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Title: PERFORMANCE INGREDIENTS IN FILM PARTICLES

Abstract: A granular detergent composition comprising a plurality of film particles, each film particle comprising at least 30% polymer and 0.01 to 1 wt% of a benefit ingredient selected from the group comprising: shading dye, shading pigment, photo bleach, fluorescences antioxidant, transition metal catalyst and mixtures thereof characterised in that the cross sectional area of each film particle is between 4mm² and 100mm².
PERFORMANCE INGREDIENTS IN FILM PARTICLES

This invention relates to granular detergent compositions comprising a plurality of film particles.

BACKGROUND

It is known to include visually contrasting particles in granular laundry detergent compositions. The contrasting particles may deliver a functional ingredient or may simply provide a visual cue to the user.

In US 4082682, a minor proportion of contrastingly colored elongated soap particles is added to a detergent powder. The contrasting particles comprise a non fabric-substantive dye and a fluorescer. The powder comprises a detergency builder compound. The soap particles contribute detergency to the composition and reduce foaming. Because the soap particles could sink onto the fabric it is a stated advantage of the particles that they do not cause staining of the fabric with which they come into contact.

In GB2358403A a powder detergent composition having a major proportion of white or light-coloured particles has dry mixed into it a minor proportion of lamellar visually contrasting bodies of significantly larger average particle size in at least one dimension than the average particle size of the white or light-coloured particles. The examples used contrasting circular or star shaped bodies made of
coloured water-soluble polymer film. The visually contrasting bodies may optionally contain detergent functional ingredients.

WO200 6/079416 proposes to use a highly soluble film particle as a visual cue. It is suggested to be possible to include functional ingredients within the film e.g. surface active agents, perfume, antioxidant, antifoam. Examples in this application compare detergent powders containing 0.1 wt% visual cues made from polyvinyl alcohol with visual cues made from gum Arabic. Suitably, the film particles could be chosen to pass a 1400 μm sieve, but not a 500 μm sieve.

It is known to add sensitive ingredients to laundry powders as separately manufactured granules. This process may be referred to as dry mixing or post dosing.

US4176079 describes an alternative to post dosing granules. An enzyme is incorporated into a water soluble film and the functional film so produced is cut into squares, rectangles or strips and added to a detergent powder. Typical film additive compositions are polyvinyl alcohol 48.7 % and nonionic surfactant 43.8 % (balance water and enzyme). The cut functional film additive has a surface area of 300 mm².

US 2005/0075261 A1 relates to a water-soluble and/or water dispersible particle comprising an active ingredient, preferably an enzyme, in a matrix comprising from 20-95% of the particle of a specified polyvinylalcohol polymer. The examples make the particle by applying a chopping action to an extruded noodle. This would tend to make a granular
(spherical) particle. Other active ingredients suggested for inclusion at levels of 0.1 to 55% include: bleaches, bleach activators, bleach catalysts, brighteners and photobleaches. The particle size ranges from 200 µm to 2000 µm, preferably 250 µm to 800 µm. In an embodiment where the extruded (cylindrical) particle is not chopped up it can be up to 20 mm long, but it is preferably less than 1 mm long and has a preferred particle size distribution of 100 µm to 800 µm.

There remain a number of problems relating to the use of film particles in granular detergent compositions, especially granular laundry detergents.

A major problem is to make a visual cue film particle that aids cleaning. Surprisingly, we have now found new benefits from delivery of specific benefit ingredients from a film particle.

SUMMARY OF THE INVENTION

According to the present invention there is provided a granular detergent composition comprising a plurality of film particles, each film particle comprising at least 30% polymer and 0.01 to 1 wt% of a benefit ingredient selected from the group comprising: shading dye, shading pigment, photobleach, fluorescer, antioxidant, transition metal catalyst and mixtures thereof characterised in that the thickness of each film particle is less than 0.5 mm and the
cross sectional area of each film particle is between 4 mm$^2$ and 100 mm$^2$.

5 DETAILED DESCRIPTION OF THE INVENTION

Granular laundry detergent compositions are mainly composed of surfactants and electrolytes. Typical surfactants include linear alkyl benzene sulphonates, primary alcohol sulphates, linear alcohol ethoxysulphates and alcohol ethoxylates. Typical electrolytes are inorganic materials such as sodium sulphate, sodium chloride, sodium tripolyphosphates, sodium carbonate, silicas, and zeolites and organic materials such as polycarboxylates and citric acid.

