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Abstract: A granular detergent composition comprising anionic surfactant and a plurality of lamellar visual cues, each lamellar visual cue comprising at least 30% polymer and 0.01 to 50 wt% of perfume characterised in that the cross-sectional area of each lamellar visual cue is less than 100 mm².
This invention relates to granular detergent compositions comprising anionic surfactant and a plurality of contrasting lamellar visual cues, in particular to compositions comprising perfume.

BACKGROUND

It is known to include visually contrasting particles in granular detergent compositions. The visually 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 particles comprise a non fabric-substantive dye and fluoroscer. 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 polymer film. Mixed green and white circle film additives were added at a total level of 0.4 percent and red stars were added at a level of 0.1. The film additives may optionally also contain unspecified amounts of unspecified detergent functional ingredients.

WO2006/079416 proposes to use a high solubility film additive as a visual cue. It is suggested to be possible to include unspecified amounts of functional ingredients within the film e.g. surface active agents, perfume, antioxidant, antifoam. Examples in this application compare detergent powders containing 0.1% visual cues made from polyvinyl alcohol lamellae with visual cues made from gum Arabic lamellae. Suitably the film additives could be chosen to pass a 1400 µm sieve, but not a 500 µm sieve, thus the cross sectional area of each film additive would be at most about 2 mm².

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. Granules to add perfume in this way are known.

Film compositions per se have been suggested for use as cleaning products. FR2120295 gives examples of such compositions. Example 15 comprises glycerol, Sodium Lauryl sulphate, Carboxymethylcellulose, perfume and water. The
final film composition is not given. On a solids basis the perfume would be included in the film at a level of 0.18 wt%.

EP 1275368A1 discloses addition of a perfume composition to a water soluble polymeric film. The polymer is preferably selected from polyvinyl alcohol, modified polyvinyl alcohol, polyvinylpyrrolidone, starch, starch derivatives and modified cellulose. The examples all use large cross sectional areas of perfumed film: 50 cm$^2$, 25 cm$^2$. There is no suggestion to use the film pieces with a granular detergent composition.

EP1614743 discloses that addition of fragrance to laundry via a water soluble film is superior to direct addition of the same fragrance to the laundry detergent. The examples use a single sheet of polymer film with a perfume level of approx 25 wt%. The cross-sectional area of the film used is 113 cm$^2$. The examples show an improved perfume effect, in terms of perfume intensity on washed articles, for cellulosic film over polyvinyl alcohol film.

There remain problems relating to the use of polymer film as visual cues in perfumed granular detergent compositions, especially laundry detergents.

An object of the present invention is a granular composition comprising a plurality of lamellar contrasting visual cues that add functionality to the composition. Surprisingly we have discovered that there are advantages if perfume is delivered from specific sized lamellar visual cues.
SUMMARY OF THE INVENTION

According to the present invention there is provided a granular detergent composition comprising anionic surfactant where the fraction \([\text{wt}\% \text{ non-ionic surfactant}] / [\text{wt}\% \text{ anionic surfactant}]\) is 0 to 1 comprising a plurality of contrasting lamellar visual cues, each visual cue comprising at least 30 wt\% polymer and 0.01 to 50 wt\% perfume wherein the cross-sectional area of each visual cue is less than 100 mm\(^2\). For optimum visibility of the visual cue, the cross-sectional area should also be greater than 8 mm\(^2\).

The specified range of cross-sectional areas for the lamellar visual cues provides improved perfume intensity. This is most advantageous in wash solutions that contain anionic surfactant and where the fraction \([\text{wt}\% \text{ non-ionic surfactant}] / [\text{wt}\% \text{ anionic surfactant}]\) is 0 to 1. Thus, the total surfactant ratio of nonionic to anionic in the composition should lie in this range.

Additionally the perfume containing lamellar visual cues of these dimensions also confer the advantage that a wide range of perfumes are stabilised from decomposition by high pH or bleach in the granular composition.

DETAILED DESCRIPTION OF THE INVENTION

Granular laundry powder detergents are mainly composed of surfactants and electrolytes. Typical anionic surfactants include linear alkyl benzene sulphonates, primary alcohol
sulphates, linear alcohol ethoxysulphates and typical non-ionic surfactants are 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, high performance materials such as fluorescers, shading dyes, enzymes, photobleaches antioxidant and catalysts may be added at low levels to the composition. Such high performance materials are most cost-effective when added at low levels, typically less than 0.1 wt% of the full composition. The materials are usually granulated and then post-dosed into the composition.

