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(54) **GRANULES**

GRANULAT

GRANULES

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**WO-A-2007/096052**
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EP 2 245 133 B1

## Description

### FIELD OF INVENTION

**[0001]** The present invention relates to the reduction in migration of actives from granules.

### BACKGROUND OF THE INVENTION

**[0002]** Powder detergents for clothes washing are formulated at high pH and often contain percarbonate or perborate as a bleach. To give additional benefits to the washer, high performance organic chemicals (HPOC's) such as anti-oxidants, shading dyes and shading pigments may be added to the formulation. These compounds are frequently chemically unstable to high pH and bleach, so that on storage they are destroyed. To prevent this, they may be segregated from the formulation, by adding them to the formulation in separate post-dosed granules. An acidic polymer may be added to the granule used to increase stability as described in W02007/039042 (Unilever).

**[0003]** It is advantageous to use non-ionic surfactants in such granules, to initially mix the HPOC's in and to aid dispersion and delivery of the ingredients in the wash, as described in W02006/053598 (Unilever). This is especially the case when the HPOC's are hydrophobic materials.

**[0004]** Under storage conditions in powder detergents at high temperature and humidity the non-ionic containing granules, leach non-ionic over the whole formulation, again exposing the HPOC's to high pH and bleach. The problem is particularly severe in powder detergent formulations that contain high levels of non-ionic surfactant. The leaching from the granule can also lead to powder discolouration, especially for dyes and pigments.

### SUMMARY OF THE INVENTION

**[0005]** We have found that granules of the present invention provide reduced bleeding of HPOC.

**[0006]** In one aspect the present invention provides a granule comprising:

(i) from 5 to 30 wt% of a non-ionic surfactant having mixed therein between 0.00001 to 5% wt % of a high performance organic compound selected from the group consisting of dye, pigment, and antioxidant
(ii) from 20 to 90 wt% of silica; and,
(iii) from 20 to 60 wt% of a binder that is other than a non-ionic surfactant,

wherein the fraction (wt% binder)/(wt% non-ionic) is greater then 1, preferably greater than 2 most preferably greater than 2.5.

**[0007]** Preferably the non-ionic surfactant having the HPOC mixed therein is in contact with the silica and coated with the binder.

### DETAILED DESCRIPTION OF THE INVENTION

### HIGH PERFORMANCE ORGANIC CHEMICALS

**[0008]** High performance organic chemicals are organic chemicals added to the formulation at low levels, preferably between 0.00001 to 0.5 wt% to give benefits beyond detergency to the user.

**[0009]** The HPOC is limited to an anti-oxidant, a shading dyes, a shading pigment or mixtures thereof.

**[0010]** The HPOC is most preferably a dye.

### DYE

**[0011]** Dyes preferably selected from the groups of basic dye, acid dyes, direct dyes, hydrophobic dyes selected from solvent dyes and disperse dyes.

**[0012]** Dyes may be selected from those listed in the colour index (Society of Dyers and Colourists and American Association of Textile Chemists and Colorists).

**[0013]** Blue and violet thiazolium mono-azo dyes may also be used as described in WO 2007/084729.

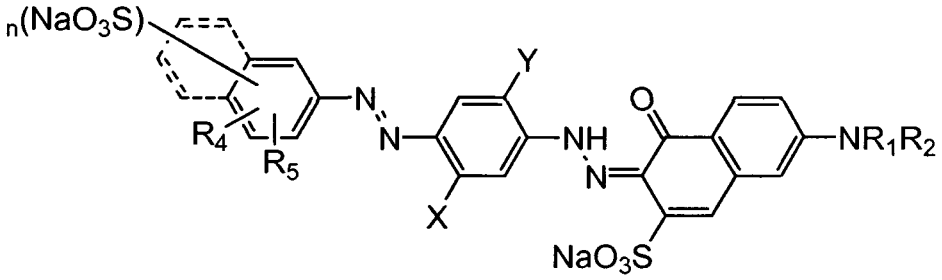
**[0014]** Preferably the granule contains 0.01 to 1.0 wt% of a shading dye for fabric whiteness.