To give additional wash benefits, benefit ingredients; namely fluorescers, shading dyes, photobleaches antioxidant and catalysts, may be included at low levels. Such benefit ingredients are most cost-effective when added at very low levels, typically less than 0.1wt% of the composition. The benefit ingredients are usually granulated and then post-dosed into the granular composition. This inevitably results in localised high concentrations of the benefit ingredient, which can cause problems if they come into contact with certain fabrics before they have had an opportunity to dissolve or disperse into the wash liquor. This problem is caused by the localised high concentration of the benefit ingredient and not by the timing of its release. The problem occurs particularly for low molecular weight benefit ingredients that cause damage to fabrics when
present at very high concentrations, particularly if delivered from a carrier substrate that has a higher solubility and/or dispersibility than the benefit ingredient.

Encapsulation of the benefit ingredient or ingredients within soluble polymeric film particles provides a solution to this problem. The amount of benefit ingredient in the film particle is preferably 0.05 to 1.0 wt% of the film particle.

The film particles are desirably rendered visible by non fabric-substantive dye that gives them a contrasting colour from the granules making up the remainder of the granular composition.

Granular detergent compositions of lighter colour than the film particles advantageously include some fluorescer and/or shading dye in the granules to give a higher contrast between the granules and the film particles.

The granular detergent composition is preferably highly alkaline when dissolved in deionised water. A 0.1% solution at 25 °C is > pH 10.5. To achieve this pH the granular detergent composition may advantageously comprise silicate and/or carbonate.

The film particle is preferably more near to a neutral pH to protect the benefit ingredient or ingredients contained therein. It has a pH of 3 to 9, preferably 6 to 8 when dissolved to form a 0.1% solution in deionised water.
Although many soluble polymers could be suitable for inclusion in the film particle, a preferred polymeric material is polyvinyl alcohol. To improve its solubility and to facilitate easy inclusion of the benefit ingredients the film particles desirably further comprise 5 to 50 wt% surfactant. Preferred surfactant content of the film particles is at least 5 wt% anionic surfactant, most preferably an alkyl sulphate.

Preferred film compositions are those that comprise a polymer and a surfactant. Optionally a colorant is also included as a preferred ingredient of the film, in addition to the performance ingredient.

Optional further ingredients are: adjuncts to assist in the manufacture of the film, for instance release agents and water. Besides its effect of control of relative humidity of the film, water also assists in plasticising the film and regulates its solubility.

The polymer may be selected from water soluble film forming polymers, especially those used in formulation of detergent powders. Preferred polymers include polymers which dissolve and disperse completely in water within 30 minutes with agitation at a temperature anywhere in the range of from 293 to 333K.

Preferred water soluble polymers are those capable of being cast into a film or solid mass, for example as described in Davidson and Sittig, Water-Soluble Resins, Van Nostrand Reinhold Company, New York (1968). Preferred water-soluble
resins include polyvinyl alcohol, cellulose ethers, polyethylene oxide, starch, polyvinylpyrrolidone, polyacrylamide, polyvinyl methyl ether-maleic anhydride, polymaleic anhydride, styrene maleic anhydride, hydroxyethylcellulose, hydroxypropylmethylcellulose, polyethylene glycols, carboxymethylcellulose, polyacrylic acid salts, alginates, acrylamide copolymers, guar gum, casein, ethylene-maleic anhydride resin series, polyethyleneimine, ethyl hydroxyethylcellulose, ethyl methylcellulose, hydroxyethyl methylcellulose, sugars. Lower molecular weight water-soluble, polyvinyl alcohol film-forming resins are preferred.

Polyvinyl alcohols preferred for use therein have an average molecular weight anywhere between 1,000 and 1,000,000, preferably between 5,000 and 250,000, for example between 15,000 and 150,000. Hydrolysis, or alcoholysis, is defined as the percent completion of the reaction where acetate groups on the resin are substituted with hydroxyl, -OH, groups. A hydrolysis range of from 60-99% of polyvinyl alcohol film-forming resin is preferred, while a more preferred range of hydrolysis is from about 70-90% for water-soluble, polyvinyl alcohol film-forming resins. The most preferred range of hydrolysis is 80-89%. As used in this application, the term "polyvinyl alcohol" includes polyvinyl acetate compounds with levels of hydrolysis disclosed herein.

