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(54) **REDUCED SPOTTING GRANULES**

GRANULAT MIT REDUZIERTER FLECKENBILDUNG

GRANULÉS À TACHAGE RÉDUIT

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Description

FIELD OF INVENTION

[0001] The present invention relates to the delivery of shading dyes to fabrics.

BACKGROUND OF THE INVENTION

[0002] WO 2005/003274, to Unilever, discloses that shading dyes are added to laundry detergents to increase whiteness. One drawback with these powders is that under certain conditions localised spotting occurs on fabric treated with the detergent powder. WO 2006 /020162 and WO 2006/053598 disclose laundry compositions comprising granules containing a dye.

SUMMARY OF THE INVENTION

[0003] A shading dye granule present in a laundry detergent formulation is susceptible to providing unwanted spotting of fabrics.

[0004] This problem is ameliorated by having an anti-dye transfer agent present in the shading dye granule.

[0005] In one aspect the present invention provides a shading dye granule comprising:

(i) from 0.001 to 95 wt% of a shading dye;

(ii) from 0.1 to 99.999 wt% of a dye transfer polymer selected from: polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles;

(iii) from 0 to 80 wt% of a non-ionic surfactant;

(iv) from 0 to 20 wt % of an anionic or cationic surfactant;

(v) from 0 to 99.5 wt% of a carrier; and,

(vi) from 0 to 50 wt% of a binder, wherein the weight ratio of the dye transfer polymer:the charged surfactant is from 1:0 to 1:1, wherein the shading dye is blue or violet.

[0006] In another aspect the present invention provides a granular laundry detergent composition comprising:

1. (a) from 0.00005 to 10 wt% of visually distinct laundry detergent granule as defined in any one of claims 1 to 3;
2. (b) from 99.99995 % to 90 wt % of a granular base powder, wherein the granular laundry detergent composition comprises 10 to 50 wt % of an anionic surfactant.

[0007] The surfactant that comes from the base powder may be a mixture of different types of surfactants but the total concentration of anionic surfactant in the granulate laundry detergent is in the range from 10 to 50 wt %. The surfactant that comes from the base powder is preferably greater than 70% anionic surfactant.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Preferably, the shading dye granule is visually distinct (VD) from a granular background powder in order to provide a visual cue.

[0009] The shading dye granule is for adding to a base powder (main detergent powder).

[0010] Preferably the shading dye granule does not contain an anionic surfactant. When the shading dye granule is admixed with the base powder, which must contain an anionic surfactant, there may be some migration of anionic surfactant to the shading dye granule.

[0011] The ratio of the dye transfer polymer:the charged surfactant prevents spotting whilst permitting dye deposition of substantive dyes from the wash liquors.

Shading Dye

[0012] The shading dye is blue or violet. It is preferred that the shading dye(s) have a peak absorption wavelength of from 550nm to 650nm, preferably from 570nm to 630nm. A combination of dyes 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 provided for example by mixing a red and green-blue dye to yield a blue or violet shade.

[0013] Dyes are coloured organic molecules which are soluble in aqueous media that contain surfactants. Dyes are described in 'Industrial Dyes', Wiley VCH 2002, K.Hunger (editor).

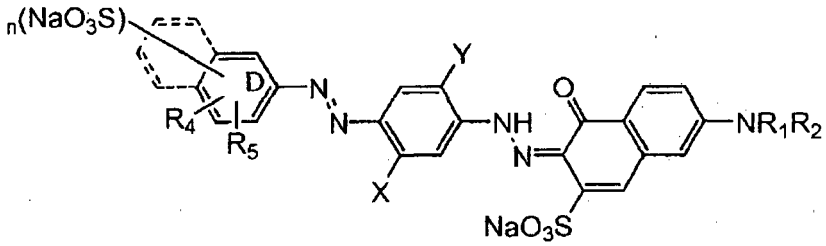
[0014] Dyes are listed in the Color Index International published by Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. Dyes are preferably selected from the classes of basic, acid and direct dyes.

Direct dyes

[0015] Direct violet and direct blue dyes are preferred. Preferably the dyes are *bis*-azo or *tris*-azo dyes. The carcinogenic benzidene based dyes are not preferred.

[0016] Bis-azo copper containing dyes such as direct violet 66 may be used.

