Title: IMPROVEMENTS RELATING TO FABRIC TREATMENT COMPOSITIONS

Abstract: A laundry detergent composition, which comprises: (i) an encapsulated volatile benefit agent; (ii) an encapsulated phase change active having a phase transition temperature of from 24 to 39°C; (iii) at least one anionic surfactant; and (iv) at least one non-ionic surfactant; wherein the composition further comprises a non-encapsulated volatile benefit agent.
IMPROVEMENTS RELATING TO FABRIC TREATMENT COMPOSITIONS

Technical Field

The present invention relates to laundry detergent compositions comprising volatile benefit agent in encapsulated and non-encapsulated forms, encapsulated phase change material and an anionic and a non-ionic surfactant.

Background

Fragrances are a valuable and ubiquitously employed benefit agent in home and personal care applications. The use of perfumes in laundering signals to the consumer that the washing process has been achieved to an acceptable level.

Encapsulated perfume technologies are known for use in laundry products. Such technologies provide enhanced fragrance delivery over conventional free perfume oil by overcoming the issue of perfume loss during the drying process by protecting the perfume in the capsule. Encapsulation also ensures that perfume is released at the optimal time to enable the provision of a perceivable benefit to the wearer of laundered garments. Examples of the mode of action of encapsulates include: shear sensitive action, where the perfume core is released in response to mechanical rupture of the encapsulate, and diffusive action, wherein perfume is released by diffusion through the outer wall of the encapsulate. Some encaps are capable of both release mechanisms. One type of capsule that has been used in laundry compositions has a melamine formaldehyde shell and a perfume core. Release of perfume from melamine formaldehyde capsules is friction based, the benefit becoming apparent after a rubbing process is applied to the treated fabric. This benefit is provided by a boost in perfume intensity during wear.

WO 201 0/060677 (Henkel AG & Co KGAA) discloses scented washing or cleaning agents, comprising anionic and non-ionic surfactants, encapsulated
scents and non-encapsulated scents. A preferred embodiment further comprises an encapsulated active comprising urea or other skin conditioning agents.

We have now found that the inclusion of a low level of encapsulated phase change material significantly increase the shear release effect associated with a fabric cleaning formulation containing conventional encapsulated volatile benefit agents, for example perfume.

**Definition of the Invention**

In a first aspect, the present invention provides a laundry detergent composition, which comprises:

(i) an encapsulated volatile benefit agent;

(ii) an encapsulated phase change active having a phase change temperature of from 24 to 39 °C;

(iii) at least one anionic surfactant;

(iv) at least one non-ionic surfactant; and

(v) a non-encapsulated volatile benefit agent.

In a second aspect of the present invention there is provided a process for treating fabric comprising the step of treating a fabric article with a composition as defined by the first aspect.

**Detailed Description of the Invention**

**The Encapsulated Volatile Benefit Agent**

The encapsulated volatile benefit agent comprises a capsule and a volatile benefit agent. The capsule comprises a shell and a core.
The capsule comprising the volatile benefit agent comprises a shell that is comprised of materials including but not limited to polyurethane, polyamide, polyolefin, polysaccarhride, protein, silicone, lipid, modified cellulose, gums, polyacrylate, polyphosphate, polystyrene, polyesters or combinations of these materials. Other encapsulating material which may be used effectively in the present invention, such as polymethylmethacrylate. Preferred encapsulating polymers include those formed from melamine formaldehyde or urea formaldehyde condensates, as well as similar types of aminoplasts. Most preferably the shell comprises melamine formaldehyde.

Additionally, microcapsules made via the simple or complex coacervation of gelatin are suitable for use in compositions of the invention.

A representative process used for aminoplast encapsulation is disclosed in 3516941 USAU.S. Patent No. 3,516,941 though it is recognised that many variations with regard to materials and process steps are possible. A representative process used for gelatin encapsulation is disclosed in 2800457 USAU.S. Patent No, 2,800,457 though it is recognized that many variations with regard to materials and process steps are possible. Both of these processes are discussed in the context of fragrance encapsulation for use in consumer products in 4145184 USAU.S. Patent Nos. 4,145,184 and 5,112688 USA5,1 12,688 respectively.

Encapsulation can provide pore vacancies or interstitial openings depending on the encapsulation techniques employed.

Fragrance capsules known in the art and suitable for use in the present invention comprise a wall or shell comprising a three-dimensional cross-linked network of an aminoplast resin, more specifically a substituted or un-substituted acrylic acid polymer or co-polymer cross-linked with a urea-formaldehyde pre-condensate or a melamine-formaldehyde pre-condensate.
Microcapsule formation using mechanisms similar to the foregoing mechanism, using (i) melamine-formaldehyde or urea-formaldehyde pre-condensates and (ii) polymers containing substituted vinyl monomeric units having proton-donating functional group moieties (e.g. sulfonic acid groups or carboxylic acid anhydride groups) bonded thereto is disclosed in 44068162USBU.S. Patent 4,406,816 (2-acrylamido-2-methyl-propane sulfonic acid groups), 2062570GBAUK published Patent Application GB 2,062,570 A (styrene sulfonic acid groups) and 2006709GBAUK published Patent Application GB 2,006,709 A (carboxylic acid anhydride groups).

