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(54) **White powder**

(57) The present invention provides a product and method of whitening the appearance of a detergent powder formulation, especially when incorporating more yellow linear alkyl benzene sulphonates.

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Description**FIELD OF INVENTION**

5 **[0001]** The present invention relates to the aesthetic qualities of detergent powders.

BACKGROUND OF THE INVENTION

10 **[0002]** Granular laundry powder detergents are mainly composed of surfactants and inorganic materials. Typical surfactants include linear alkyl benzene sulphonates, linear alcohol sulphates, linear alcohol ethoxysulphates and alcohol ethoxylates. Typical inorganic materials include sodium carbonate, sodium bicarbonate, sodium sulphate, sodium chloride, sodium tripolyphosphates, silica's, and zeolites. To reduce costs and impact on the environment it is preferable that these materials are used with as little processing as possible. This has a disadvantage that it can leave them with a yellow hue. This is particularly true for linear alkyl benzene sulphonates. Use of low quality linear alkyl benzene
 15 sulphonates in laundry powders gives the powders an unattractive yellow hue and gives the product the appearance of poor quality. The yellowness leads the user to fallaciously believe the powder cannot clean properly. The yellowness cannot be removed with the use of fluorescers.

[0003] Linear alkyl benzene sulphonates are synthesized by reaction of linear alkyl benzene with sulphuric acid. The linear alkyl benzene is produced by alkylation of benzene starting from n-paraffins feedstock. In each step unless careful
 20 control of reaction conditions and starting materials is maintained large amounts of yellow by-products are produced.

[0004] US 3,762,859, to Palmolive, in Example 10, discloses that a water soluble disazo dye stuff, a bluing agent, may serve to increase the whiteness of a detergent powder.

SUMMARY OF THE INVENTION

25 **[0005]** The dyes disclosed in US 3,762,859 and either degrade in the composition during storage or are green-blue and do not provide a good whiteness appearance.

[0006] We have found that storage stable white powders with the appearance of high quality/cleaning may be produced using low quality linear alkyl benzene sulphonates by addition of low levels of a limited set of blue dyes or organic
 30 pigments. Furthermore it is surprisingly found that some of these systems may be applied to bleach containing products.

[0007] Colourant may be selected from organic dyes and pigments. Thousands of different dye and pigment structures are known [ref: K. Hunger Industrial Dyes 2003 Wiley-VCH ISBN 3-527-30426-6; H. Zollinger Color Chemistry 2003 Wiley-VCH ISBN 3-906390-23-3]. In these compounds the colour arises due to extend conjugation of unsaturated double bonds. Due to this high level of unsaturation such compounds are highly susceptible to decomposition reaction.

35 **[0008]** Dyes and pigments suitable for shading detergent powder must stable to the high pH of the formulation (which can reach effective pH of 12 in the powder), stable with respect to other ingredients such as sequesterants and bleach, and stable to the presence of trace impurities such as hydroperoxides and metal ions. Many dyes are not stable under these conditions, for example triphenyl methane dyes decompose at high pH, as do many other dyes, particularly those dyes which have a proton with a pKa less than 12; dyes which contain transition metals, such as direct violet 48 and
 40 direct violet 66 rapidly decompose at high pH in the presence of the common laundry builder/sequesterant sodium tripolyphosphate, as the transition metal is removed from the dye; many dyes react rapidly with bleach; many dyes can sequester trace transition metals ions in the powder, leading to a colour change. Adding to the problem, nearly all dyes and many pigments listed as blue are in fact green-blue and the wrong hue. Many violet dyes and pigments are red and the wrong hue to impart whiteness.

45 **[0009]** Consequently Dyes and pigments of the correct hue for shading that are stable to the formulation and are safe to use are not known.