A further ingredient that is normally added to commercial laundry compositions is perfume. Laundry products are appreciated by the consumer according to their smell. The smell of the product in the pack, the smell of the washing and water during the washing and drying process and the smell on the clothes after drying have all been the focus of much research and many patents. The smell in use in the wash is usually closely related to the smell in the pack.

Many consumers soak their clothes in a solution of detergent composition. Often the clothes are placed into water, the composition sprinkled on top and clothes left for 2 to 200 minutes. In this procedure, the consumer is exposed to the smell evolved from the water during the initial phases of the soak and also during the post soak washing operation. The perception of fragrance is often a key factor in
assessing the suitability of a particular laundry product for their needs. We have found that the fragrance may be enhanced and modified if it is included within a soluble polymer film that has been cut into discrete pieces having a low surface area of less than 100 mm². The lamellar visual cues may be rendered clearly visible in the powder and in the water by adding to them a dye that gives them a contrasting colour from the granules and by making them have a cross sectional area greater than 8 mm². The lamellar visual cues so formed are desirably dyed and shaped to look like tiny flowers with petals or some other such natural object.

Lamellar visual cues are essentially two dimensional particles made from a planar film. They have first and second dimensions larger than detergent granules so they are highly visible. The thickness of the film is preferably less than 0.5mm, more preferably less than 0.3mm and most preferably less than 0.2mm. The film is of relatively uniform thickness to allow predictable dissolution characteristics. The thickness tolerance is preferably at most plus or minus 20%, more preferably plus or minus 10%.

The polymer in the lamellar visual cues preferably comprises polyvinyl alcohol. The lamellar visual cues advantageously further comprise 5 to 50 wt% surfactant to enhance their solubility.

Preferably, the surfactant comprises at least 5 wt% anionic surfactant, most preferably an alkyl sulphate.
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-Cl5; primary and secondary alkylsulphates, particularly Cs-Cl5 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-C15, 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.

When the lamellae are used as visual cues they need to be easily visible in wash liquor as well as against the background of the detergent formulation, therefore the film 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 0.03. Suitable colorants include any that are used to colour detergent liquids or powders. Yellow, blue, violet, purple, red, lilac, orange, green, pink are preferred colours.

The lamellar visual cues may further comprise optional additional benefit ingredients at a level of 0.001 to 20%, selected from shading dyes, photobleach, fluorescer, antioxidant, enzymes, dye transfer inhibitors, decoupling polymers, sequestrants and bleach catalysts. Preferred additional benefit agents are shading dyes and fluorescer. The compositions comprising a plurality of such lamellar visual cues have the additional advantage of keeping the perfume and optionally other sensitive high performance materials away from the aggressive high pH of the granular components. Preferably, the granular composition is highly alkaline when dissolved in deionised water (0.1% solution at 25°C is >pH 10.5). This avoids the need to include any antioxidant or preservative in the film formulation. Such ingredients can interfere with perfume. To achieve such an alkaline pH it is typical that the granular detergent powder comprises significant quantities of silicate and / or carbonate.

Furthermore, to reduce the effect that the film formulation may have on the perfume and other benefit ingredients it may contain, it is desirable that the lamellar visual cues have a pH of 3 to 9, preferably 6 to 8 when they are separately dissolved to form a 0.1% solution in deionised water.
It is particularly desirable that the lamellar visual cues float when first added to water. This enhances the visibility of the visual cues in use, provides a clear cue that the perfume is present and, if the optional further benefit ingredients are present in the film, it can also assist with the reduction of spotting or other fabric damage due to the dissolution of the visual cue taking place on the surface, remote from most of the fabrics being washed. The evolution of perfume from a wash solution made form a composition comprising a plurality of floating lamellar visual cues of the type claimed also appears to be beneficial. To ensure that the visual cues float it is preferred that their relative density is less than 0.8, more preferably less than 0.5 and most preferably less than 0.4.