The capsules for use in the invention may further comprise a carrier oil in the core. The carrier oils are hydrophobic materials that are miscible in the volatile benefit agent materials used in the present invention. Suitable oils are those having reasonable affinity for the benefit agent. Where the benefit agent is a perfume, suitable materials include, but are not limited to triglyceride oil, mono and diglycerides, mineral oil, silicone oil, diethyl phthalate, polyalpha olefins, castor oil and isopropyl myristate. Preferably, the oil is a triglyceride oil, most preferably a capric/caprylic triglyceride oil.

For liquid laundry detergent compositions, the capsules may be used in the form of a slurry, which preferably comprises about 40% solids.

Particle size and average diameter of the capsules can vary from about 10 nanometers to about 1000 microns, preferably from about 50 nanometers to about 100 microns, more preferably from about 2 to about 40 microns, even more preferably from about 4 to 15 microns. A particularly preferred range is from about 5 to 10 microns, for example 6 to 7 microns. The capsule distribution can be narrow, broad or multimodal. Multimodal distributions may be composed of different types of capsule chemistries.
The shell may further comprise a deposition aid, which is preferably covalently attached.

A preferred deposition aid is a polysaccharide. The polysaccharide preferably has a $\beta$-1,4-linked backbone.

Preferably the polysaccharide is a cellulose, a cellulose derivative, or another $\beta$-1,4-linked polysaccharide having an affinity for cellulose, such as polymannan, polyglucan, polyglucomannan, polyxyloglucan and polygalactomannan or a mixture thereof. More preferably, the polysaccharide is selected from the group consisting of polyxyloglucan and polygalactomannan.

Highly preferred polysaccharides are selected from locust bean gum, tamarind gum, xyloglucan, non-ionic guar gum, cationic starch and mixtures thereof. Most preferably, the deposition aid is locust bean gum.

Preferably, the polysaccharide backbone has only $\beta$-1,4 linkages. Optionally, the polysaccharide has linkages in addition to the $\beta$-1,4 linkages, such as $\beta$-1,3 linkages. Thus, optionally some other linkages are present. Polysaccharide backbones which include some material which is not a saccharide ring are also within the ambit of the present invention (whether terminal or within the polysaccharide chain).

The polysaccharide may be straight or branched. Many naturally occurring polysaccharides have at least some degree of branching, or at any rate at least some saccharide rings are in the form of pendant side groups (which are therefore not in themselves counted in determining the degree of substitution) on a main polysaccharide backbone.

Preferably, the polysaccharide is present at levels of between 0.1% to 10% w/w by weight of the total amount of the particle.
The deposition aid, which is preferably a polysaccharide, is attached to the particle by means of a covalent bond, entanglement or strong adsorption, preferably by a covalent bond or entanglement and most preferably by means of a covalent bond. By entanglement as used herein is meant that the deposition aid is adsorbed onto the particle as the polymerisation proceeds and the particle grows in size, part of the adsorbed deposition aid becomes buried within the interior of the particle. Hence at the end of the polymerisation, part of the deposition aid is entrapped and bound in the polymer matrix of the particle, whilst the remainder is free to extend into the aqueous phase.

By strong adsorption as used herein is meant strong adsorption of the deposition aid to the surface of the particle; such adsorption can, for example, occur due to hydrogen bonding, Van Der Waals or electrostatic attraction between the deposition aid and the particle.

The deposition aid is thus mainly attached to the particle surface and is not, to any significant extent, distributed throughout the internal bulk of the particle. This is distinct from graft copolymers in which e.g. a polysaccharide may be grafted along the length of a polymer chain. A particle which is formed from a graft copolymer would, therefore, contain polysaccharide throughout the internal bulk of the particle as well as on the particle surface and the present invention is not intended to cover such a particle. Thus the particle which is produced when using a polysaccharide as the deposition aid according to the process of the invention can be thought of as a "hairy particle", which is different from a graft copolymer. This feature of the invention provides significant cost reduction opportunities for the manufacturer as much less deposition aid is required to achieve the same level of activity as systems which utilise polysaccharide copolymers.

The deposition aid is present in the outermost portion of the shell, which is made of melamine formaldehyde polymer having a thickness of from 5 to 20 nm.
Polyesters of terephthalic and other aromatic dicarboxylic acids having soil release properties, in particular, the so-called PET/POET (polyethylene terephthalate/polyoxyethylene terephthalate) and PET/PEG (polyethylene terephthalate/polyethylene glycol) polyesters may be employed as deposition aids.

