une quelconque des revendications 1 à 7, où le liant est un copolymère, comprenant de préférence des moitiés acide acrylique et est encore mieux un copolymère d'acide maléique et d'acide acrylique.

9. Granulé de colorant selon l'une quelconque des revendications 1 à 8, où le granulé de colorant présente une dimension de 180 à 1 000 microns sur la base de l'aptitude à passer à travers un tamis calibré.

10. Granulé de colorant selon l'une quelconque des revendications 1 à 9, où la quantité totale de tensioactif de carboxylate d'alkyléther est de 10 à 40 % en masse et où la quantité totale de colorant est de 0,001 à 0,1 % en masse.

11. Composition de détergent de lessive granulaire comprenant :

a) des granulés de colorant selon l'une quelconque des revendications 1 à 10 dans une quantité telle à fournir de 0,0005 à 0,5 % en masse de colorant sur la base de la masse totale de la composition de détergent de lessive granulaire,

b) 2 à 70 % en masse de tensioactif, sur la base de la masse totale de la composition de détergent de lessive granulaire,
c) de 5 à 50 % en masse d'adjuvant, sur la base de la masse totale de la composition de détergent de lessive granulaire,
d) de 0,05 à 50 % en masse de support solide soluble dans l'eau sur la base de la masse totale de la composition de détergent de lessive granulaire,

où la somme des ingrédients a), b), c) et d) est d'au moins 80 % en masse, sur la base de la masse totale de la composition.

12. Procédé pour fournir une composition de détergent de lessive granulaire comprenant l'étape de mélange des granulés de colorant selon l'une quelconque des revendications 1 à 10 avec des granulés de détergent pour fournir une composition de détergent de lessive granulaire.

13. Procédé selon la revendication 12, où les granulés de détergent comprennent au plus 10 % en masse de la quantité totale de colorant et au plus 25 % en masse de la quantité totale de tensioactif de carboxylate d'alkyl éther.

14. Procédé de traitement d'un textile, le procédé comprenant les étapes de :

(i) traitement d'un textile avec une solution aqueuse de la composition de détergent de lessive granulaire selon la revendication 11, la solution aqueuse comprenant de 1 ppb à 5 ppm de colorant de nuançage et de 0,2 g/L à 3 g/L de tensioactif ; et
(ii) rinçage et séchage du textile.

15. Procédé de traitement d'un textile selon la revendication 14, où la température maximum de la solution aqueuse dans l'étape (i) est de 50 degrés Celsius, de préférence 45 degrés Celsius et encore mieux 40 degrés Celsius.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2005003274 A **[0003] [0041]**
- WO 2005003275 A **[0004]**
- EP 1814974 A **[0005]**
- EP 3081625 A1 **[0006]**
- DE 3135946 **[0034]**
- DE 2816127 **[0034]**
- EP 0304763 A **[0034]**
- WO 2006032327 A, Unilever **[0041]**
- WO 2006032397 A, Unilever **[0041]**
- WO 2006045275 A, Unilever **[0041]**
- WO 2006027086 A, Unilever **[0041]**
- WO 2008017570 A, Unilever **[0041]**
- WO 2008141880 A, Unilever **[0041]**
- WO 2009132870 A, Unilever **[0041]**
- WO 2009141173 A, Unilever **[0041]**
- WO 2010099997 A, Unilever **[0041]**
- WO 2010102861 A, Unilever **[0041]**
- WO 2010148624 A, Unilever **[0041]**
- WO 2008087497 P, P&G **[0041]**
- WO 2011011799 A, P&G **[0041]**
- WO 2012054820 P, P&G **[0041]**
- WO 2013142495 P, P&G **[0041]**
- WO 2013151970 P, P&G **[0041]**
- WO 2013142495 A **[0044]**
- WO 2008087497 A **[0044]**
- WO 201254058 A **[0047]**
- WO 2010151906 A **[0047]**
- EP 0384070 A **[0057] [0101]**
- WO 9219709 A **[0111]**
- WO 9219708 A **[0111]**

Non-patent literature cited in the description

- Anionic Surfactants Organic Chemistry. Marcel Dekker, 1996 **[0029]**
- Industrial Dyes: Chemistry, Properties, Applications. Wiley-VCH, 2003 **[0036]**
- *CHEMICAL ABSTRACTS,* 72749-80-5 **[0051]**
- International Buyers Guide. CFTA Publications, 1992 **[0112]**
- Chemicals Buyers Directory 80th Annual Edition. Schnell Publishing Co, 1993 **[0112]**