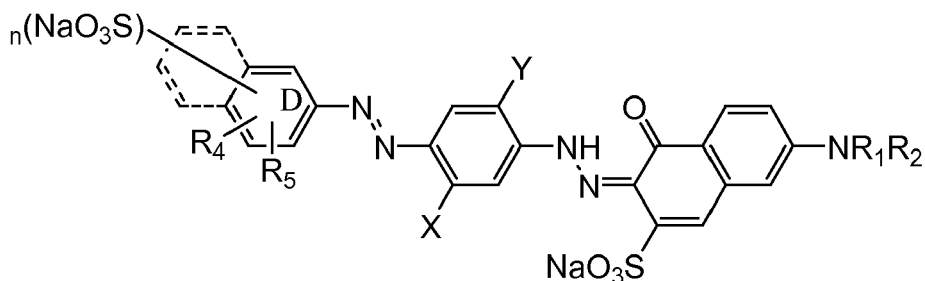
[0010] The present invention provides a way of using low colour quality yellow/brown linear alkyl benzene sulphonates. The colour quality, **CoQu**, of the linear alkyl benzene sulphonates is determined by measuring the optical absorption at 400nm of a 3.5g/L solution of linear alkyl benzene sulphonate in water. If the linear alkyl benzene sulphonates is too
 50 yellow, the colour quality is not ameliorated to aesthetically acceptable product.

[0011] In one aspect the present invention provides a granular laundry detergent powder comprising:

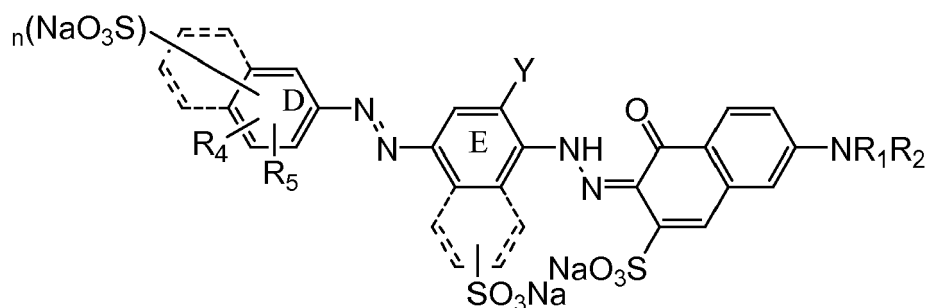
- a) from 4 to 50 wt % of a linear alkyl benzene sulphonate, wherein the optical absorption of a 3.5g/L solution of the linear alkyl benzene sulphonate at 400nm in water in a 5cm cell is between 0.005 to 0.2, preferably 0.005 to 0.08, most preferably 0.005 to 0.06;
- b) from 0 to 0.5 wt% fluorescer; and,
- c) from 0.00005 to 0.0007 wt%, preferably 0.0001 to 0.0005 wt% of a colourant that is a blue pigment or a blue dye, wherein the colourant gives a colour to the powder with a hue angle of from 250 to 310 degrees, preferably 270 to

295 degrees, wherein the colourant is selected from:

solvent violet 13; acid violet 43; food black 1; acid blue 98; organic pigments; mixtures of green-blue anthraquinone dyes with acid red mono-azo dyes or acid red fluorescent xanthene based dyes; mixtures of green-blue anthraquinone dyes with a bis-azo direct dye or anthraquinone violet dyes; and, mixtures of green-blue phthalocyanine compound with a bis-azo direct dye, and wherein the bis-azo direct dye is selected from:



or



wherein:

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

R₁ is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;

R₂ is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;

R₃ and R₄ 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.

[0012] The linear alkyl benzene sulphonate measured at 400nm in water is conducted at pH 2.

[0013] Other than any added, post dosed, coloured bodies the hue of the powder is preferably uniform. This may be obtained by spraying of the colourant as a solution or dispersion onto a powder containing the linear alkyl benzene sulphonate.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Linear alkyl benzene sulphonates may be bleached in order to improve whiteness. The bleaching may be conducted using hypochlorite or other bleaching agents. It is preferred that the linear alkyl benzene sulphonates in the granular laundry detergent powder has not been subjected to a bleaching step.

[0015] The measurement is conducted on the main bulk of the powder.