The polymer must have at least one mole free OH group per mole polymer, to allow covalent binding to the reactive dye(s). Most preferably the polymer comprises at least two free OH groups. Preferably the OH groups are the terminal groups of the polymer.

Preferably, the oxyalkyleneoxy [-O(CH$_2$)$_n$O-] is selected from: oxy-1,2-propyleneoxy [-OCH$_2$CH(Me)O-]; oxy-1,3-propyleneoxy [O-CH$_2$CH$_2$CH$_2$O-]; and, oxy-1,2-ethyleneoxy [-OCH$_2$CH$_2$O-] (t is an interger). As is evident one or more of the CH$_2$ groups of the oxyalkyleneoxy may be substituted by C1 to C4 alkyl group(s).

The polyoxyalkyleneoxy facilitates water solubility of the polymer. Preferably, the polyoxyalkyleneoxy [-O(CH$_2$)$_w$]-O- is selected from: polyoxy-1,2-propyleneoxy [-O(CH$_2$CH(Me))-SO-]; polyoxy-1,3-propyleneoxy [O-CH$_2$CH$_2$CH$_2$]-O-; and, polyoxy-1,2-ethyleneoxy [O-CH$_2$CH$_2$]-O-. The polyoxyalkyleneoxy may be a mixture of different oxyalkyleneoxy. Different polyoxyalkyleneoxy types may present in the polymer. (s and w are intergers).

Preferably the phenyl dicarboxylate is a 1,4-phenyl dicarboxylate. Preferably the phenyl dicarboxylate is of the form: -OC(O)C$_6$H$_4$C(O)O-. Examples of preferred polymers are a PET/POET (Polyethylene terephthalate/polyoxyethylene terephthalate), PEG/POET (Polyethyleneglycol/polyoxyethylene terephthalate) or PET/PEG (Polyethylene terephthalate/Polyethyleneglycol) polymer. Most preferable a PET/POET.
The structure of a preferred polymer is found below.

\[
\begin{array}{c}
\text{R}_2 \quad \text{H}_2 \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{C} \quad \text{O} \\
\text{H} \quad \text{R}_2 \quad \text{O} \quad \text{C} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\end{array}
\]

wherein

- \( R_2 \) is selected from H or CH\(_3\), preferably H;
- \( b \) is 2 or 3, preferably 2;
- \( y \) is 2 to 100, preferably 5 to 50;
- \( n \) and \( m \) are independently 1 to 100, preferably 2 to 30; and, the terminal (end) groups of the polymer are \((\text{CH}_2)_b\text{OH}\).

The polymers may be synthesised by a variety of routes, for example an esterification reaction of dimethyl terephthalate with ethyleneglycol and polyethyleneglycol, this reaction is discussed in Polymer Bulletin 28, 451-458 (1992). Another example would be the direct esterification of terephthalic acid with ethylene glycol and/or propylene glycol and polypropylene glycol.

A further example would be a transesterification of a polyethyleneterephthalate with a polyethyleneglycol or polypropylene glycol.

It is preferred that the number average molecular weight of the polymer is in the range from 1000 to 50,000, preferably the average molecular weight of the polymer is in the range of from 1000 to 15000, more preferably from 2000 to 10000.
The Volatile Benefit Agent

The volatile benefit agent is an agent which is volatile and which confers a benefit to fabric.

Suitable volatile benefit agents include but are not limited to perfumes, insect repellents, essential oils, sensates such as menthol and aromatherapy actives, preferably perfumes. Mixtures of volatile benefit agents may be used.

The total amount of volatile benefit agent is preferably from 0.01 to 10 % by weight, more preferably from 0.05 to 5 % by weight, even more preferably from 0.1 to 4.0 %, most preferably from 0.15 to 4.0 % by weight, based on the total weight of the composition.

The preferred volatile benefit agent is a perfume. The compositions of the compositions of the invention also comprise an unconfined (also called non-encapsulated) volatile benefit agent. Where the volatile benefit agent is a perfume, the perfumes described below are suitable for use as the encapsulated volatile benefit agent and also as the unconfined perfume component.

Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming, flavouring, and/or aromatizing consumer products, i.e., of imparting an odour and/or a flavour or taste to a consumer product traditionally perfumed or flavoured, or of modifying the odour and/or taste of said consumer product.
By perfume in this context is not only meant a fully formulated product fragrance, but also selected components of that fragrance, particularly those which are prone to loss, such as the so-called 'top notes'.

Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Examples of well known top-notes include citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol. Top notes typically comprise 15-25%wt of a perfume composition and in those embodiments of the invention which contain an increased level of top-notes it is envisaged at that least 20%wt would be present within the encapsulate.

Some or all of the perfume or pro-fragrance may be encapsulated, typical perfume components which it is advantageous to encapsulate, include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100-250 Celsius and pro-fragrances which can produce such components.