Surprisingly, it is found to be advantageous if the specified lamellar visual cues comprising polymer and perfume are used in compositions which comprise anionic surfactant and where the fraction \([\text{wt\% non-ionic surfactant}] / [\text{wt\% anionic surfactant}]\) is 0 to 1. Preferably the fraction \([\text{wt\% non-ionic surfactant}] / [\text{wt\% anionic surfactant}]\) is 0 to 0.1, most preferably 0. Linear alkyl benzene sulphonate is the most preferred anionic surfactant. To our surprise, the now preferred formulations give much higher perfume intensities in the wash liquor.

The level of anionic surfactant in the granular composition is preferably between 4 and 60 wt\%. More preferably between 6 and 20 wt\%.
Perfume

The amount of perfume in the lamellar visual cue is 0.01 to 50 wt%, preferably 0.1 to 40 wt% of the visual cue.

It is desirable if the perfume is an encapsulated perfume and the amount of perfume encapsulate in the lamellar visual cue is 15 to 40 wt% of the visual cue.

Examples of perfumes that may be used are found in WO2004/111174, WO2004/111171, WO2004/111172 and WO2005/059077. A perfume is not generally a single compound but usually a complex mixture made up of a mix of various fragrance notes. The present invention includes the use of individual compounds (fragrance notes) and complex mixtures.

The invention is particularly suited to perfumes that are not stable to high pH or bleach. In particular perfumes which decompose by more than 20% in aqueous solution at pH 11 for 7 days, or perfumes which decompose by more than 20% when exposed to aqueous solution containing 2 mM hydrogen peroxide or peracetic acid at pH 11, for 7 days. Percentages refer to loss in concentration in moles per litre. Tests should be performed at 293K with 1 mM perfume. To solubilise the perfumes, surfactants, preferably 1g/L Sodium dodecyl sulphate (SDS), may be used.

This includes compounds with a wide degree of different functional groups, for example, alcohols, ketones, esters, lactones, aldehydes, terpenes, and phenols.
Preferred examples of aldehydic perfumes are: cyclamen aldehyde, hydroxycitronellal, hydrocinnamic aldehyde, lilial, lyral, nonadienal, and phenylacetaldehyde.

Preferred examples of phenolic containing perfumes are: raspberry ketone, vanillin, ethyl vanillin, 4-propyl-2-methoxyphenol, 4-allyl-2-methoxyphenol, 4-propenyl-2-methoxyphenol, hexyl salicylate, cis-3-hexenyl salicylate, and methyl salicylate.

Perfumes are readily available for such firms as: International Flavors and Fragrances (IFF), Firmenich SA and Givaudan.

The following is a list of preferred perfumes that may be used with the present invention: Alpha demascone; Delta demascone; Iso E super; Cinnamic aldehyde; Hexylcinnamic aldehyde; Aldehyde butylcinnamic; benzaldehyde; anisique aldehyde; Linalol; Tetrahydrolinalol; Undecavertol; Geraniol; Nerol; Citronellol; citral; Oxyde de Rose; Geranyl acetate; Citronellyl acetate; Coumarine; Linalyl acetate; Geranyl nitrate; Citronellyl nitrile; Cinnaminitrile; Citronitrile; pinane; veloutone; Alpha-methylionone; damascenone; Gamma-terpinene; trifernal; lilial; citronellal; cyclosal; heliopropanal; zestover; Aldehyde C12; tridecylenicaldehyde; Cyclosia base; octenal; pulegone; Vertofix® Coeur, a methyl cedryl ketone from IFF; and, terpinolene.

Particularly advantageous perfume release effects are obtained if the perfumes that are included in the lamellar
visual cues are encapsulated. An encapsulated perfume is a perfume that is mixed with a polymeric material to form a particle of maximum dimension of 100 microns. Preferably the vapour pressure of the perfume is reduced in the encapsulated particle at 293K and 1 atmosphere pressure. Typical materials used to encapsulate perfumes are modified starches, cellulosics, amino-plast-resins and polyacrylates.

SHADING DYES

Optionally, the lamellar visual cues further comprise 0.1 to 1 wt% of a shading dye or pigment, for fabric whiteness. Such ingredients are compatible with perfume and can be incorporated into the film in the same way as the perfume.

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 medium 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,
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 preferred. 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

![Chemical structure](image)

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.