[0016] Colour coordinates and colour differences are expressed using the internationally standardized CIELAB tristimulus values:

a^* = red-green (+,-)

b^* = yellow-blue (+,-)

L^* = lightness (light = 100)

C^* = chroma

H^* = hue (angle of 0° = red, 90° = yellow, 180° = green, 270° = blue), and the colour differences ΔE^* , ΔH^* , ΔC^* , ΔL^* , Δa^* , and Δb^* , together with an identification number of the sample.

[0017] Measurements are taken with UV-excluded.

[0018] This internationally accepted system has been developed by CIE ("Commission Internationale de l'Éclairage"). It is for example part of DIN 6174: 1979-01 as well as DIN 5033-3: 1992-07.

PREFERRED COLOURANTS

[0019] The colour of a powder may be defined by measuring its CIELAB co-ordinates. Powder is poured onto a flat background and a thin transparent flat glass or plastic slide placed over it, then the reflectance spectrum taken through the slide.

[0020] Preferred colourants may be selected from the group of dyes and pigments. Most dyes listed as blue dyes in the colour index are unsuitable as they are green-blue in colour, for example acid blue 113. Triphenyl methane dyes are unsuitable as they are not stable to alkaline pH. Metal complexed azo dyes such as Cu containing bis azo dyes, direct violet 48 and direct violet 66 are unsuitable as the metal is removed on storage by sequesterants in the powder. Sequesterants, such as sodium tripolyphosphates, are widely used in laundry powders.

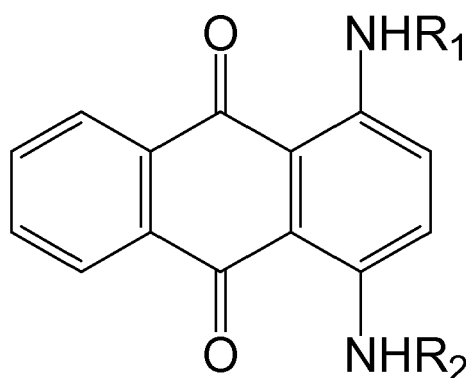
[0021] Preferred dyes are solvent violet 13; acid violet 43; food black 1; acid blue 98; mixtures of green-blue anthraquinone dyes with acid red mono-azo dyes or acid red fluorescent xanthene based dyes; mixtures of green-blue anthraquinone dyes with bis-azo and anthraquinone violet dyes; and mixtures of green-blue phthalocyanine compound with bis azo direct dyes.

[0022] Green-blue phthalocyanin dyes such as acid blue 279 and water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1 to 4 SO_3X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba) may be used in place of anthraquinone dyes but are not preferred.

[0023] When green-blue anthraquinone dyes are used they should show very low substantivity to nylon and cotton fabrics to avoid fabric discolouration on multiple washing.

[0024] Preferably, the green-blue anthraquinone dye has two amino groups.

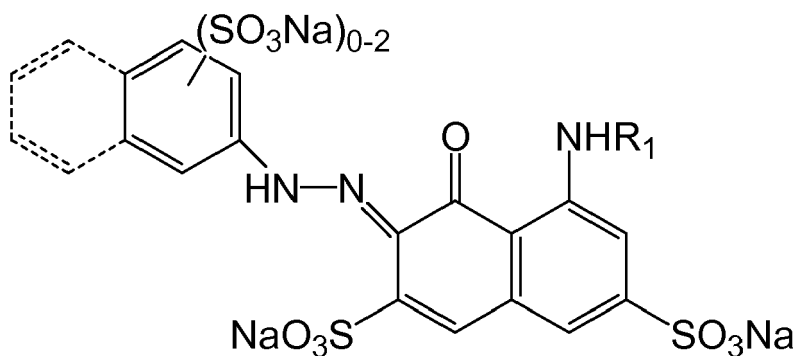
[0025] Preferred green-blue anthraquinone dyes have the structure:



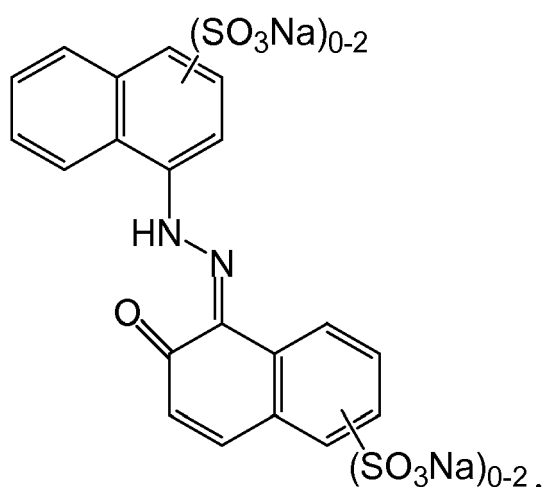
[0026] Where R_1 and R_2 are independently selected from hydrogen, aliphatic and aromatic organic groups. Preferred aliphatic groups are C1 to C10 alkyl. A Preferred aromatic organic group is phenyl; the phenyl may be substituted by up to three methyl groups. The dye is preferably substituted with at least one sulphonate group, more preferably at least two sulphonate groups.

[0027] Preferred green-blue anthraquinone dyes include acid blue 80, acid blue 204, acid blue 221, acid blue 331, acid blue 327, acid blue 288, acid blue 287, acid blue 272, most preferably acid blue 80.

[0028] Preferred acid red mono-azo dyes are selected from the following structures:



15 where R₁ is selected from selected from hydrogen, aliphatic and aromatic organic groups; and,



35 **[0029]** In the red mono-azo it is preferred that the aliphatic and aromatic organic groups are C₁ to C₁₀ alkyl and phenyl respectively; the phenyl may be substituted by up to three methyl groups.

[0030] Preferred acid red azo dyes are acid red 27, acid red 18, acid red 33, acid red 1.

40 **[0031]** Preferred acid red fluorescent xanthene based dyes are acid red 52, acid violet 9, acid red 50, acid red 87, acid red 98, acid red 92, acid red 51, most preferably acid red 52 and acid red 50. Xanthene dyes are most preferred to use in dye mixtures as they lead to a brightening of the powder.

[0032] Preferred bis-azo 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.

[0033] For bleach containing formulation the most favoured dye mixture is a green-blue acid anthraquinone dye and a bis-azo dye. Other dye combinations are not suitably stable to the presence of bleach.

45 **[0034]** Preferably the dye should not have a pK_a less than 12, to avoid deprotonation and decomposition of the dye within the powder.

[0035] Preferred pigments are selected from pigment blue 1, 1:2, 1:3, 2, 2:1, 2:2, 3, 4, 5, 7, 9, 10, 10:1, 11, 12, 13, 14, 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 18, 19, 20, 21, 22, 23, 25, 26, 27, 28, 29, 30, 31, 32, 34, 35, 36, 56, 57, 58, 59, 60, 61, 61:1, 62, 63, 64, 65, 66, 67, 69, 71, 72, 73, 74, 75, 79, 80, 83 and pigment violet 1, 1:1, 1:2, 2, 3, 3:1, 3:3, 3:4, 5, 5:1, 7:1, 8, 9, 11, 12, 13, 14, 15, 16, 18, 19, 23, 25, 27, 28, 29, 31, 32, 35, 37, 39, 41, 42, 43, 44, 45, 47, 48, 50, 54, 55 and 56.

[0036] Most Preferred pigments are pigment violet 3, pigment violet 39 and pigment violet 23 in combination with a green-blue dye or pigment. Preferred green-blue pigments are pigment blue 15, 15:1, 15:2, 15:3, 15:4 and 15:6.

55 **[0037]** The colourant may be sprayed or dry mixed onto the finished powder from an organic solvent, perfume water or surfactant solution. Dry mixing of the powder with a surfactant solution of the colourant is preferred as this give most even coverage of the powder.

[0038] Most preferably the colourant should be added to the surfactant slurry before granulation to avoid colourant spots. To avoid precipitation of the colourant in the slurry due to the high ionic strength present, the colourant may be

added from a surfactant solution, preferably a non-ionic surfactant solution.