It is also advantageous to encapsulate perfume components which have a low Clog P (i.e. those which will be partitioned into water), preferably with a Clog P of less than 3.0. These materials, of relatively low boiling point and relatively low Clog P have been called the "delayed blooming" perfume ingredients and include the following materials:

Allyl Caproate, Amyl Acetate, Amyl Propionate, Anisic Aldehyde, Anisole, Benzaldehyde, Benzyl Acetate, Benzyl Acetone, Benzyl Alcohol, Benzyl Formate, Benzyl Iso Valerate, Benzyl Propionate, Beta Gamma Hexenol, Camphor Gum, Laevo-Carvone, d-Carvone, Cinnamic Alcohol, Cynamyl Formate, Cis-Jasmone, cis-3-Hexenyl Acetate, Cuminic Alcohol, Cyclal C, Dimethyl Benzyl Carbinol, Dimethyl Benzyl Carbinol Acetate, Ethyl Acetate, Ethyl Aceto Acetate, Ethyl Amyl Ketone, Ethyl Benzoate, Ethyl Butyrate, Ethyl Hexyl Ketone, Ethyl Phenyl Acetate, Eucalyptol, Eugenol, Fenchyl Acetate, Flor Acetate (tricyclo Decenyl Acetate),
Frutene (tricyclco Decenyl Propionate), Geraniol, Hexenol, Hexenyl Acetate,
Hexyl Acetate, Hexyl Formate, Hydratropic Alcohol, Hydroxycitronellal, Indone,
Isoamyl Alcohol, Iso Menthone, Isopulegyl Acetate, Isoquinolone, Ligustral,
Linalool, Linalool Oxide, Linalyl Formate, Menthone, Menthyl Acetphenone,
Methyl Amyl Ketone, Methyl Anthranilate, Methyl Benzoate, Methyl Benyl Acetate,
Methyl Eugenol, Methyl Heptone, Methyl Heptine Carbonate, Methyl Heptyl
Ketone, Methyl Hexyl Ketone, Methyl Phenyl Carbinyl Acetate, Methyl Salicylate,
Methyl-N-Methyl Anthranilate, Nerol, Octalactone, Octyl Alcohol, p-Cresol, p-
Cresol Methyl Ether, p-Methoxy Acetphenone, p-Methyl Acetophenone, Phenoxy
Ethanol, Phenyl Acetaldehyde, Phenyl Ethyl Acetate, Phenyl Ethyl Alcohol, Phenyl
Ethyl Dimethyl Carbinol, Prenyl Acetate, Propyl Bornate, Pulegone, Rose Oxide,
Safrole, 4-Terpinenol, Alpha-Terpinenol, and/or Viridine.

Preferred non-encapsulated perfume ingredients are those hydrophobic perfume
components with a ClogP above 3. As used herein, the term "ClogP" means the
calculated logarithm to base 10 of the octanol/water partition coefficient (P). The
octanol/water partition coefficient of a perfume raw material (PRM) is the ratio
between its equilibrium concentrations in octanol and water. Given that this
measure is a ratio of the equilibrium concentration of a PRM in a non-polar solvent
(octanol) with its concentration in a polar solvent (water), ClogP is also a measure
of the hydrophobicity of a material-the higher the ClogP value, the more
hydrophobic the material. ClogP values can be readily calculated from a program
called "CLOGP" which is available from Daylight Chemical Information Systems
Inc., Irvine Calif., USA. Octanol/water partition coefficients are described in more
detail in U.S. Pat. No. 5,578,563.