Another suitable polymer is a polyvinyl alcohol film, made of a polyvinyl alcohol copolymer having a comonomer having a carboxylate function.
The preferred grade of PVA picks up water only at an RH well above that of granular detergent compositions. Thereby, it protects the other film ingredients from decomposition by water and soluble dyes from bleeding.

The visual cue film particle may comprise 10 to 80% polymer or polymer mixture.

Although any suitable surfactant or surfactant system may be used, the surfactant is preferably an anionic surfactant, especially if the granular composition comprises a builder.

Suitable anionic surfactants include are well-known to those skilled in the art. Examples of high-foaming sulphonate or sulphate type surfactants include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of Cs-Ci₅; primary and secondary alkylsulphates, particularly Cs-Ci₅ primary alkyl sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Further information is given in the open literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred anionic surfactants are alkylbenzene sulphonates, more especially linear alkylbenzene sulphonate (LAS), which is preferably present in an amount of from 12 to 24 wt%, more preferably from 12 to 22 wt% and especially from 15 to 22 wt%.
Even more preferred are primary alcohol sulphates (PAS), particularly Cs-Cis, preferably C12-C15, primary alcohol sulphates. A particularly preferred surfactant is primary alcohol sulphate (PAS) with a carbon chain length of 12.

Visual cue Film particles containing up to 50 % PAS, may be used.

The film may additionally include a second surfactant. The second surfactant is preferably chosen from amphoteric surfactants, zwitterionic surfactants, nonionic surfactants and ethoxylated anionic surfactants.

Preferred amphoteric second surfactants are amine oxides. The most preferred amine oxide is coco dimethylamine oxide.

Preferred zwitterionic second surfactants are betaines, and especially amidobetaines, for example, coco amidopropyl betaine.

Preferred nonionic second surfactants include the primary and secondary alcohol ethoxylates, especially the C8-C20 aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C10-C15 primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

Preferred ethoxylated anionic second surfactants, include alkyl ether sulphates (ethoxylated alcohol sulphates).
Also suitable for use as second surfactants in the visual cues of the present invention are Cs-Cis alkyl monoethanolamides, for example, coco monoethanolamide.

The second surfactant system used in the film particle may additionally comprise minor amounts, e.g. less than 5% of the film, of cationic surfactant.

Surfactant may be included at a level of up to 90 wt%, preferably up to 75 wt%, most preferably up to 60 wt% in the film.

The visual cue needs to be easily visible in wash liquor as well as against the background of the detergent formulation, therefore it is preferably coloured. Non fabric-substantive colorants may be included in the film composition at a level of 0.001 to 0.5 wt%, preferably 0.1 to 0.3 wt% of the film.

Suitable colorants include any that are used to colour detergent liquids or powders. Yellow, blue, violet, purple, red, orange, green, pink are preferred colours.

To get most effective use of their washing products many consumers soak their clothes in a solution of a laundry detergent composition. Often the clothes are placed into water, the laundry detergent composition sprinkled on top and clothes then left for 2 to 200 minutes. In this procedure, a granular laundry detergent composition may not fully dissolve and spotting of the clothes fabric with the benefit ingredients may occur. Spotting involves the incomplete dissolution of the granules and the subsequent
forming of a localised high concentration of the benefit ingredient in contact with the fabric of the clothes, this highly concentrated and localised overdose of benefit ingredient may then gel and it is then inhibited from further dispersion or dissolution. This problem is most pronounced and obvious with dyes and photobleaches where clear coloured spots occur on the fabric of the clothes. The phenomenon also reduces the effectiveness of the benefit ingredients, because not all of the ingredient is made available to the full wash.

This problem may be overcome by incorporating the benefit ingredients in a soluble polymer film that is then cut into discrete pieces having a low cross sectional area of less than 100mm$^2$. Such film particles may also serve the purpose of visual cues if they also include dye. Their function as a visual cue may be further enhanced by cutting the film particles into the shape of a flower with petals, or some other such natural object. The cross-sectional area should be at least 4mm$^2$. By cross-sectional area we mean the actual surface area of one side of the planar film particle.