FLUORESCENT AGENT

[0039] 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 0.3 wt %. Preferred classes of fluoescer 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.

[0040] Preferred fluoescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[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-sulfoslyryl)biphenyl. Most preferred are disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

BLEACH

[0041] The present invention has particular utility when bleaching agents are present. Dyes of particular utility in this regard are mixtures of green-blue phthalocyanine compound with a bis-azo direct dye as defined above. These dyes are used with sodium percarbonate or sodium perborate at a level in the range from 1 to 25 wt %. These peroxygen bleaches are preferably used with an activator such as TAED or SNOBS

PERFUME

[0042] 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.

COLOURED BODIES

[0043] It is preferred that the granular laundry detergent powder comprises from 0.01 to 5 wt % of coloured bodies. The coloured bodies are an important aesthetic part to the consumer. The combination of a white powder together with the contrast of a coloured body gives the powder a quality appearance. The cost effective use of a yellow linear alkyl benzene sulphonate which has been colour enhanced to a white appearance using a dye counter balances the extra cost of aesthetically pleasing coloured bodies. The coloured body is of greater contrast in a dye white enhanced powder than a powder of same intrinsic perceived whiteness.

[0044] The coloured bodies have a deltaE difference from the bulk powder of at least 15. The measurements are taken as described above. The powder without coloured bodies is poured onto a flat background and a thin transparent flat glass or plastic slide placed over it, then the reflectance spectrum taken through the slide. The coloured bodies are measured analogously.

[0045] The coloured bodies may be granular or flat. The coloured bodies may be of any shape, for example, circular, triangular, square, hexagonal etc.

[0046] Preferably the coloured body has a maximum dimension of 5mm in any one direction.

[0047] Suitable coloured bodies are described in GB2358403, published 25 July 2001.

[0048] All compositions are defined with respect to weight percentage unless otherwise specified.

Experimental

Example 1

[0049] A laundry detergent powder was made of the following formulation (10% Linear alkyl benzene sulphonate, 40% sodium chloride, 30% sodium carbonate, remainder moisture and minors). The powder was yellow in colour. The linear alkyl benzene sulphonate used was of low quality.

[0050] Identical laundry detergent was made except various levels of the dye solvent violet 13 was added to the Linear

alkyl benzene sulphonate before granulation. The powder had the following colour:

- (a) 0 wt% Solvent violet 13 added - yellow powder
- (b) 0.00025wt% solvent 13 added - white powder
- (c) 0.0005 wt% solvent violet 13 added - white powder
- (d) 0.001wt% solvent violet 13 - grey-white powder.

Example 2

[0051] Powders (a) and (c) of example 1 were measured using a reflectometer. The Powder was poured onto a flat white piece of paper and a thin transparent flat plastic slide placed over it, then the reflectance spectrum taken with UV-excluded. The Lab values are given below:

Powder (a) $L^* = 91.3$, $a^* = 0.8$, $b^* = 0.25$

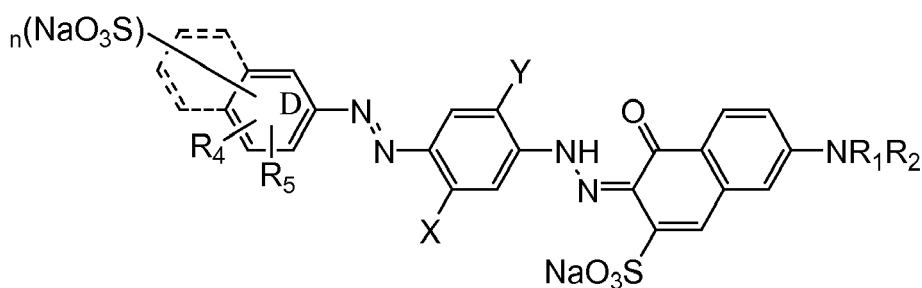
Powder (c) $L^* = 90.4$, $a^* = 0.9$, $b^* = -2.7$

[0052] Solvent Violet 13 causes changes predominately in b^* .