**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: $H$, a branched or linear C1 to C7-alkyl chain, benzyl, a phenyl, and a naphthyl;
the dye is substituted with at least one $S\theta^3$ 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 group;
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.

**Hydrophobic dyes**
The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, naphtoquinone, 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.

10 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's 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. Examples are Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue, 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 are not preferred.

Photobleach

Optionally, the lamellar visual cues contain 0.01 to 1 wt% of a photobleach, in addition to the perfume, for fabric whiteness and cleaning. Combinations of shading dye and photobleach are particularly preferred. The photobleach can be incorporated at the same time as the other additives; perfume and optional shading dye.

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

\[
\begin{align*}
PB & + \text{light} \rightarrow PB^* \\
PB^* & + ^3O_2 \rightarrow PB + ^1O
\end{align*}
\]

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 singlet oxygen 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 SO3X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (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.
Quantum yields for photosensitized formation of singlet oxygen may be found in J. Phys. Chem. Ref. Data 1993, vol 22, no1 pp13-262. It is preferred if the quantum yield for singlet oxygen formation measured in an organic solvent or D20 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**

Optionally, the lamellar visual cues may further comprise 0.01 to 1 wt% of a 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 laundry treatment composition is from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred fluorescers are: sodium 2-(4-styryl-3-sulfophenyl)-2H-napthol [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-sulfo styryl) biphenyl.
The invention will now be further described with reference to the following non-limiting examples.

**Example 1**

A polymer film containing 33 wt% of a perfume encapsulate (Denali, ex IFF) was made as follows:

A 30% solution of polymer (polyvinyl alcohol) and surfactant (Lauryl ether Sulphate) were dissolved in water at 60°C. After complete dissolution, the microencapsulated perfume (ex IFF) was dispersed into the solution. This final dispersion was then spread as a thin layer over a glass plate of 24 x 34 cm and dried.

After complete drying, the resulting film was taken from the glass plate and cut up.

**Example 2**

Two, 10 gram samples of a granular laundry detergent composition were prepared. It contained 18% sodium LAS. 73% salts (silicate, sodium tripolyphosphate, sodium sulphate, sodium carbonate), remainder impurities water and minors (enzymes and fluorescer). The powder contained no perfume. The samples were labelled A and B.

To A was added 0.13g of a perfume encapsulate (Denali, ex IFF). To B was added 0.4g of the cut perfume film of example 1. Therefore, initially A and B contained identical
amount of perfume. The perfume film was cut into rectangles of 5-6 mm by 1-2 mm. The two powders were thoroughly mixed, and the perfume intensity of the powder measured by an assessor.

The samples were then stored in open jars in a humidity cabinet at 310K and 70% relative humidity. The perfume odour was monitored by the same assessor over time. Before each assessment, the powder was vigorously shaken to release volatiles.

The results are shown in table 1.

Perfume intensity measured on a scale 0 (none) to 5 (high)

<table>
<thead>
<tr>
<th>Storage time</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4 Fruity peach melon</td>
<td>2 spicy</td>
</tr>
<tr>
<td>2 hours</td>
<td>2 fruity</td>
<td>3 Fruity + Spicy</td>
</tr>
<tr>
<td>20 hours</td>
<td>2 Peachy</td>
<td>3 Fruity + Spicy + rich aromatic</td>
</tr>
</tbody>
</table>

From the results, A has initial a much higher and more intricate smell then B, shown by the higher score and more descriptors (in italics). However very quickly on storage, B gains a higher score and has a more intricate smell.
Inclusion of the perfume in the film provided the granular composition with an improved perfume effect.

**Example 3**

The perfume film of example 1 was cut into samples of different size:

- C 2 x 3 cm pieces
- D 2 x 2 mm pieces

0.15 g of each sample size were weighed out and added to 40 ml solutions containing 0.5g/L of total surfactant at 293K, without agitation. The surfactants used for the study were linear alkyl benzene sulphonate (LAS), a non-ionic, \( R-(OCH_2CH_2)_nOH \), where \( R \) is a C12 to C15 alkyl chain \( n \) is 7 (NI), and a 1:1 mix of LAS:NI.

The odours of the liquid solutions were assessed immediately and after standing for 4 minutes at 293K. Perfume intensity measured on a scale 0 (none) to 5 (high).