The film particles have the additional advantage of keeping the often sensitive benefit ingredients away from the aggressive high pH of a base laundry detergent composition. It provides a clear visual cue to the user that the benefit ingredient is present. It is particularly desirable that the film particle floats when first added to water. This enhances the visibility of the film particle in use and can also assist with the reduction of spotting or other fabric damage due to the initial dissolution taking place on the
surface, which is likely to be remote from most of the fabrics being washed. To ensure that the film particle floats it is preferred that its relative density is less than 0.8, more preferably less than 0.5 and most preferably less than 0.4.

The thickness of the planar film of the film particle is at most 0.5mm. Preferably it is less than 0.3mm, most preferably 0.2mm. The film is of relatively uniform thickness to allow predictable dissolution characteristics. The thickness tolerance is at most plus or minus 20%, preferably plus or minus 10%.

**SHADING DYES**

It is highly preferred that the film particles comprise 0.01 to 1 wt% of a benefit ingredient selected from shading dye and pigment, for fabric whiteness.

The shading dye, or pigment, is selected from:

**Pigments**

Pigments are coloured particles preferably of 0.05 to 10 micron size, which are practically insoluble in aqueous media that contain surfactants. Preferred pigments are blue or violet.

Inorganic pigments such as pigment blue 29 or pigment violet 15 may be used, however, organic pigments are preferred.
Pigment blue 1, 1:2, 1:3, 2, 2:1, 2:2, 3, 4, 5, 7, 10, 10:1, 11, 12, 13, 14, 15, 15:1, 15:2, 15:3, 15:4, 15:6. 18, 19, 20, 21, 22, 23, 25, 26, 27, 28, 29, 30, 31, 32, 34, 35, 36, 37, 58, 59, 60, 61, 61:1, 62, 63, 64, 65, 66, 67, 69, 71, 72, 73, 74, 75, 80, 83 and pigment violet 3,, 3:1, 3:3, 3:4, 5, 7:1, 8, 9, 11, 12, 13, 14, 15, 16, 18, 19, 23, 25, 27, 28, 29, 31, 35, 37, 39, 41, 43, 44, 45, 47, 48, 50, 54, 55 and 56 may be used.

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.

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

The most preferred is pigment violet 23.

White pigments may also be used; these are especially suitable if the granular detergent composition is a deep hue, for example green or blue. Suitable White pigments are listed in the color index (Society of Dyers and Colourists
and American Association of Textile Chemists and Colorists 2002), pigment white 1 through pigment white 35 may be used to whiten the petal. Preferred are pigment white 18, pigment white 26, pigment white 27, pigment white 6, pigment white 4 and metal stearate salts where the metals are selected from Ba, Ca, Mg or Zn.

White pigments are described in detail in 'Industrial Inorganic Pigments' (3rd edition 2005 G.Buxbaum, G.Pfaff eds, Wiley VCH) and include TiO2, zinc white (ZnO), zinc sulfide and lithopone.

**Direct dyes**

Direct violet and direct blue dyes are even more preferred than pigments. Preferably, the dyes 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

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{NaO3S}n
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or

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25
where

\( R_i \) 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.

**Acid dyes**

Cotton substantive acid dyes give benefits to cotton containing fabrics. 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, a branched or linear Cl 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 NO2.

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.

**Hydrophobic dyes**

The benefit ingredient may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, naphthoquinone, anthraquinone and mono-azo or di-azo dye chromophores.

Hydrophobic dyes are dyes that 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.

**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.

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

**Reactive dyes**

Reactive dyes are dyes that 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 reacted with an organic species such as a polymer, so
Dyes may be selected from the reactive violet and reactive blue dyes listed in the colour index. Examples are reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue 96.

Dye conjugates

Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles via physical forces. Dependent on the choice of polymer or particle they deposit on cotton or synthetics. A description is given in WO2006/055787. They may be used as benefit ingredients but are not preferred.

Photobleach

Preferably, the benefit ingredient in the film particles comprises 0.01 to 1wt% of a photobleach for fabric whiteness and cleaning.

Singlet oxygen photo-bleaches are preferred.