**[0015]** The shading dye is preferably selected from:

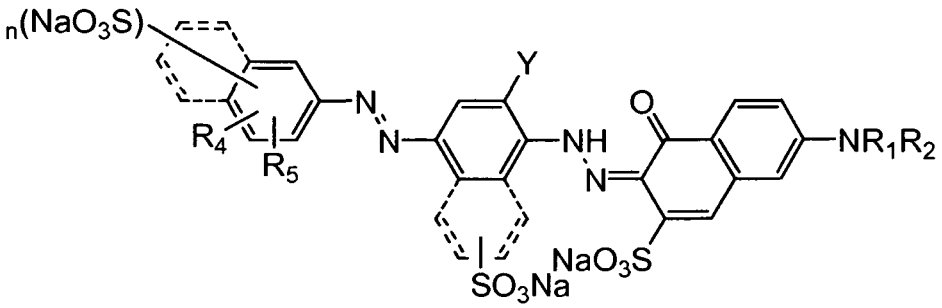
(1) Direct dyes
Direct violet and direct blue dyes are preferred. Preferably the dye are *bis* or *tris* - azo dyes. The carcinogenic

benzidene based dyes are not preferred.

Most preferably the direct dye is a direct violet of the following structure



or



where

$R_1$ is hydrogen or alkyl

$R_2$ is hydrogen, alkyl or substituted or unsubstituted aryl, preferably phenyl

$R_3$ and $R_4$ are independently hydrogen or alkyl

X and Y are independently hydrogen, alkyl or alkoxy, preferably the dye has X= methyl and Y = methoxy.

n is 0, 1 or 2, preferably 1 or 2.

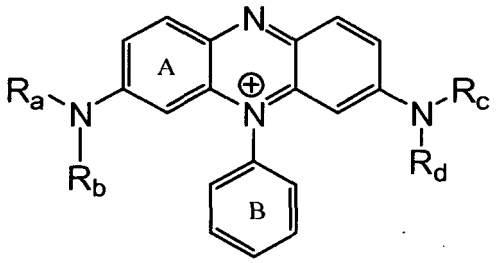
Preferred dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99.

In another embodiment the direct dye may be covalently linked to a photobleach, for example as described in WO2006/024612.

(2) Acid dyes

Cotton substantive acid dyes give benefits to cotton containing garments. Preferred dyes and mixes of dyes are blue or violet. 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 $NO_2$.

Preferred azine dyes are: acid blue 98, acid violet 50, and acid blue 59, more preferably acid violet 50 and acid blue 98.

(ii) acid violet 17, acid violet 50, acid black 1, acid red 51, acid red 17 and acid blue 29.

(3) Hydrophobic dyes

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.

Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

(4) Reactive dyes

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. Preferably the reactive group is hydrolysed or the dye has been reactive group 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.

(5) Shading Photobleaches

Shading photo-bleaches (PB) are dyes which form reactive bleach species on exposure to light. They are best used in combination with other shading dyes and pigments to give a blue or violet colour.

They function as follows:

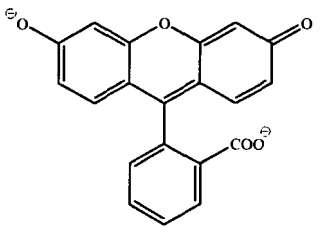
$$PB + light \rightarrow PB^*$$

$$PB^* + {}^3O_2 \rightarrow PB + {}^1O_2$$

The photo-bleach molecule absorbs light and attains an electronical excited state, PB*. This electronically excited state is quenched by triplet oxygen, ${}^3O_2$, in the surroundings to form singlet ${}^1O_2$. Singlet oxygen is a highly reactive bleach.

Suitable Shading photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Zl where Zl is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably, the phthalocyanine has 1-4 $SO_3X$ groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in W02005/014769 (Ciba).

Xanthene type dyes are preferred, particularly based on the structure:




where the dye may be substituted by halogens and other elements/groups. Particularly preferred examples are Food Red 14 and Rose Bengal, Phloxin B, Eosin Y.