The results are given in table 2.
The smaller maximum cross-sectional area film, $D$, gives much more perfume over the wash liquor, than the larger cross-sectional area film $C$. More perfume is detected from the LAS containing formulations and most from the nonionic free formulation.

Example 4

0.15 grams of the perfume film of Example 1 was added to 5 grams of the washing powder of Example 2. Four samples were made with the same total area of perfume film cut into rectangles of different individual cross-sectional areas. 120 ml of demineralised water was added to the powder, and the solution shaken for 1 minute. The odour of the wash liquor was assessed three times within 5 minutes. Perfume intensity measured on a scale 0 (none) to 5 (high). The results are shown in table 3.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>LAS</th>
<th>1:1 LAS:NI</th>
<th>NI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>D</td>
<td>C</td>
</tr>
<tr>
<td>Initial</td>
<td>1</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>4 minutes</td>
<td>0</td>
<td>4</td>
<td>0.5</td>
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Table 3

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<th>Perfume film dimensions</th>
<th>Perfume intensity</th>
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<td>2 x 3cm (600 mm²)</td>
<td>0.2</td>
</tr>
<tr>
<td>1 x 1.5cm (150 mm²)</td>
<td>0.5</td>
</tr>
<tr>
<td>1 x 0.75cm (75 mm²)</td>
<td>1.3</td>
</tr>
<tr>
<td>2 x 2mm (4 mm²)</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The samples with the smaller cross-sectional area give higher perfume scores than the larger.

Example 5

The perfume film of example 1 was cut into samples of different size:

- C  5 x 20 mm piece
- D  2 x 2 mm piece

One of each sample size were weighed out and added to 100ml solutions containing 0.5g/l of total surfactant at 293K, without agitation. The surfactants used for the study were linear alkyl benzene sulphonate (LAS), a non-ionic, \( R-(OCH_2CH_2)_nOH \), where \( R \) is a C12 to C15 alkyl chain and \( n \) is 7 (NI), and a 1:1 mix of LAS:NI.

The total weight of film added to the LAS solution was 0.048g. The total weight of film added to the LAS:NI solution was 0.042g. The total weight of film added to the NI solution was 0.046g. Thus, the weight of perfume encaps added via the film was 0.018g at maximum.
The odours of the liquid solutions were assessed immediately and after standing for 4 minutes at 293K. Initially the odour of the wash liquors were

\[ \text{LAS} > \text{LAS} : \text{NI} > \text{NI} \]

Very little perfume could be detected from the NI surfactant solution, but considerably more perfume from the LAS:NI which was almost as strong an odour as the pure LAS solution. After 4 mins the order of perfume intensity remained the same.

After 4 mins, the film pieces were still visible in all the liquors and visibly intact. The smaller piece was removed, dried and reweighed. The %wt remaining was 62% for the LAS, 57% for the LAS:NI, 75% for the NI. These differences in solubility are too small to explain the observed difference in perfume. The perfume is released by a complex diffusion mechanism which is not fully understood.

The experiment was repeated but adding 0.03g of the Denali perfume encaps directly to the wash liquor. Initially no perfume could be detected from any of the wash liquors, unlike in the case of the perfume films. To release perfume the solutions were shaken and left for 20 minutes. The perfume remained very weak in all samples and the order of smell intensity was

\[ \text{NI} > \text{LAS} \sim \text{LAS : NI} \]

The difference between the solutions was much smaller than in the film example.

To show that the temperature of manufacture of the film did not account for the observed difference we added 0.09g of
Denali perfume encaps to 100g water at 293K and 333K. The warmer sample was then cooled to 293K and both samples assessed for perfume intensity. No difference was discernable.
**Exemplary Granular Detergent Compositions A, B, C, D**