Singlet oxygen photo-bleaches (PB) function as follows:

\[
PB + \text{light} \rightarrow PB^* \\
PB^* + O_2 \rightarrow PB + O_2
\]

The photo-bleach molecule absorbs light and attains an electronical excited state, PB*. This electronically excited state is quenched by triplet oxygen, \(O_2^\text{3}\), in the surroundings to form singlet \(O_2^\text{1}\). Singlet oxygen is a highly reactive bleach.
Suitable singlet oxygen photo-bleaches may be selected from, 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 phthalocyanine has 1-4 SO3X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769.

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

![Structure Image]

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.

Quantum yields for photosensitized formation of singlet oxygen may be found in J.Phys.Chem.Ref. Data 1993, vol 22, nol ppl3-262. It is preferred if the quantum yield for singlet oxygen formation measured in an organic solvent or D2O is greater than 0.05, more preferably greater than 0.1.

Other singlet oxygen producing compounds include chlorophyll, coumarin, porphyrins, myoglobin, riboflavin, bilirubin, and methylene blue.
Fluorescer

Preferably, the film particles comprise as benefit ingredient 0.01 to 1 wt% of a fluorescent agent (fluorescer), for fabric whiteness.

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 a laundry detergent composition is from 0.005 to 2 wt%, more preferably 0.01 to 0.1 wt%. Preferred fluorescers are: sodium 2-(4-styryl-3-sulfo phenyl)-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-sulfostyryl) biphenyl.
Antioxidant

Preferably, the film particles comprise as benefit ingredient 0.01 to 1 wt% of an antioxidant, to enhance the lifetime of the fabric.

If an antioxidant is present in the film particle, a bleach catalyst (other than photobleach) should not be present.

One class of antioxidants suitable for use in the present invention is alkylated phenols having the general formula:

\[
\text{OH} \quad [R_1]x \quad R
\]

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.

Another class of antioxidants 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-C₉ 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.

Other suitable antioxidants are found as follows. A derivative of α-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, and alkyl esters of gallic acid, especially octyl gallate and dodecyl gallate.

Another example of suitable antioxidants is the class of hindered amine light stabilisers (HALS), particularly those based 2,2,6,6-tetramethylpipiridines.

Non-limiting examples of antioxidants 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. Mixtures of antioxidants may be used and in particular mixtures that have synergic antioxidant effects as found in, for example, WO02/072746.
Bleach catalyst

Preferably, the film particles comprise 0.01 to 1 wt% of a transition metal catalyst, as benefit ingredient, to enhance cleaning of fabric.

Preferably, the catalyst is formed from a ligand containing 3 to 5 nitrogen atoms that coordinate to the transition metal. Ligands containing pyridine substituents are especially preferred. Of the transition metals Fe and Mn are particularly preferred ions.

The ligand is preferably in the form of a complex of the general formula (A1):

\[ [M_{\alpha}L_{\beta}X_{\gamma}]Y_{m} \]  

(A1)

in which:
M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably selected from Fe(II)-(III)-(IV)-(V), Mn(II)-(III)-(IV)-(V) or Co(I)-(II)-(III)-(IV)-(V)-(VI), most preferably Fe(II)-(III)-(IV)-(V), or Mn(II)-(III)-(IV)-(V);
L represents a ligand as herein defined, or its protonated or deprotonated analogue; X represents a coordinating species selected from any mono, bi or tridentate manner, preferably selected from O^2−, RBO₂^2−, RCOO^−, RCONR^−, OH^−, NO₃^−, NO, S^2−, RS^−, PO₄^3−, PO₃OR^3−, H₂O, CO₃^2−, HCO₃^−, ROH, N(R)₃, ROO^−, O₂^2−, O₂^−,
RCN, Cl\^-, Br\^-, OCN\^-, SCN\^-, CN\^-, N_3\^-, F\^-, I\^-, RO\^-, ClO_4\^-, and CF_3SO_3\^-, and more preferably selected from O^{2-}, RBO_2^{2-}, RCOO\^-, OH\^-, NO_3\^-, S^{2-}, RS\^-, PO_4^{3-}, H_2O, CO_3^{2-}, HCO_3\^-, ROH, N(R)\_3\^-, Cl\^-, Br\^-, OCN\^-, SCN\^-, RCN, N_3\^-, F\^-, I\^-, RO\^-, ClO_4\^-, and CF_3SO_3\^-. Y represents any non-coordinated counter ion, preferably selected from ClO_4\^-, BR_4\^-, [MX_4]\^-, [MX_4]^{2-}, PF_6\^-, RCOO\^-, NO_3\^-, RO\^-, N^+(R)\_4\^-, ROO\^-, O_2^{2-}, O_2\^-, Cl\^-, Br\^-, F\^-, I\^-, CF_3SO_3\^-, S_2O_6^{2-}, OCN\^-, SCN\^-, H_2O, RBO_2^{2-}, BF_4\^- and BPh_4\^-, and more preferably selected from ClO_4\^-, BR_4\^-, [FeCl_4]\^-, PF_6\^-, RCOO\^-, NO_3\^-, RO\^-, N^+(R)\_4\^-, Cl\^-, Br\^-, F\^-, I\^-, CF_3SO_3\^-, S_2O_6^{2-}, OCN\^-, SCN\^-, H_2O and BF_4\^-; 