**(6) Basic dyes**

Basic dyes are organic dyes that 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. Preferred examples include triarylmethane basic dyes, 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.

Pigments

**[0016]** Pigments are coloured particles preferably with an average particle size in the range of 0.01 to 0.1 micron size,

which are practically insoluble in aqueous medium that contain surfactants. Preferred pigments are blue or violet.

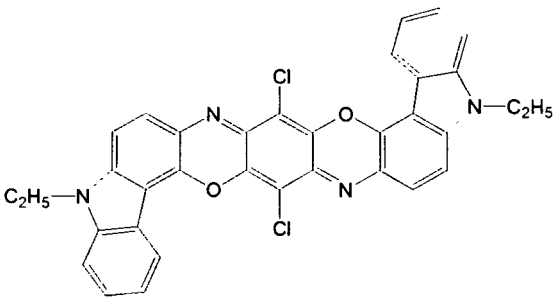
**[0017]** Pigments may be selected from the blue and blue pigments listed in the colour index.

**[0018]** Inorganic pigments such as pigment blue 29 or pigment pigment violet 15 may be used, however organic pigments are preferred.

**[0019]** Preferred organic pigments are pigment violet 1, 1:1, 1:2, 2, 3, 5:1, 13, 19, 23, 25, 27, 31, 32, 37, 39, 42, 44, 50 and Pigment blue 1, 2, 9, 10, 14, 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 18, 19, 24:1, 25, 56, 60, 61, 62, 66, 75, 79 and 80.

**[0020]** More preferred pigments are pigment violet 3, 13, 23, 27, 37, 39, pigment blue 14, 25, 66 and 75.

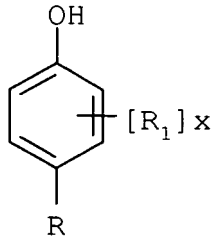
**[0021]** The most preferred is pigment violet 23.




Pigment Violet 23

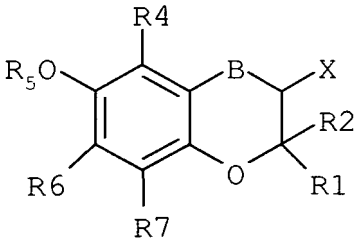
ANTIOXIDANT

**[0022]** One class of anti-oxidants suitable for use in the present invention is alkylated phenols having the general formula:




wherein R is C1-C22 linear or branched alkyl, preferably methyl or branched C3-C6 alkyl; C3-C6 alkoxy, preferably methoxy; R1 is a C3-C6 branched alkyl, preferably tert-butyl; x is 1 or 2. Hindered phenolic compounds are preferred as antioxidant.

**[0023]** Another class of anti-oxidants suitable for use in the present invention is a benzofuran or benzopyran derivative having the formula:




wherein R1 and R2 are each independently alkyl or R1 and R2 can be taken together to form a C5-C6 cyclic hydrocarbyl moiety; B is absent or CH2; R4 is C1-C6 alkyl; R5 is hydrogen or -C(O)R3 wherein R3 is hydrogen or C1-C19 alkyl; R6 is C1-C6 alkyl; R7 is hydrogen or C1-C6 alkyl; X is - CH2OH, or -CH2A wherein A is a nitrogen comprising unit, phenyl, or substituted phenyl. Preferred nitrogen comprising A units include amino, pyrrolidino, piperidino, morpholino, piperazino, and mixtures thereof.

**[0024]** Other suitable antioxidants are found as follows. A derivative of $\alpha$-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocophero, and alkyl esters of gallic acid, especially octyl gallate and dodecyl gallate.

**[0025]** Another example of suitable antioxidants are the class of hindered amine light stabilisers (HALS), particularly those based 2,2,6,6-tetramethylpipiridines.

**[0026]** Non-limiting examples of anti-oxidants suitable for use in the present invention include phenols *inter alia* 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, mixtures of 2 and 3- tert-butyl-4-methoxyphenol.

**[0027]** Mixtures of antioxidants may be use and in particular mixtures that have synergic antioxidant effects as found in, for example, WO02/072746.