Perfume components with a ClogP above 3 comprise: Iso E super, citronellol,
Ethyl cinnamate, Bangalol, 2,4,6-Trimethylbenzaldehyde, Hexyl cinnamic
aldehyde, 2,6-Dimethyl-2-heptanol, Diisobutylcarbinol, Ethyl salicylate, Phenethyl
isobutyrate, Ethyl hexyl ketone, Propyl amyl ketone, Dibutyl ketone, Heptyl methyl
ketone, 4,5-Dihydrotoluene, Caprylic aldehyde, Citral, Geranial, Isopropyl
benzoate, Cyclohexanepropionic acid, Campholene aldehyde, Caprylic acid, Caprylic alcohol, Cuminaldehyde, 1-Ethyl-4-nitrobenzene, Heptyl formate, 4-Isopropylphenol, 2-Isopropylphenol, 3-Isopropylphenol, Allyl disulfide, 4-Methyl-1-phenyl-2-pentanone, 2-Propylfuran, Allyl caproate, Styrene, Isoeugenyl methyl ether, Indonaphthene, Diethyl suberate, L-Menthone, Menthone racemic, p-Cresyl isobutyrate, Butyl butyrate, Ethyl hexanoate, Propyl valerate, n-Pentyl propanoate, Hexyl acetate, Methyl heptanoate, trans-3,3,5-Trimethylcyclohexanol, 3,3,5-Trimethylcyclohexanol, Ethyl p-anisate, 2-Ethyl-1-hexanol, Benzyl isobutyrate, 2,5-Dimethylthiophene, Isobutyl 2-butenoate, Caprylnitrile, gamma-Nonalactone, Nerol, trans-Geraniol, 1-Vinylheptanol, Eucalyptol, 4-Terpinenol, Dihydrocarveol, Ethyl 2-methoxybenzoate, Ethyl cyclohexanecarboxylate, 2-Ethylhexanal, Ethyl amyl carbinol, 2-Octanol, 2-Octanol, Ethyl methylphenylglycidate, Diisobutyl ketone, Coumarone, Propyl isovalerate, Isobutyl butanoate, Isopentyl propanoate, 2-Ethylbutyl acetate, 6-Methyl-tetrahydroquinoline, Eugenyl methyl ether, Ethyl dihydrocinnamate, 3,5-Dimethoxytoluene, Toluene, Ethyl benzoate, n-Butyrophenone, alpha-Terpineol, Methyl 2-methylbenzoate, Methyl 4-methylbenzoate, Methyl 3, methylbenzoate, sec. Butyl n-butyrate, 1,4-Cineole, Fenchyl alcohol, Pinanol, cis-2-Pinanol, 2,4, Dimethylacetophenone, Isoeugenol, Safrole, Methyl 2-octynoate, o-Methylanisole, p-Cresyl methyl ether, Ethyl anthranilate, Linalool, Phenyl butyrate, Ethylene glycol dibutyrat e, Diethyl phthalate, Phenyl mercaptan, Cumic alcohol, m-Toluquinoline, 6-Methylquinoline, Lepidine, 2-Ethylbenzaldehyde, 4-Ethylbenzaldehyde, o-Ethylphenol, p-Ethylphenol, m-Ethylphenol, (+)-Pulegone, 2,4-Dimethylbenzaldehyde, Isoxylaldehyde, Ethyl sorbate, Benzyl propionate, 1,3-Dimethylbutyl acetate, Isobutyl isobutanoate, 2,6-Xylenol, 2,4-Xylenol, 2,5-Xylenol, 3,5-Xylenol, Methyl cinnamate, Hexyl methyl ether, Benzyl ethyl ether, Methyl salicylate, Butyl propyl ketone, Ethyl amyl ketone, Hexyl methyl ketone, 2,3-Xylenol, 3,4, Xylenol, Cyclopentadenanolide and Phenyl ethyl 2 phenylacetate 2.

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there
will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components from the list given of delayed blooming perfumes given above and/or the list of perfume components with a ClogP above 3 present in the perfume.

The volatile benefit agent may be an insect repellent. In chemical terms, most repellent actives belong to one of four groups: amides, alcohols, esters or ethers. Those suitable for use in the present invention are liquids or solids with a relatively low melting point and a boiling point above 150 °C, preferably liquids. They evaporate slowly at room temperature. Where the volatile benefit agent is an insect repellent, the repellents described below are suitable for use as the encapsulated volatile benefit agent and also as the unconfined repellent component.

Many suitable insect repellents are related to perfume species (many fall into both classes). The most commonly used insect repellents include: DEET (N,N-diethyl-m-toluamide), essential oil of the lemon eucalyptus (Corymbia citriodora) and its active compound p-menthane-3,8-diol (PMD), Icaridin, also known as Picaridin, D-Limonene, Bayrepel, and KBR 3023, Nepetalactone, also known as "catnip oil", Citronella oil, Permethrin, Neem oil and Bog Myrtle.

Known insect repellents derived from natural sources include: Achillea alpina, alpha-terpinene, Basil oil (Ocimum basilicum), Callicarpa americana (Beautyberry), Camphor, Carvacrol, Castor oil (Ricinus communis), Catnip oil (Nepeta species), Cedar oil (Cedrus atlantica), Celery extract (Apium graveolens), Cinnamon (Cinnamomum Zeylanicum, leaf oil), Citronella oil (Cymbopogon fleusus), Clove oil (Eugenic Caryophyllata), Eucalyptus oil (70%+ eucalyptol, also known as cineol), Fennel oil (Foeniculum vulgare), Garlic Oil (Allium sativum), Geranium oil (also known as Pelargonium graveolens), Lavender oil (Lavandula officinalis), Lemon eucalyptus (Corymbia citriodora) essential oil and its active
ingredient p-menthane-3,8-diol (PMD), Lemongrass oil (Cymbopogon flexuosus), Mangolds (Tagetes species), Marjoram (Tetranychus urticae and Eutetranychus orientalis), Neem oil (Azadirachta indica), Oleic acid, Peppermint ( Mentha x piperita), Pennyroyal (Mentha pulegium), Pyrethrum (from Chrysanthemum species, particularly C. cinerariifolium and C. coccineum), Rosemary oil (Rosmarinus officinalis), Spanish Flag Lantana camara (Helopeltis theivora), Solanum villosum berry juice, Tea tree oil (Melaleuca alternifolia) and Thyme (Thymus species) and mixtures thereof.