a represents an integer from 1 to 10, preferably from 1 to 4; 
k represents an integer from 1 to 10; 
m represents an integer from 1 to 10, preferably from 1 to 4; 
and each R independently represents a group selected from hydrogen, hydroxyl, -R' and -OR', wherein R' = alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R' being optionally substituted by one or more functional groups E, wherein E independently represents a functional group selected from -F, -Cl, -Br, -I, -OH, -OR', -NH_2, -NHR', -N(R')_2, -N(R')_3^+, -C(O)R', -OC(O)R', -COOH, -COO\^- (Na\^+, K\^+), -COOR', -C(O)NH_2, -C(O)NHR', -C(O)N(R')_2, heteroaryl, -R', -SR', -SH, -P(R')_2, -P(O)(R')_2, -P(O)(OH)_2, -P(O)(OR')_2, -NO_2, -SO_3H, -SO_3\^- (Na\^+, K\^+), -S(O)_{2R'}, -NHC(O)R', and -N(R')C(O)R', wherein R' represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br,
- 25 -

-I, -NH\textsubscript{3}\textsuperscript{+}, -SO\textsubscript{3}H, -SO\textsubscript{3}\textsuperscript{-} (Na\textsuperscript{+}, K\textsuperscript{+}), -COOH, -COO\textsuperscript{-} (Na\textsuperscript{+}, K\textsuperscript{+}), -P(O) (OH)\textsubscript{2}, or -P(O) (O (Na\textsuperscript{+}, K\textsuperscript{+}))\textsubscript{2}, and preferably each R independently represents hydrogen, optionally substituted alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or Cl\textsubscript{-4} alkyl.

The counter ions Y in formula (Al) balance the charge z on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as RCOO\textsuperscript{-}, BPh\textsubscript{4}\textsuperscript{-}, ClO\textsubscript{4}\textsuperscript{-}, BF\textsubscript{4}\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-}, RSO\textsubscript{3}\textsuperscript{-}, RSO\textsubscript{4}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, F\textsuperscript{-}, Cl\textsuperscript{-}, Br\textsuperscript{-}, or I\textsuperscript{-}, with R being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl) ammonium cation.

Suitable counter ions Y include those that give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from R\textsuperscript{7}COO\textsuperscript{-}, ClO\textsubscript{4}\textsuperscript{-}, BF\textsubscript{4}\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-}, RSO\textsubscript{3}\textsuperscript{-} (in particular CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{-}), RSO\textsubscript{4}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, F\textsuperscript{-}, Cl\textsuperscript{-}, Br\textsuperscript{-}, and I\textsuperscript{-}, wherein R represents hydrogen or optionally substituted phenyl, naphthyl or Cl-C\textsubscript{4} alkyl.

The following are preferred ligands. Ligands of the form:
Ligands of the form:

\[
R_1 N - N - R_2 N - N - R_3 N - N - R_4
\]

In the cyclic structures R1 to R4 may be the same or different and are H, and linear or branched, substituted or unsubstituted C1-C20 alkyl, alkyaryl, alkenyl or alkynyl. Alternatively, opposite R groups may together form a bridge, preferably an ethylene bridge, and
Ligands may be substituted as appropriate. For example they may be substituted by sulphonlic and carboxylic acid groups; amines; quaternary amines; alkyl and alkoxy groups such as methyl, methoxy, ethyl and ethoxy; halogens; CN; and NO2.