NON-IONIC SURFACTANT

**[0028]** Preferred non-ionic surfactants are, for example, polyethoxylated alcohols, ethoxylated alkyl phenols, anhydrosorbitols, and alkoxylated anhydrosorbitol esters. An example of a preferred nonionic surfactant is a polyethoxylated alcohol manufactured and marketed by the Shell Chemical Company under the trademark "Neodol". Examples of preferred Neodols are Neodol 25-7 which is a mixture of 12 to 15 carbon chain length alcohols with about 7 ethylene oxide groups per molecule; Neodol 23-65, a C12-13 mixture with about 6.5 moles of ethylene oxide; Neodol 25-9, a C12-13 mixture with about 9 moles of ethylene oxide; and Neodol 45-7, a C14-15 mixture with about seven moles of ethylene oxide. Other nonionic surfactants useful in the present invention include trimethyl nonyl polyethylene glycol ethers such as those, manufactured and marketed by Union Carbide Corporation under the Trademark Tergitol, octyl phenoxy polyethoxy ethanols sold by Rohm and Haas under the Trademark Triton, and polyoxyethylene alcohols, such as Brij 76 and Brij 97, trademarked products of Atlas Chemical Co. The hydrophilic lipophilic balance (HLB) is preferably below about 13, and more preferably below 10.

SILICA

**[0029]** Preferably, the silica has a pore volume of from 0.2 to 2.5 ml/g, most preferably 1.2 to 2 ml/g. The pore volume is measured by mercury intrusion porosimetry or water saturation method at 293K. The water saturation method is preferred; here a known weight of the silica is slowly mixed with a known volume of water, such that excess water is present. The container is sealed and left till the silica becomes fully saturated (i.e. all pores are filled). The excess water is then removed and the volume measured. Pore volume is then given by the equation:

$$(\text{pore volume}) = [(\text{total volume of water}) - (\text{excess water})]/\text{weight of silica}.$$

**[0030]** The pore volume served to provide cavities into which the non-ionic/HPOC migrates during application.

**[0031]** Preferably, the silica has an average particle size, APS, from 0.1 to 100 microns, preferably 1 to 15 microns. Preferably this is as measured by a laser diffraction particle size analyser, preferably a Malvern HP with 100mm lens.

**[0032]** For general discussion of the measurement of particle size see OECD 110 and EUR 20268 EN(2002).

**[0033]** Preferably the silica is a neutral or acidic silica.

**[0034]** Preferably the silica is amorphous.

**[0035]** Preferably the silica is without a wax surface treatment. This permits ready delivery of the HPOCs to the wash medium.

BINDER

**[0036]** 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.

**[0037]** Preferably, the binder has a melting point above 30°C.

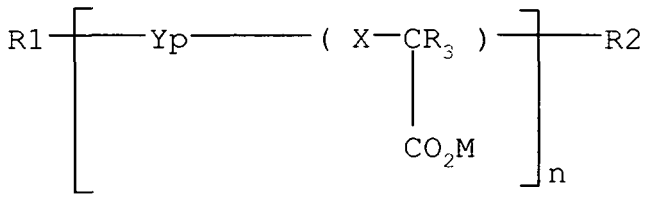
**[0038]** Preferably the binder is selected from the group consisting of a polyacrylate, polyethylene glycol, and polyacrylate/maleate copolymer.

**[0039]** The binder may serve as a coating agent and a cogranulent for the silica particles.

**[0040]** 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.

**[0041]** 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. Suitable polymers for use herein have a molecular weight in the range of from 1000 to 280,000, preferably from 1500 to 150,000.

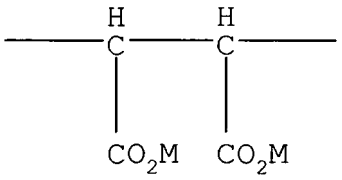
**[0042]** Suitable polymers which meet the above criteria and are therefore particularly useful in the present invention, include those having the following empirical formula I



(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.

**[0043]** 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)

**[0044]** Such polymers are available from BASF under the trade name Sokalan® CP5 (neutralised form) and Sokajan® CP45 (acidic form).