[0017] Most preferably the direct dye is a direct violet of the following structures:



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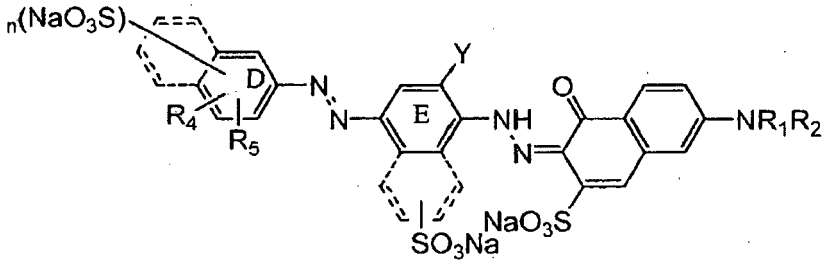


wherein:

ring D and E may be independently naphthyl or phenyl as shown;

R_1 is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;

R_2 is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;

R_3 and R_4 are independently selected from: hydrogen and C1-C4-alkyl, preferably hydrogen or methyl;

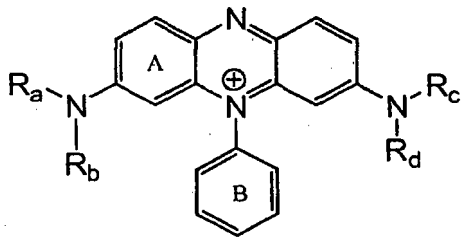
X and Y are independently selected from: hydrogen, C1-C4-alkyl and C1-C4-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

[0018] Preferred dyes 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, and direct violet 99.

Acid dyes

[0019] Cotton substantive acid dyes give benefits to cotton containing garments. Preferred acid dyes are:

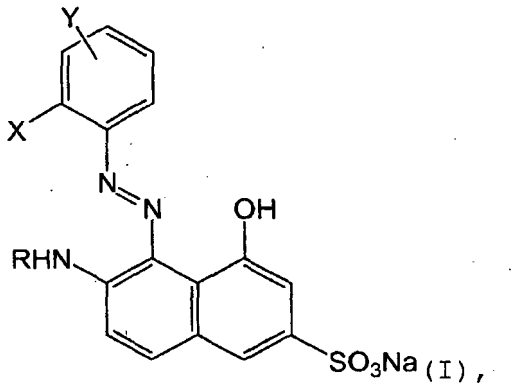
(i) azine dyes, wherein the dye is of the following core structure:



wherein R_a, R_b, R_c and R_d are selected from: H, an branched or linear C1 to C7-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.

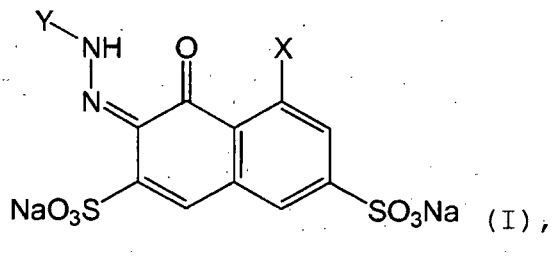
[0020] Preferred azine dyes are: acid violet 50 and acid blue 98.

(ii)DANSA dyes of the following core structure:-



wherein R is selected from: H; a branched or linear C1 to C7-alkyl chain; COR_1 wherein R_1 is a branched or linear C1 to C7-alkyl chain; and, a $-SO_2Ar$ group, wherein Ar is phenyl or methyl substituted phenyl group;
Y is selected from: NO_2; CN; I; Br; Cl; F; H; $OCOR_2$; $NHCOR_3$; R_4; R_5O; and, NR_6R_7, wherein R_2, R_3, R_4, and R_5 are independently selected from a branched or linear C1 to C7-alkyl chain and R_6 and R_7 are independently selected from: H; a branched or linear C1 to C7-alkyl chain that is unsubstituted or is substituted by groups independently selected from: OH; Cl; F; $OCOCH_3$; $COOCH_3$; $OCOC_2H_5$; and, $COOC_2H_5$; and,
X is selected from: H; SO_2N (R_8) $COCH_3$; SO_2N (R_8) -Ar; SO_2N (R_8) -Ar; and SO_2-Ar, wherein Ar is an aromatic group and R_8 is H, CH_3 or C_2H_5,
with the proviso that the Y ring does not carry a negatively charged group or salt thereof.

(iii) MAAD dyes the following core structure:



(I),

wherein:

X is selected from -OH, CH_3O-, CH_3CH_2O-, and -NR_1R_2, wherein R_1 and R_2 are independently selected from: H, a branched or linear -C1-C7-alkyl chain, -COR_3, wherein R_3 is a branched or linear -C1-C7-alkyl chain, and a -SO_2Ar group, wherein Ar is a phenyl or methyl substituted phenyl group;

Y is an aromatic group selected from: phenyl and napthyl, and Y may be substituted by R_4O-, R_4CONH-, R_4-, C1, Br, I, F, NO_2, and -NR_4R_5, wherein R_4 and R_4 are independently selected from: H, a branched or linear -C1-C7-alkyl chain or a phenyl group.