A preferred ligand is of the form:

wherein $R^1$ is independently selected from H, and linear or branched, substituted or unsubstituted C1-C20 alkyl, alkylary, alkenyl or alkynyl. Preferably $R^1$ is methyl, most preferably ethyl.

A preferred ligand is of the form:
wherein -NR6R7 is selected from the group consisting of -
\[
\begin{array}{c}
  \text{NMe}_2 \\
  \text{NEt}_2 \\
  \text{N(i-Pr)}_2
\end{array}
\]

It is preferred that the ethylene bridge carrying the tertiary nitrogen is substituted by an alkyl group, preferably a methyl group. Most preferably the alkyl group is alpha to the bicyclo nitrogen carrying tertiary nitrogen.

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

**Example 1**

A film containing the [nitrolotris (2, 1-ethanediylxylo) ] tris [propanol] salt of direct violet 9 was prepared as follows:

A 30% solution of polymer (Polyvinyl alcohol) and surfactant (Lauryl Ether Sulphate) are dissolved in water at 60°C. After complete dissolution, 0.8% of the [nitrolotris (2, 1-ethanediylxylo) ] tris [propanol] salt of direct violet 9 is added and dissolved. This final solution is then spread as a thin layer over a glass plate of 24 x 34 cm and dried at 70-90°C in a drying oven.

After complete drying, the resulting film is taken from the glass plate and cut into the desired film particle shapes.
When film particles were dissolved in water to make a 0.284 wt% solution, the solution had an optical absorption at 550 nm (1cm path length) of 0.875.

Example 2

Sodium carbonate granules containing nominally 0.1 wt% of the [nitrolootris (2,1-ethanediyloxy) tris (propanol)] salt of direct violet 9, were created by mixing an aqueous solution of the dye with sodium carbonate and drying. The dye is an effective shading agent benefit ingredient for fabric whiteness.

When granules were dissolved in water to make a 1.83 wt% solution, the solution had an optical absorption at 550 nm (1cm path length) of 0.442. Therefore, the film particle is calculated to contain 13 times more dye per weight than the granules.

Example 3

Three 3 gram samples of a washing powder were prepared. The powder contained 18 wt% sodium LAS, 73 wt% salts (silicate, sodium tripolyphosphate, sodium sulphate, sodium carbonate), remainder impurities water and minors (enzymes and fluorescer). The three samples were labelled A, B and C. To A was added 0.100g of the carbonate granule of Example 2. To B was added 0.011g of the dye benefit ingredient containing film particles of Example 1. To C was added 0.084g of the film particles of Example 1. Thus, the
amounts of shading dye benefit ingredient in the samples were in the ratio A:B:C of 1:1.4:11.

In Examples B and C the dye film was cut into film particles with a cross sectional area of 5 to 6 mm².

Samples were thoroughly mixed before use.

A 1.7g piece of bleached non-mercerised, white woven cotton sheeting was placed in a beaker, so that the fabric filled the bottom of the beaker in a single flat layer. To this was added 100ml of demineralised water, then sample A was sprinkled over the cloth. The solution was gently agitated for a minute then left for 5 minutes. The cloth was removed and thoroughly rinsed twice, and left to dry.

The experiment was repeated with samples B and C.

Once the cloths had dried the number of dye spots on the cloths were counted. The results are shown in table 1.

<table>
<thead>
<tr>
<th>Example</th>
<th>No. of large spots</th>
<th>No. of small spots</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18</td>
<td>106</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

Large spots have a diameter of greater than 1 mm. Small spots have a diameter of less than 1 mm.
Although samples B and C contain more dye than A, there is a huge reduction in spotting.
**Exemplary Granular Laundry Compositions A, B, C, D**