**[0045]** 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.

GRANULE

**[0046]** The granule is preferably of the size from 250 to 1400 microns. The granule size is as determined by passing through a mesh sieve. Preferably the size is in the range...

**EXAMPLES**

**Example 1**

**[0047]** The dye solvent violet 13 was mixed in non-ionic surfactant (7EO) to form a 0.5 wt% solution.

**[0048]** The non-ionic was added to the carrier in a high shear mixer. Following this the binder was added to granulate the mixture. There resultant granules were dried in an oven at 353K finally sieved to give granules in the size range 500 to 1000 microns.

**[0049]** The granules had the following composition. All percentages refer to weight.

| | Carrier | Non-ionic containing 0.5 wt% dye | Binder |
|---|---|---|---|
| Granule 1 | 37% gasil 230 | 16 | 47% CP5 |
| Granule 2 | 68% gasil 200TP | 27 | 5% CP13 |
| Granule 3 | 64% gasil 200TP | 26 | 10% CP5 |
| Granule 4 | 60% gasil 200 DF | 34 | 16% CP5 |
| Granule 5 | 71% bentonite | 17 | 12% CP5 |

**[0050]** Gasil 230 is a neutral silica with an APS of 3.6 microns and a pore volume of 1.6 ml/g.
**[0051]** Gasil 200DF is an acidic silica with an APS of 4.3 microns and a pore volume of 0.4 ml/g. Gasil 200TP is similar to Gasil 200DF.

**Example 2 Bleeding tests**

**[0052]** The granules of example 1 were added to detergent powders of the following formulations, so that the powder contained 0.01 wt% solvent violet 13. The powders were stored in open cups at 310 K, and 70% Relative humidity for 1 month.
**[0053]** Formulation (1) surfactant system: 18% sodium LAS. Builder system: 28% Sodium tripolyphosphate, sodium carbonate and sodium disilicate. Bleach system: none. Remainder sodium sulphate.
**[0054]** Formulation (2) surfactant system: 7% sodium LAS, 3% non-ionic (7EO). Builder system: 45% Sodium tripolyphosphate, sodium carbonate, sodium disilicate. Bleach system: none. Remainder sodium sulphate.
**[0055]** Formulation (3) surfactant system: 10% sodium LAS, 5% non-ionic (7EO). Builder system: 35% zeolite 4A, sodium carbonate, Bleach systems 16% sodium percarbonate and TAED. Remainder sodium sulphate.
**[0056]** After storage the powders were visually inspected for bleeding and compared to fresh powders. The results are given in the table below.

| | Formulation | | |
|---|---|---|---|
| | (1) | (2) | (3) |
| Granule 1 | No bleeding | No bleeding | No bleeding[1] |
| Granule 2 | Low level bleeding | Bleeding | No bleeding[1] |
| Granule 3 | Bleeding | Bleeding | No bleeding[1] |
| Granule 4 | Bleeding | Bleeding | No bleeding[1] |
| Granule 5 | No bleeding | Bleeding | White[2] |
| [1] blue coloured granules still observed in powder<br>[2] no coloured granules observed in powder after storage Granule 1 the silica granule with high level of CP5 gave the best overall performance. | | | |

**[0057]** The disappearance of colour in granule 4 indicates that the dye is destroyed over time by the bleach present in the formulation.
**[0058]** Performance test showed that some dye was also destroyed in formulation (3) with time, this was least with granule (2) with the acidic binder CP13.
**[0059]** No dye losses were seen from formulation (1) and (2) for any of the granules.

**Claims**

**1.** A granule comprising:

(i) from 5 to 30 wt% of a non-ionic surfactant having mixed between 0.00001 to 5% wt % of a high performance organic compound selected from the group consisting of dye, pigment, and antioxidant,
(ii) from 20 to 90 wt% of silica; and,

(iii) from 20 to 60 wt% of a binder that is other than a non-ionic surfactant,

wherein the fraction (wt% binder)/(wt% non-ionic) is greater than 1.