[0021] Other preferred acid dyes are acid violet 17, acid black 1, acid red 17 and acid blue 29.
[0022] Preferably the acid dye is present at 0.001 wt% to 0.006 wt% of the formulation.

Hydrophobic dyes

[0023] The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, napthoquinone, anthraquinone and mono-azo or di-azo dye chromophores. Hydrophobic dyes are dyes which do not contain any charged water solubilising group. Hydrophobic dyes may be selected from the groups of disperse and solvent dyes. Blue and violet anthraquinone and mono-azo dye are preferred.
[0024] Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.
[0025] Preferably the hydrophobic dye is present at 0.0005 wt% to 0.004 wt% of the formulation.

Basic dyes

[0026] Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in composition that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International.
[0027] Preferred examples include triarylmethane basic dyes, azo basic dye, methane basic dye, anthraquinone basic dyes, basic blue 16, basic blue 65, basic blue 66, basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141 and thiazolium dyes.

Reactive dyes

[0028] Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton.
[0029] Preferably the reactive group is hydrolysed or reactive group of the dyes has been reacted with an organic species such as a polymer, so as to the link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.
[0030] Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue, reactive blue 96.

ANTI-DYE TRANSFER POLYMER

[0031] The shading dye granule according to the present invention comprising from 0.1 to 99.999 wt%, preferably from 0.5 to 18 wt%, more preferably from 0.5 to 2 wt% by weight of an anti-dye transfer polymer (ADTP) selected from: polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers,

polyvinyloxazolidones and polyvinylimidazoles.

[0032] The anti-dye transfer polymers (ADTPs) discussed above are well known in the art and commercially available, reference in made to US6833336 and references found therein.

[0033] The preferred anti-dye transfer polymer is PVP.

CARRIERS

[0034] The shading dye granule preferably contains a carrier preferred examples of carrier are bentonite, sodium chloride, zeolite, and sodium sulphate.

BINDER .

[0035] A binder is a material used to bind together two or more other materials in mixtures. Its two principal properties are adhesion and cohesion. The binder is other than a non-ionic surfactant. Binders are standard in the art of laundry detergent granules, examples of which are: Sokalan® CP45, Sokalan® CP5, ethylene glycol, surfactants, anionic surfactants, polyethylene glycol, polyvinyl pyrrolidone, polyacrylates, citric acid and mixtures thereof.

[0036] Preferably, the binder has a melting point above 30 °C.

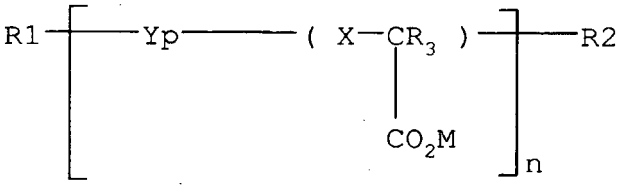
[0037] Preferably the binder is selected from the group consisting of a polyacrylate, polyethylene glycol, and polyacrylate/maleate copolymer.

[0038] 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.

[0039] The binder is preferably an acidic polymer. By an acidic polymer, it is meant herein that a 1% solution of said polymers has a pH of less than 7, preferably less than 5.5.

[0040] Suitable polymers for use herein have a molecular weight in the range of from 1000 to 280,000, preferably from 1500 to 150,000.

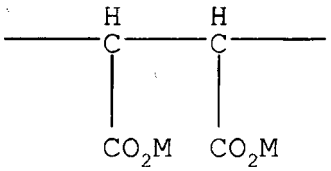
[0041] Suitable polymers which meet the above criteria and are therefore particularly useful in the present invention, include those having the following empirical formula I



(I)

wherein X is 0 or CH2; Y is a comonomer or comonomer mixture; R1 and R2 are bleach-stable polymer-end groups; R3 is H, OH or C1-4 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. The proportion of M being H in such polymers is preferably such as to ensure that the polymer is sufficiently acidic to meet the acidity criteria as hereinbefore defined.

[0042] Polymers according to formula I are known in the field of laundry detergents, and are typically used as chelating agents, as for instance in GB-A-1,597,756. 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, R3 is H or C1-4 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)

[0043] Such polymers are available from BASF under the trade name Sokalan® CP5 (neutralised form) and Sokajan® CP45 (acidic form).