<table>
<thead>
<tr>
<th>Composition</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaLAS</td>
<td>15</td>
<td>20</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>N1(7EO)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Na tripolyphosphate</td>
<td>7</td>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Soap</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Zeolite A24</td>
<td>-</td>
<td>-</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>23</td>
<td>20</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>40</td>
<td>30</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Carboxymethylcellulose</td>
<td>0.2</td>
<td>0.3</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Percarbonate</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>TAED</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Protease</td>
<td>0.005</td>
<td>0.01</td>
<td>-</td>
<td>0.005</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.15</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Perfume (petal)</td>
<td>0.01</td>
<td>-</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Petal**</td>
<td>1</td>
<td>0.5</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Amylase (petal)</td>
<td>0.001</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cellulase</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fluorescer</td>
<td>0.1</td>
<td>0.15</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>Direct Violet 9 (petal)</td>
<td>0.0002</td>
<td>0.0005</td>
<td>-</td>
<td>0.0004</td>
</tr>
<tr>
<td>Direct Violet 99</td>
<td>-</td>
<td>-</td>
<td>0.0003</td>
<td>-</td>
</tr>
<tr>
<td>Solvent Violet 13</td>
<td>-</td>
<td>0.002</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solvent Violet 13 (petal)</td>
<td>-</td>
<td>-</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Food Red 14 (petal)</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulfonated Zn</td>
<td>0.002</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pthalocyanine photobleach</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water/impurities/minors</td>
<td>remainder</td>
<td>remainder</td>
<td>remainder</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

**The petal is a film particle with cross-sectional area of 10 to 20 mm² and a film composition consisting of primary alkyl sulphate surfactant and polyvinyl alcohol polymer.**
The quantity given in this line includes the minor quantities of benefit ingredients included in the film particle and identified separately by "(petal)".

5 Enzyme levels are given as percent pure enzyme. Levels of direct violet 9, direct violet 99, solvent violet 13 and Sulfonated Zn Pthalocyanine photobleach are given as pure dye. NI (7EO) refers to R-(OCH₂CH₂)nOH, where R is an alkyl chain of C12 to C15, and n is 7.
CLAIMS

1. A granular detergent composition comprising a plurality of film particles, each film particle comprising at least 30% polymer and 0.01 to 1 wt% of a benefit ingredient selected from the group comprising: shading dye, shading pigment, photobleach, fluorescer, antioxidant, transition metal catalyst and mixtures thereof characterised in that the cross sectional area of each film particle is between 4 mm² and 100 mm².

2. A granular detergent composition according to claim 1 in which the film particles are rendered visible by non fabric-substantive dye that gives them a contrasting colour from the granular detergent composition.

3. A granular detergent composition according to claim 2 in which fluorescer and/or shading dye in the granules gives higher contrast between the granules and the film particles.

4. A granular detergent composition according to any preceding claim in which the composition is highly alkaline when dissolved in deionised water (0.1% solution at 25 deg C is >pH 10.5 and the film particles have a pH of 3 to 9), preferably 6 to 8 when separately dissolved to form a 0.1% solution in deionised water.

5. A granular detergent composition according to claim 4 in which the granular detergent powder comprises silicate and/or carbonate.
6. A granular detergent composition according to any preceding claim in which the polymer in the film particle comprises polyvinyl alcohol.

7. A granular detergent composition according to any preceding claim in which the film particle further comprises 5 to 50 wt% surfactant.

8. A granular detergent composition according to claim 7 in which the surfactant comprises at least 5 wt% anionic surfactant, preferably an alkyl sulphate.

9. A granular detergent composition according to any preceding claim in which the film particles comprise shading dye as the benefit ingredient.

10. A granular detergent composition according to any preceding claim in which the film particles are made from a soluble film material that floats on the wash liquor formed by the dissolution of the granular detergent composition.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D17/06 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

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 database consulted during the international search (name of database and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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<td>US 2005/075261 A1 (BAECK ANDRE CESAR [BE] ET AL) 7 April 2005 (2005-04-07) paragraphs [0012], [0019] - [0028], [0037] - [0040], [0044] - [0046], [0084], [0089], [0107] - [0125]; examples 4,5</td>
<td>1-10</td>
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Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search
6 February 2009

Date of mailing of the international search report
17/02/2009

Name and mailing address of the ISA/ European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HW Rijswijk, Tel (+31-70) 340-2040, Fax (+31-70) 340-3016

Authorized officer
Culmann, J
<table>
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<th>Publication date</th>
<th>Patent family member(s)</th>
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<td>US 2005075261</td>
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*Form PCT/ISA/210 (patent family annex) (April 2009)*