Preferred encapsulated insect repellents are mosquito repellents available from Celessence, Rochester, England. Celessence Repel, containing the active ingredient Saltidin™ and Celessence Repel Natural, containing the active Citrepel™ 75. Saltidin is a man made molecule developed originally by the Bayer Corporation. Citrepel is produced from eucalyptus oils and is high in p-menthane-3,8-diol (PMD). A preferred non-encapsulated repellent is Citriodiol™ supplied by Citrefine.

Another group of volatile benefit agents with which the present invention can be applied are the so-called ‘aromatherapy’ materials. These include components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian.

The Encapsulated Phase Change Active

Phase change actives are materials that can absorb, store and release heat whilst the material changes its physical form. This is known as a phase change. Water changing from solid (ice) to liquid is an example of this phenomenon. During these phase changes large amounts of heat are absorbed or released.
The phase change active has a thermal phase transition temperature (TPTT) in the range 24 to 39°C. The TPTT may conveniently be measured by the Perkin & Elmer thermal analysis system.

The Perkin & Elmer thermal analysis system measures the heat flow into a material to be heated as a function of the temperature of the material. By investigating a material at various temperatures, a temperature profile is obtained. Such a temperature profile usually has one or more peaks, each peak corresponding to a maximum for the heat flow into the material at a specific temperature. The temperature corresponding to the major peak in the temperature profile is referred to as the thermal phase transition temperature. Generally a high TPTT corresponds to a high softening temperature of the material. The material has a TPTT in the range 24 to 39°C, preferably from 25 to 39°C, more preferably from 26 to 38°C and most preferably from 26 to 30°C.

Phase change actives possess a latent heat and show a phase transition phenomena between phases at a phase transition temperature. The phase transition of the present invention incorporated solid to liquid, liquid to vapor, solid to vapor, gel to liquid-crystalline phase changes. In the present invention, preferable phase transitions are solid to liquid phase or liquid to solid phase changes. At these phase changes, PTMs reversibly absorb or release heat from the environment at around the phase transition temperature, which is accompanied with a corresponding change in the ambient temperature.

The phase change active may be in the form of a composition (or mixture) provided that the total composition has a TPTT in the range 24 to 39°C, preferably from 25 to 39°C, more preferably from 26 to 38°C and most preferably from 26 to 30°C.

Suitable compositions may comprise hydrocarbon materials comprising a linear or branched alkyl chain and preferably comprising an average of from 12 to 50
carbon atoms per molecule, preferably from 12 to 30 carbon atoms. Preferably, the hydrocarbon materials are either alkanes or alkenes. Relatively small amounts of non-alkyl substituent groups may be present provided the hydrocarbon nature of the product is not substantially affected. Mixtures of these materials may be used.

Examples of suitable hydrocarbon materials for use in the hydrocarbon composition are the liquid hydrocarbon materials of natural source. Other liquid hydrocarbon materials including the liquid fractions derived from crude oil, such as mineral oil, liquid paraffins, cracked hydrocarbons and mixtures thereof. A preferred material is paraffin wax (n-Octadecane).

Examples of solid or semi-solid hydrocarbon materials are the paraffinic materials of longer chain length, and hydrogenated versions of some of the liquid materials mentioned above.

A particularly useful combination of hydrocarbon materials is a mixture of mineral oil (for example, M85 ex Daltons Company) and petroleum jelly (for example, Silkolene 910 ex Daltons), wherein the weight ratio of mineral oil to petroleum jelly is chosen such that the TPTT of the mixture is in the range of from 24 to 39 °C. In our experiments this result was obtained by using a ratio of mineral oil to petroleum jelly of less than 3:1, preferably from 2:1 to 1:3. The mineral oil was a liquid mixture of linear and branched hydrocarbons having an average number of carbon atoms per molecule of 26. Petroleum jelly was a semi-solid mixture of linear and branched hydrocarbons having an average number of carbon atoms per molecule of 26, and having a softening temperature of about 50°C.

The encapsulated phase change active comprises a capsule and a phase change active. The capsule comprises a shell and a core. The capsule for the phase change material preferably has a shell that is permeable to the unconfined volatile
benefit agent in the composition. A mixture of encapsulated phase change actives may be present.

The phase change active is encapsulated in a polymer shell to form encapsulated particles having a preferred particle size of from 10 nm to 1000 µm, preferably 50 nm to 100 µm, more preferably 0.2 to 30 µm. The use of encapsulated materials has the advantage that the materials may be readily dispersed without interference or interaction with the fabric softener compound. An additional advantage in that the encapsulated material does not cause a "messiness" feeling when deposited on the fabric which may be present with materials of a semi-liquid nature.