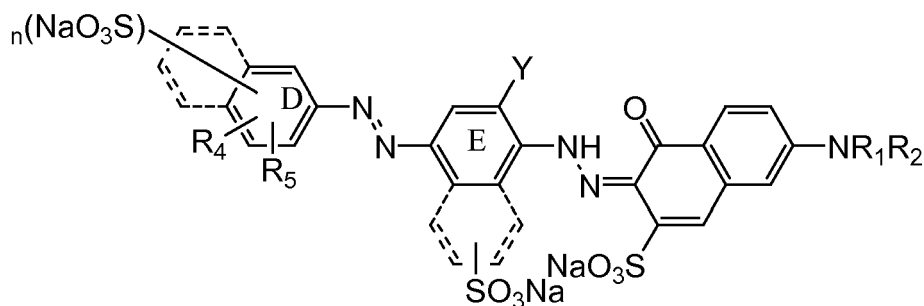
Claims

1. A granular laundry detergent powder comprising:

- a) from 4 to 50 wt % of a linear alkyl benzene sulphonate, wherein the optical absorption of a 3.5g/L solution of the linear alkyl benzene sulphonate at 400nm in water in a 5cm cell is between 0.005 to 0.2;
- b) from 0 to 0.5 wt% fluorescer; and,
- c) from 0.00001 to 0.0007 wt% of a colourant that is a blue pigment or a blue dye, wherein the colourant gives a colour to the powder with a hue angle of from 250 to 310 degrees, wherein the colourant is selected from: solvent violet 13; acid violet 43; food black 1; acid blue 98; organic pigments; mixtures of green-blue anthraquinone dyes with acid red mono-azo dyes or acid red fluorescent xanthene based dyes; mixtures of green-blue anthraquinone dyes with a bis-azo direct dye or anthraquinone violet dyes; and, mixtures of green-blue phthalocyanine compound with a bis-azo direct dye, and wherein the bis-azo direct dye is selected from:



or



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.

2. A granular laundry detergent powder according to claim 1, wherein green-blue anthraquinone dye has two amino groups.
3. A granular laundry detergent powder according to claim 1, wherein the acid red azo dyes are: acid red 27, acid red 18, acid red 33, acid red 1.
4. A granular laundry detergent powder according to claim 1, wherein the acid red fluorescent xanthene based dye is selected from the group consisting of: acid red 52, acid violet 9, acid red 50, acid red 87, acid red 98, acid red 92, acid red 51, most preferably acid red 52 and acid red 50.
5. A granular laundry detergent powder according to claim 1, wherein the bis-azo dye is selected from the group consisting of: 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.
6. A granular laundry detergent powder according to claim 1, wherein the colourant is a pigment and is selected from the group consisting of: pigment blue 1, 1:2, 1:3, 2, 2:1, 2:2, 3, 4, 5, 7, 9, 10, 10:1, 11, 12, 13, 14, 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 18, 19, 20, 21, 22, 23, 25, 26, 27, 28, 29, 30, 31, 32, 34, 35, 36, 56, 57, 58, 59, 60, 61, 61:1, 62, 63, 64, 65, 66, 67, 69, 71, 72, 73, 74, 75, 79, 80, 83 and pigment violet 1, 1:1, 1:2, 2, 3, 3:1, 3:3, 3:4, 5, 5:1, 7:1, 8, 9, 11, 12, 13, 14, 15, 16, 18, 19, 23, 25, 27, 28, 29, 31, 32, 35, 37, 39, 41, 42, 43, 44, 45, 47, 48, 50, 54, 55 and 56.
7. A granular laundry detergent powder according to any preceding claim, wherein the linear alkyl benzene sulphonate is unbleached linear alkyl benzene sulphonate.
8. A granular laundry detergent powder according to any preceding claim, wherein the granular laundry detergent powder comprised from 0.01 to 5 wt % of coloured bodies, the coloured bodies having a deltaE difference from the bulk powder of at least 15.

REFERENCES CITED IN THE DESCRIPTION

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