[0044] Binder materials are commercially readily available. The water soluble polymers of the Sokalan® type sold by BASF® are preferred. 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.

Granules

[0045] The granules are preferably of the 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.

EXAMPLES

Example 1

[0046] The dye solvent violet 13 was mixed in non-ionic surfactant (7EO) to form a 0.5 wt% solution. To this was added the [nitrolotris(2,1-ethanediyloxy)] tris[propanol] salt of direct violet 9, DV9, (Ex Ciba Speciality Chemicals). The non-ionic was added to the carrier in a high shear mixer. Following this the binder, Sokalam CP5 (ex BASF) was added. Where appropriate polyvinylpyrrolidone, PVP, was added to the starting non-ionic solution.

[0047] The resultant granules were dried in an oven at 353K finally sieved to give granules in the size range 500 to 1400 microns.

[0048] The granules had the following composition. All percentages refer to dry weight%.

Granule	bentonite	7EO	DV9	PVP	CP5
1*	69.93	20.56	0.20	0.00	9.41
2	69.71	20.68	0.20	0.21	9.51
3	69.41	20.65	0.08	0.21	9.83
4*	69.38	20.93	0.08	0.00	9.58
* comparative examples					

Example 2

[0049] The granules of example 1 were separately added to a detergent powder (20% linear alkyl benzene sulphonate, 30% sodium carbonate, 40% sodium chloride, remainder minors including fluorescer and moisture), at 2 wt%. 10 g of the powder was sprinkled onto a 25 by 25 cm piece of white cotton sheeting, immersed in 1 cm of demineralised water. The cloth was soaked for 90 minutes, then thoroughly rinsed and dried. Each experiment was repeated four times. Cloths soaked with Granule 1 and 2 were compared, and Granule 3 and 4 were compared, as they had equivalent levels of DV9. The eight clothes from each comparison were ranked in terms of the degree of dye staining/spotting. The cloth with the least staining/spotting received a score of 1, that with the second lowest level of staining a score of 2, and so on, so that the most stained/spotted cloth had a score of 8.

[0050] The total score across the 4 cloths for each granule were then compared:

Granules containing 0.20 wt% DV9

Granule 1	(no PVP)	total score = 24
Granule 2	(PVP)	total score = 12

Granules containing 0.08 wt% DV9

Granule 3	(PVP)	total score = 11
Granule 4	(no PVP)	total score = 25

[0051] The granules containing the dye transfer inhibition polymer show reduced levels of spotting/staining.

Example 3

[0052] The granules of example 1 were added to the base washing powder of example 2, such that when the washing powder was dissolved at 2g/L the wash liquor contained 200ppb of SV13.

[0053] To the wash liquor was added pieces of woven cotton and knitted nylon-elastane fabric such the liquor:cloth was 100:1. The liquor was agitated for 60 minutes at 293K, the clothes rinsed twice and the colour change measured by reflectometry and expressed as CIE L*a*b* values.

[0054] The results are given below expressed as the ΔE values relative to the control washed without dye

[0055] All granules gave good deposition of the dyes to the fabrics evidenced by the ΔE values.

Granule	Cotton ΔE	Nylon-elastane ΔE
1	4.2	4.0
2	3.3	4.2
3	1.4	4.2
4	1.3	4.2

Example 4

Exemplary Base Powder Formulation A, B, C and D

[0056]

Formulation	**A**	**B**	**C**	**D**
NaLAS	15	20	10	14
NI(7EO)	-	-	-	10
Na tripolyphosphate	-	15	-	-
Soap	-	-	-	2
Zeolite A24	7	-	-	17
Sodium silicate	5	4	5	1
Sodium carbonate	25	20	30	20
Sodium sulphate	40	33	40	22
Carboxymethylcellulose	0.2	0.3	-	0.5
Sodium chloride	-	-	-	5
Lipase	0.005	0.01	-	0.005
Protease	0.005	0.01	-	0.005
Amylase	0.001	0.003	-	-
Cellulase	-	0.003	-	-
Fluorescer	0.1	0.15	0.05	0.3
Water/impurities/minors	remainder	remainder	remainder	remainder

[0057] Granule 2 and granule 3 were individually added to exemplary powder formulations A, B, C and D at 1 wt % to generate final formulations for use in washing and shading textiles.

