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(54) **Title:** SHADING DYE GRANULE ITS USE IN A DETERGENT FORMULATION AND PROCESS TO MAKE IT

(57) **Abstract:** A shading dye granule for use as an additive in a laundry powder composition, the granule having a particle size distribution such that 90 wt% of the particles are less than 300 microns, preferably 250 microns, in diameter, the granule comprising: 0.05 to 0.5 wt% water soluble fabric substantive shading dye (solids) absorbed into at least 80 wt% hydratable salt.

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SHADING DYE GRANULE ITS USE IN A DETERGENT FORMULATION AND PROCESS TO MAKE IT

This invention relates to powdered laundry detergent compositions that include a shading dye or fabric substantive dye, it relates particularly to inclusion of a shading dye granule into an essentially uncoloured detergent composition.

White fabrics may be treated with dye in order to enhance whiteness. The dye used is typically blue or violet. When these treated fabrics have been repeatedly washed with a detergent composition the dye may be removed from the fabric, leading to yellowing of the fabric.

The prior art has suggested remedying this effect by delivering shading dye to the fabric during the laundry washing process. For example 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.

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%.

Granules may be formed by loading an inorganic salt with soluble dye solution. A problem with this is that the solution may leak from the granule when it is mixed with the remainder of the laundry detergent composition. This is especially likely if the composition is moist and/or warm: for example, during storage. The phenomenon of leaking of the dye into the surrounding composition is termed bleeding. It is a particularly significant problem for pale coloured or uncoloured detergent powder compositions.

Coloured granules containing a dye have also been used in detergent powder formulations as coloured speckles to provide visual cues. These granules or particles are large and contain as little dye as possible due to its non-functional nature. The dye is not fabric substantive and a shading dye is therefore unsuitable for this purpose. EP 0336 635 describes a process for preparing a coloured granular alkali metal silicate. This is a visual cue type of speckle and uses a non-substantive dye. Non- substantive dyes may be incorporated at a higher level without fear of spotting damage if the dye granule comes into direct contact with a fabric. It is stated in this document that the

amount of colorant in the speckle granule should be low, so as not to interfere with the washing process. The process involves spraying the inorganic material with dye or pigment and a solvent. It is taught that the silicate may be mixed with other inorganic materials such as zeolite, sodium sulphate or sodium phosphate. The preferred particle size of the coloured granules is 0.8 to 1.6 mm. The dye is suggested to be incorporated at a low level: 0.1 to 2 wt% of the granules and it is said to be present as a coating on the silicate.

WO 2000/27980 also relates to visible speckles. The particle size being preferably 500 to 1440 mu m. The speckle comprises a dye on a crystalline material that can be a hydrated salt, such as crystalline silicate. The preferred level of dyestuff may be below 0.1 wt% of the speckle particle.

US 5073295 relates to coated granules containing, for example, soluble dyestuff. The coatings provide excellent protection against decomposition and separation from other components, for example in detergent compositions. The preferred particle size of the dye granules is 200 to 700 microns.

According to the present invention there is provided a shading dye granule comprising 0.05 to 0.5 wt% shading dye absorbed onto a hydratable inorganic salt, such as sodium carbonate. When sodium carbonate is used it is preferably a light soda ash with a particle size range such that at least 90% of the particles have a diameter less than 250 microns.

The salt may be used in admixture with zeolite in an amount of 0 to 20 wt%.

In this specification "shading dye" means one, or a combination of, water-soluble, photostable dyes, substantive to cotton, which, on cotton has a peak absorption wavelength of from 540nm to 650nm, preferably from 570nm to 630nm. Such shading dyes are solid at room temperatures and are typically made into processable liquids by dissolving or dispersing in an aqueous medium. In this specification references to quantities of shading dye mean the amount of shading dye solids and not the amount of shading dye solution or dispersion.

Also according to a second aspect of the present invention there is provided a method of manufacturing a shading dye granule comprising the steps of dry mixing inorganic carrier materials and then spraying on to the mixture a liquid comprising shading dye and water. Shading dye may be supplied as a dispersion or solution in water. It can be used as supplied or it can be further diluted by adding water. If it is used undiluted, care must be taken about the rate of addition of dye to the inorganic material. If it is used further diluted then the ratio of added water to shading dye solution should preferably be at least 2:1. Dilution of the shading dye with water enables a better control of the amount being added and aids dispersion of the dye over the inorganic solids. The mixing and spraying preferably takes place in a drum mixer. The amount of liquid sprayed on should be less than that which would lead to agglomeration of the inorganic carrier materials. This

allows the retention of spare liquid carrying capacity in the inorganic material. It has been found that by retaining at least 10% of the total liquid carrying capacity of the inorganic material the bleeding performance of the granule may be significantly improved.