<table>
<thead>
<tr>
<th>Composition</th>
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<th>B</th>
<th>C</th>
<th>D</th>
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<tr>
<td>NaLAS</td>
<td>15</td>
<td>20</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Ni(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>
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<tr>
<td>Soap</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Zeolite A24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17</td>
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<td>Sodium silicate</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>1</td>
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<td>Sodium carbonate</td>
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<td>20</td>
<td>30</td>
<td>20</td>
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<td>Sodium sulphate</td>
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<td>30</td>
<td>40</td>
<td>20</td>
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<td>Carboxymethylcellulose</td>
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<td>0.3</td>
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<td>0.5</td>
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<td>Percarbonate</td>
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<td>-</td>
<td>10</td>
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<tr>
<td>TAED</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>4</td>
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<td>Protease</td>
<td>0.005</td>
<td>0.01</td>
<td>-</td>
<td>0.005</td>
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<td>Perfume</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Perfume (visual cue)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.03</td>
<td>0.3</td>
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<tr>
<td>Lamellar visual cue**</td>
<td>1</td>
<td>0.5</td>
<td>0.1</td>
<td>2</td>
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<tr>
<td>Cellulase</td>
<td>-</td>
<td>0.003</td>
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<td>Fluorescer</td>
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<td>0.15</td>
<td>0.05</td>
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<tr>
<td>Direct Violet 9 (visual cue)</td>
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<td>Direct Violet 99</td>
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<td>0.01</td>
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<tr>
<td>Sulfonated Zn</td>
<td>0.002</td>
<td>0.004</td>
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<tr>
<td>Pthalocyanine photobleach</td>
<td>Remainder</td>
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<td>remainder</td>
<td>Remainder</td>
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<tr>
<td>Water/impurities/minors</td>
<td>Remainder</td>
<td>remainder</td>
<td>remainder</td>
<td>Remainder</td>
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**The lamellar visual cue has a 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 "(visual cue)".

Levels of direct violet 9, direct violet 99, solvent violet 13 and Sulfonated Zn Phthalocyanine 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.
1. A granular detergent composition comprising anionic surfactant and optionally nonionic surfactant where the fraction [wt% non-ionic surfactant]/[wt% anionic surfactant] is 0 to 1 and further comprising a plurality of lamellar visual cues, each lamellar visual cue comprising at least 30% polymer and 0.01 to 50wt% of perfume characterised in that the cross-sectional area of each lamellar visual cue is less than 100 mm².

2. A granular detergent composition according to claim 1 in which the amount of perfume in the lamellar visual cue is 0.1 to 40 wt% of the additive.

3. A granular detergent composition according to claim 1 in which the perfume is an encapsulated perfume and the amount of perfume encapsulate in the lamellar visual cue is 15 to 40 wt% of the additive.

4. A granular detergent composition according to any preceding claim in which the lamellar visual cues are rendered visible by comprising dye or pigment that gives them a contrasting colour from the granules.

5. A granular detergent composition according to any preceding claim in which the composition is highly alkaline when dissolved in deionised water (1% solution at 25deg C is >pH 10.5 and the lamellar visual cue has a pH of 3 to 9, preferably 6 to 8 when it is separately dissolved to form a 1% solution in deionised water.
6. A granular detergent composition according to claim 5 in which the granular detergent powder comprises silicate and/or carbonate.

7. A granular detergent composition according to any preceding claim in which the polymer in the lamellar visual cues comprises poly vinyl alcohol.

8. A granular detergent composition according to any preceding claim in which the lamellar visual cues further comprise 5 to 50wt% surfactant.

9. A granular detergent composition according to any preceding claim in which the fraction [wt% non-ionic surfactant]/[wt% anionic surfactant] is 0 to 0.1, preferably 0.

10. A granular detergent composition according to any preceding claim in which the anionic surfactant in the granules is Linear alkyl benzene sulphonate.

11. A granular detergent composition according to any preceding claim in which the lamellar visual cues further comprise additional benefit ingredients at a level of 0.001 to 20% selected from shading dyes, photobleach, fluorescer, dye transfer inhibitor, sequestrant, decoupling polymer, antioxidant, enzymes, bleach catalysts and mixtures thereof.

12. A granular detergent composition according to claim 11 in which the lamellar visual cues comprise shading dyes.
13. A granular detergent composition according to claim 11 or 12 in which the lamellar visual cues comprise fluorescer.

14. A granular detergent composition according to any preceding claim in which the lamellar visual cues 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. C11D3/50 C11D17/06 C11D3/37 C11D1/02

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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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

5 February 2009

Date of mailing of the international search report

13/02/2009

Name and mailing address of the ISA/

European Patent Office, P B 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040,
Fax (+31-70) 340-3016

Authorized officer

Culmann, J

Form PCT/ISA/210 (second sheet) (April 2005)
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