Suitable encapsulating polymers include those formed from melamine-formaldehyde or urea formaldehyde condensates, as well as similar types of aminoplasts. Additionally, capsules made via the simple or complex coacervation of gelatin are also preferred for use with the coating. Capsules having shell walls comprised of polyurethane, polyamide, polyolefin, polysaccharide, protein, silicone, lipid, modified cellulose, gums, polyacrylate, polyphosphate, polystyrene, and polyesters or combinations of these materials are also functional.

Further examples of suitable phase change actives are those materials disclosed in WO 03/0144460 having a phase transition temperature of from 24 to 39 °C, referred to therein as "Phase Transition Materials" or "PTM's" at page 6, final paragraph to the penultimate line on page 8.

A preferred material is Lurapret TX PMC 28 commercially available from BASF which is a material, specifically paraffin wax (comprising n-Octadecane), encapsulated in polymethylmethacrylate having a particle size in the range 0.2 to 20 µm. This material has a phase transition temperature of about 28°C.
The phase change actives are generally deposited to apply from 0.2 to 1 %, preferably 0.2 to 0.5 % by weight of the fabric after drying. The encapsulated phase change actives are preferably present in an amount of from 0.01 to 15 wt %, more preferably 0.01 to 10 wt %, even more preferably from 0.05 to 5 wt %, still more preferably from 0.05 to 2 wt %, more preferably still from 0.05 to 1 wt % and most preferably from 0.05 to 0.5 wt % by weight of the fabric softening composition.

The encapsulated phase change material comprises a shell that is permeable to the unconfined volatile benefit agent in the composition. Suitable encapsulating polymers include those formed from melamine-formaldehyde or urea formaldehyde condensates, as well as similar types of aminoplasts. Additionally, capsules made via the simple or complex coacervation of gelatin are also preferred for use with the coating. Capsules having shell walls comprised of polyurethane, polyamide, polyolefin, polysaccharide, protein, silicone, lipid, modified cellulose, gums, polyacrylate, polyphosphate, polystyrene, and polyesters or combinations of these materials are also suitable. A preferred material is polymethylmethacrylate.

The Surfactants

The composition of the invention comprises at least one anionic surfactant and at least one nonionic surfactant.

Examples of suitable anionic surfactants include alkylbenzene sulfonates, such as linear alkylbenzene sulfonate, particularly linear alkylbenzene sulfonates having an alkyl chain length of Cs-Cis. It is preferred that the level of linear alkylbenzene sulfonate is from 0 wt% to 30 wt%, more preferably 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.
The compositions of the invention may contain other anionic surfactants in amounts additional to the percentages quoted above. Suitable anionic surfactants are well-known to those skilled in the art. Examples include primary and secondary alkyl sulfates, particularly C8-C20 primary alkyl sulfates; alkyl ether sulfates; olefin sulfonates; alkyl xylene sulfonates; dialkyi sulfosuccinates; and fatty acid ester sulfonates. Sodium salts are generally preferred.

The compositions of the invention also contain at least one non-ionic surfactant. Nonionic surfactants that may be used 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. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

It is preferred that the level of non-ionic surfactant is from 0.5 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

The Composition

The laundry detergent composition of the invention is preferably a main wash cleaning composition, or a softening-in-the-wash composition.

The compositions of the invention may be in any physical form e.g. a solid such as a powder or granules, a tablet, a solid bar, a paste, gel or liquid, for example an aqueous based liquid, a spray, a stick, an impregnated substrate, foam or mousse. In particular the compositions may be liquid, powder, or unit dose such as tablet laundry compositions.
The liquid products of the invention may have pH ranging from 6 to 12 (for fabric softening-in-the-wash compositions). This pH range preferably remains stable over the shelf life of the product.

Compositions in accordance with the invention may comprise at least one further surface-active compound, selected from soaps, cationic surfactants, zwitterionic surfactants, amphoteric surfactants and mixtures thereof. The choice of surface-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

Many suitable surface-active compounds are available and are described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, a total amount of from 5 to 40 wt% is generally appropriate. Typically the compositions will comprise at least 2 wt% total surfactant e.g. 2-60%, preferably 15-40% most preferably 25-35%.

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap.

It is possible to include certain mono-alkyl cationic surfactants which can be used in main-wash compositions for fabrics. Cationic surfactants that may be used include quaternary ammonium salts of the general formula \( R_1R_2R_3R_4N^+X^- \).
wherein the R groups are long or short hydrocarbon chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which R₁ is a C₈-C₂₂ alkyl group, preferably a C₇-C₁₂ or C₁₂-C₁₄ alkyl group, R₂ is a methyl group, and R₃ and R₄, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

Amphoteric and zwitterionic surfactants that may be used include alkyl amine oxides, betaines and sulfobetaines.