Claims

1. A shading dye granule comprising:

   (i) from 0.001 to 95 wt% of a shading dye;
   (ii) from 0.1 to 99.999 wt% of a dye transfer polymer selected from: polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles;
   (iii) from 0 to 80 wt% of a non-ionic surfactant;
   (iv) from 0 to 20 wt % of an anionic or cationic surfactant;
   (v) from 0 to 99.5 wt% of a carrier; and,
   (vi) from 0 to 50 wt% of a binder, wherein the weight ratio of the dye transfer polymer:the charged surfactant is from 1:0 to 1:1, wherein the shading dye is blue or violet.

2. A shading dye granule as defined in claim 1, wherein the charged surfactant is an anionic surfactant.

3. A shading dye granule according to any preceding claim, wherein the shading dye is selected from: acid dyes, basic dyes and direct dyes.

4. A granular laundry detergent composition comprising:

   (a) from 0.00005 to 10 wt% of visually distinct laundry detergent granule as defined in any one of claims 1 to 3;
   (b) from 99.99995 % to 90 wt % of a granular base powder, wherein the granular laundry detergent composition comprises 10 to 50 wt % of an anionic surfactant.

Patentansprüche

1. Nuancierfarbstoffgranulat, das Folgendes aufweist:

   (i) 0,001 bis 95 Gew.-% eines Nuancierfarbstoffs;
   (ii) 0,1 bis 99,999 Gew.-% eines Farbstoffübertragungspolymers, das ausgewählt ist aus: Polyamin-N-oxid-Polymeren, Copolymeren von N-Vinylpyrrolidon und N-Vinylimidazol, Polyvinylpyrrolidonpolymeren, Polyvinyloxazolidonen und Polyvinylimidazolen;
   (iii) 0 bis 80 Gew.-% eines nicht-ionischenTensides;
   (iv) 0 bis 20 Gew.-% eines anionischen oder kationischen Tensides;
   (v) 0 bis 99,5 Gew.-% eines Trägers;
   (vi) 0 bis 50 Gew.-% eines Bindemittels, wobei das Gewichtsverhältnis von Farbstoffübertragungspolymer zu geladenem Tensid 1:0 bis 1:1 beträgt und wobei der Nuancierfarbstoff blau oder violett ist.

2. Nuancierfarbstoffgranulat gemäß Anspruch 1, wobei das geladene Tensid ein anionisches Tensid ist.

3. Nuancierfarbstoffgranulat gemäß irgendeinem vorhergehenden Anspruch, wobei der Nuancierfarbstoff ausgewählt ist aus: sauren Farbstoffen, basischen Farbstoffen und Direktfarbstoffen.

4. Körnige Waschmittelzusammensetzung umfassend:

   (a) 0,00005 bis 10 Gew.-% eines visuell unterschiedlichen Waschmittelgranulats gemäß einem der Ansprüche 1 bis 3;
   (b) 99,99995 bis 90 Gew.-% eines körnigen Grundpulvers, wobei die körnige Waschmittelzusammensetzung 10 bis 50 Gew.-% eines anionischen Tensides aufweist.

Revendications

1. Granule de colorant de nuançage comprenant :

   (i) de 0,001 à 95 % en poids d'un colorant de nuançage ;

(ii) de 0,1 à 99,999 % en poids d'un polymère de transfert de colorant choisi parmi :

les polymères de polyamine N-oxyde, les copolymères de N-vinylpyrrolidone et N-vinylimidazole, les polymères de polyvinylpyrrolidone, les polyvinyloxazolidones et les polyvinylimidazoles ;

(iii) de 0 à 80 % en poids d'un tensioactif non ionique ;
(iv) de 0 à 20 % en poids d'un tensioactif anionique ou cationique ;
(v) de 0 à 99,5 % en poids d'un support ; et
(vi) de 0 à 50 % en poids d'un liant, dans lequel le rapport en poids du polymère de transfert de colorant : tensioactif chargé est de 1:0 à 1:1, dans lequel le colorant de nuançage est bleu ou violet.

2. Granule de colorant de nuançage selon la revendication 1, dans lequel le tensioactif chargé est un tensioactif anionique.

3. Granule de colorant de nuançage selon l'une quelconque des revendications précédentes, dans lequel le colorant de nuançage est choisi parmi : les colorants acides, les colorants basiques et les colorants directs.

4. Composition détergente granulaire pour le linge comprenant :

(a) de 0,00005 à 10 % en poids d'un granule détergent pour le linge visuellement distinct tel que défini selon l'une quelconque des revendications 1 à 3 ;
(b) de 99,99995 % à 90 % en poids d'une poudre de base granulaire, dans laquelle la composition détergente granulaire pour le linge comprend de 10 à 50 % en poids d'un tensioactif anionique.

REFERENCES CITED IN THE DESCRIPTION

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