Advantageously zeolite is added after the initial mixing of the aqueous dye liquid and the inorganic salt. It is also possible to spray the dye onto the zeolite and then dilute this mixture with inorganic salt.

A second problem with use of a highly loaded shading dye granule (or adjunct) is that it becomes visible against an uncoloured detergent powder, due to its contrasting colour. In this invention this is mitigated by preventing the agglomeration of shading dye containing particles during the manufacturing process. This is done by limiting the total amount of water and shading dye liquid to 15 wt%, preferably 10 wt%, of the amount of the inorganic salt. As mentioned above, such a limitation also has the advantage that the salt is not fully loaded with diluted shading dye. This means that the bleeding problem is reduced. This is thought to be due to the ability of the shading dye liquid to expand on heating without being forced out of the shading dye granule. Use of these levels of liquid loading also avoids caking problems.

The concentration of shading dye (on a solids basis) in the liquid sprayed on should not be greater than 25%, preferably not greater than 10%, most preferably not greater than 2.5%. Thus, a typical range of shading dye concentration (solids

basis) in the shading dye granule will be 0.05 to 0.4 wt% of the shading dye granule, preferably 0.07 to 0.27 wt%. It has been found that higher levels of shading dye lead to spotting damage if a fabric is left in contact with the powder. On the other hand, lower concentrations of shading dye mean that too high a proportion of shading dye granules need to be added to a powder formulation to obtain the required level of shading dye inclusion in the total formulation. This, in turn, leads to bleeding of the shading dye into the formulation over time.

Typical levels of the shading dye granule in the powder formulation are in the range 0.1 to 2.0 wt%. The granule can be used in conjunction with any laundry detergent powder formulations. It is especially useful for use with formulations that are white, or relatively lightly shaded, as these would have suffered particularly from any bleeding that occurs over time.

It has also been found that the selection of the inorganic salt has an effect on the bleeding and spotting performance of the shading dye granules. Soda ash light is found to give the best results and has the required low particle size - less than about 10% above 250 microns. However, it would also be possible to use magnesium sulphate, sodium tripolyphosphate, and zeolite either alone or in combination with sodium carbonate.

The invention will now be further described with reference to the following non-limiting examples. Two standard tests

are carried out on the examples they are the Spotting test and the Bleeding test.

Spotting Test

This test is designed to check if a powder containing a shading dye granule gives rise to staining and/or spotting of test fabrics.

A load of a half T-shirts 100% Cotton (= 73 g) is added to a three litre bucket containing one litre of water. Three replicates of one monitor (15 x 15 cm) are placed in the bucket and 10 g of the test powder is spread over them. After 2 hours the monitors are removed and assessed visually for spotting damage. The damage is classified according to the following ranking scale:

(1) - Very low damage
(2) - Low damage
(3) - Medium damage
(4) - High damage
(5) - Very high damage

Bleeding Test

This test checks shade colour change in finished powders containing shading dye granules.

A quantity of shading dye granules is incorporated into a standard detergent powder by mixing in a plastic bag. 30 grams of this product and a reference powder without any

shading dye granules are stored in open petri dishes at 37°C/70%r.h. for 4 weeks.

A visual comparison against the reference is done weekly to check if any shade colour change is observed. Evaluation is carried out in a visual cabinet under daylight. The classification is:

(Good): No, or very slight, bleeding observed.

(Acceptable): Slight bleeding observed, but the shade colour change is still ok.

(Rejected): Severe bleeding with clear shade colour change.

Examples

Example 1

A shading dye granule was manufactured with the ingredients shown below:

Light soda ash	= 89.0	
Zeolite 4A	= 2.1	
Water	= 8.15	
Shading dye	= 0.75	(0.075 shading dye solids+water and stabilisers)

The shading dye used was an aqueous dispersion of the trisethoxy tripropanol-amine salt of Direct Violet 9. The salt was present at a concentration of about 10 wt% and was stabilised at this level in aqueous dispersion/solution by surfactant and other minor ingredients. The water and dye were mixed together and sprayed onto the light soda ash in a low/medium shear batch mixer, with subsequent addition of

zeolite towards the end of the batch cycle. Except where specified otherwise the light soda ash used had 100wt% particles below 250 microns.

Example 2

A shading dye granule was manufactured using a similar process to that used for example 1 with the ingredients shown below:

Light soda ash	= 53.1	
Sodium sulphate	= 38.6	
Zeolite 4A	= 1.2	
Water	= 7.1	
Shading dye	= 0.75	(0.075 shading dye solids + water + stabilisers)

The shading dye was that same as that used in example 1. The water and dye were mixed together and sprayed onto the soda ash in a low/medium shear batch mixer, with subsequent addition of zeolite and then dilution with sodium sulphate towards the end of the batch cycle.