2. A granule according to claim 1, wherein the silica has a pore volume of from 0.2 to 2.5 ml/g.

3. A granule according to claim 1 or 2, wherein the silica has an average particle size, APS, from 1 to 15 microns.

4. A granule according to claim 3, wherein the silica is neutral or acidic.

5. A granule according to any preceding claim, wherein the binder is selected from the group consisting of: a polyacrylate, polyethylene glycol, and a polyacrylate/maleate copolymer.

6. A granule according to claim 5, wherein the binder is acidic.

7. A granule according to any proceeding claim wherein the non-ionic surfactant having mixed therein the HPOC is in contact with the silica and coated with the binder.

8. A granule according to any proceeding claim, wherein the HPOC is a dye.

**Patentansprüche**

1. Granulat, umfassend:

(i) 5 bis 30 Gew.-% eines nicht-ionischen Tensids, das zwischen 0,00001 bis 5 Gew.-% einer organischen Hochleistungsverbindung, ausgewählt aus der Gruppe, bestehend aus Farbstoff, Pigment und Antioxidans, eingemischt hat,
(ii) 20 bis 90 Gew.-% Siliciumdioxid und
(iii) 20 bis 60 Gew.-% eines anderen Bindemittels als ein nicht-ionisches Tensid, wobei der Bruch (Gew.-% Bindemittel) / (Gew.-% nicht-ionisches) größer als 1 ist.

2. Granulat gemäß Anspruch 1, wobei das Siliciumdioxid ein Porenvolumen von 0,2 bis 2,5 ml/g hat.

3. Granulat gemäß Anspruch 1 oder 2, wobei das Siliciumdioxid eine durchschnittliche Partikelgröße, APS, von 1 bis 15 Mikrometer hat.

4. Granulat gemäß Anspruch 3, wobei das Siliciumdioxid neutral oder sauer ist.

5. Granulat gemäß einem vorangehenden Anspruch, wobei das Bindemittel aus der Gruppe, bestehend aus einem Polyacrylat, Polyethylenglykol und einem Polyacrylat/Maleat-Copolymer, ausgewählt ist.

6. Granulat gemäß Anspruch 5, wobei das Bindemittel sauer ist.

7. Granulat gemäß einem vorangehenden Anspruch, wobei das nicht-ionische Tensid, das darin die HPOC eingemischt hat, mit dem Siliciumdioxid in Kontakt ist und mit dem Bindemittel beschichtet ist.

8. Granulat gemäß einem vorangehenden Anspruch, wobei die HPOC ein Farbstoff ist.

**Revendications**

1. Granule comprenant :

(i) de 5 à 30 % en poids d'un tensioactif non-ionique contenant un mélange entre 0,00001 et 5 % en poids d'un composé organique haute performance (HPOC) choisi dans le groupe constitué d'un colorant, d'un pigment et d'un antioxydant,
(ii) de 20 à 90 % en poids de silice, et

(iii) de 20 à 60 % en poids d'un liant qui est différent d'un tensioactif non-ionique,

dans lequel la fraction (% en poids de liant)/(% en poids de tensioactif non-ionique) est supérieure à 1.

**2.** Granule selon la revendication 1, dans lequel la silice a un volume de pore de 0,2 à 2,5 ml/g.

**3.** Granule selon la revendication 1 ou 2, dans lequel la silice a une taille moyenne de particule de 1 à 15 microns.

**4.** Granule selon la revendication 3, dans lequel la silice est neutre ou acide.

**5.** Granule selon l'une quelconque des revendications précédentes, dans lequel le liant est choisi dans le groupe constitué d'un polyacrylate, d'un polyéthylène glycol et d'un copolymère polyacrylate/maléate.

**6.** Granule selon la revendication 5, dans lequel le liant est acide.

**7.** Granule selon l'une quelconque des revendications précédentes, dans lequel le tensioactif non-ionique contenant le mélange de HPOC est en contact avec la silice et revêtu avec le liant.

**8.** Granule selon l'une quelconque des revendications précédentes, dans lequel le HPOC est un colorant.

## REFERENCES CITED IN THE DESCRIPTION

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