Example 3

A shading dye granule was manufactured in a high shear batch mixer using a similar process to that used for example 1, with the ingredients shown below:

STPP anhydrous	= 50.0
Sodium sulphate	= 47.0
Water	= 1.5

Shading dye = 1.5 (0.15 shading dye solids + water + stabilisers)

The shading dye was that same as that used in example 1. The water and dye were mixed together and sprayed onto STPP in a high shear batch mixer, with subsequent addition of sodium sulphate towards the end of the batch cycle.

Example 4

A shading dye granule was manufactured in a high shear batch mixer using a similar process used for example 3, with the ingredients shown below:

Magnesium Sulphate = 85.0
Water = 14.0
Shading dye = 1.0 (0.1 shading dye solids + water + stabilisers)

Example 5

A shading dye granule was manufactured in a high shear batch mixer using a similar process to that used for example 1, with the ingredients shown below:

Light soda ash = 76.0
Zeolite 4A = 20.0
Water = 3.0
Shading dye = 1.0 (0.1 shading dye solids + water + stabilisers)

The shading dye was the same as that used in example 1. The water and dye were mixed together and sprayed onto zeolite in a high shear batch mixer, with subsequent addition of light soda ash towards the end of the batch cycle.

Example 6

The shading dye granule of example 1 was added to a detergent powder, built with phosphate, at a level of 0.15 wt%. The appearance of the powder was not affected adversely by the incorporation of the shading dye granule.

Example 7

The shading dye granule of example 2 was added to a zeolite built detergent powder formulation at a level of 0.5 wt%. The appearance of the powder was not affected adversely by the incorporation of the shading dye granule.

Example 8

A shading dye granule was produced like example 1, except that a light soda ash with the following particle size was used:

90 wt% below 250 microns
10 wt% between 250-500 microns.

Example 9

A shading dye granule was produced like example 1, except that a light soda ash with the following particle size was used:

75 wt% below 250 microns
25 wt% between 250-500 microns

Example 10

A shading dye granule was produced like example 1, except that a light soda ash with the following particle size was used:

40 wt% below 250 microns
40 wt% between 250-500 microns
20 wt% above 500 microns

The granules of examples 1, 2, 3, 4, 5, 8, 9 and 10 were assessed for spotting and bleeding. The results are given in table 1.

Table 1

Dye granule type	Bleeding	Spotting Ranking (1 to 5)
Example 1	good	1
Example 2	good	1
Example 3	good	4
Example 4	good	3
Example 5	acceptable	1
Example 8	good	2
Example 9	good	3
Example 10	good	5

As can be seen from table 1 the use of the coarser grades of soda ash in examples 9 and 10 leads to poorer spotting rankings.

CLAIMS

1. A granule for use as an additive in a laundry powder composition, the granule having a particle size distribution such that 90 wt% of the particles are less than 300 microns, preferably 250 microns, in diameter, the granule comprising: 0.05 to 0.5 wt% shading dye solids as herein before defined absorbed into at least 80 wt% hydratable salt.

2. A shading dye granule according to claim 1 wherein the hydratable salt comprises light soda ash as hydratable salt.

3. A shading dye granule according to claim 2 wherein the granule further comprises sodium sulphate as hydratable salt.

4. A detergent powder composition comprising 0.1 to 2.5 wt% of a shading dye granule according to any one of claims 1 to 3.

5. A process to manufacture a shading dye granule according to any one of claims 1 to 3 including the steps of:

adding soda ash to a low/medium shear mixer,

optionally mixing aqueous shading dye solution with further water the ratio of water to shading dye solution being at least 2:1, and

spraying the aqueous shading dye solution and optional further water mixture over the soda ash while mixing, optionally adding further inorganic material with liquid carrying capacity, which may include further hydratable salt or zeolite, wherein agglomeration of the shading dye granules is prevented by using a total amount of water and shading dye solution of less than 15 wt%, preferably less than 10 wt%, of the weight of the granule produced.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/003274 A (UNILEVER PLC) 13 January 2005 (2005-01-13) cited in the application page 3, line 23 - page 6, line 15 page 8, lines 25-27 page 10, lines 19-23 examples claims	1-5
A	EP 0 336 635 A (UNILEVER PLC) 11 October 1989 (1989-10-11) cited in the application examples claims	1-5

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

[X] See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

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PCT/EP2007/000989

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00/27980 A (THE PROCTER & GAMBLE COMPANY) 18 May 2000 (2000-05-18) cited in the application page 5, line 25 - page 9, line 8 page 10, line 18 - page 11, line 16 example I; tables I,II claims	1-5
A	US 5 073 295 A (BRUTTEL ET AL) 17 December 1991 (1991-12-17) cited in the application example 1 claims	1-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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