Softening in the Wash

Where the composition is a softening from the wash composition, it may comprise a sugar polyester or a softening silicone oil.

The sugar polyester is preferably selected from the group consisting of sucrose polyesters, glucose polyesters and cellobiose polyesters, and is most preferably a sucrose polyester.

The sugar polyester may be liquid, soft solid or solid.

The preferred sucrose polyesters for use in the present invention have 2 to 4 hydrocarbon chains per sugar ring, where the hydrocarbon chain has a length of from 12 to 22 carbon atoms. A particularly preferred sucrose polyester is sucrose tetraerucate.

An example of a preferred sucrose polyester is Ryoto Sugar Ester ER290 supplied by Mitsubishi Kagaku Foods Corporation, which is a sucrose tetraerucate and according to the manufacturer’s specification is mainly Tetraerucate, Pentaerucate and Hexaerucate and has a HLB value of 2.
The sugar polyester may be pure, or may contain impurities. When present, the impurities are preferably selected from the group consisting of free fatty acid, fatty acid methyl ester, soap, inorganic salts and mixtures thereof.

The most preferred SPEs are commercially available, such as Emanon SCR-PK (ex KAO), which is a palm kernel derived SPE containing mainly C_{12-14} with about 20% C_{18} mono unsaturation and SPE-THSBO (ex Clariant), which is derived from touch hardened soy bean oil, having mainly C_{16-18} chains with about 80% mono and di unsaturation. The average degree of esterification of the above preferred SPEs is between 4.2-4.7.

SCR-PK contains up to 20% impurities but SPE-THSBO is pure. SCR-PK contains from 4 to 6 wt% of K soap, 2.5 wt% of free fatty acid, from 10 to 15 wt% of fatty acid methyl ester and less than 1% of KCl.

The sugar polyester, being non-ionic oil, requires an emulsifier, that is to say, the sugar polyester must be in an emulsified form. The emulsifier is preferably selected from cationic surfactant, anionic surfactant, non-ionic surfactant, and mixtures thereof.

Alternatively, the ultra-fine particles of the invention themselves can act as stabilizer and emulsifier for the nonionic softeners such as sugar polyesters (SPEs). Recently the interest in study of solid particles as emulsifies has been re-awakened (Binks, B. P. Current Opinions in Colloid Interface Science, 2002, 7, 21).

Most of recent activities on surface active colloidal particles have focused on very low aspect ratio (spherical) particles. Only recently Alargova et al, Langmuir, 2006, 22, 765-774, have shown that high aspect ratio particles can be used for emulsion stabilisation.
The compositions of the invention, when used as main wash fabric washing compositions, will generally also contain one or more detergency builder. The total amount of detergency builder in the compositions will typically range from 0 to 80 wt%, preferably from 0 to 60 wt%.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514 B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and triply phosphate are also suitable for use with this invention.

The compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 5 to 60% by weight (anhydrous basis), preferably from 10 to 50 wt%, especially from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: 0.8-1.5 Na₂O : Al₂O₃ : 0.8-6 SiO₂. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.
The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. In an alternative embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

In the case of zeolite MAP, zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00, is especially preferred. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

The zeolites may be supplemented by other inorganic builders, for example, amorphous aluminosilicates, or layered silicates such as SKS-6 ex Clariant.

The zeolite may be supplemented by organic builders. Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethoxy succinates, carboxymethoxymalonates, dipicolinates, hydroxyethyl iminodiacetates, alkyl- and alkenylmalonates and succinates; and sulfonated fatty acid salts. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 1 to 30 wt%, preferably from 5 to 30 wt%, more preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.
Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Builders are suitably present in total amounts of from 10 to 80 wt%, more preferably from 20 to 60 wt%. Builders may be inorganic or organic. A built composition in accordance with the invention may most preferably comprise from 10 to 80 wt% of a detergency builder (b) selected from zeolites, phosphates, and citrates.

The laundry detergent composition will generally comprise other detergent ingredients well known in the art. These may suitably be selected from bleach ingredients, enzymes, sodium carbonate, sodium silicate, sodium sulphate, foam controllers, foam boosters, perfumes, clays, soil release polymers, dye transfer inhibitors, photobleaches, fluorescers and coloured speckles.

Compositions according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulfates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).
The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%. The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and pernonanoic acid precursors. Especially preferred bleach precursors suitable for use in the present invention are \(\text{N},\text{N},\text{N}',\text{N}''\)-tetracetyl ethylenediamine (TAED) and sodium nonanoyloxybenzene sulphonate (SNOBS).

The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971 A (Unilever), and the cationic bleach precursors disclosed in EP 284 292 A and EP 303 520 A (Kao) are also of interest.

The bleach system can be either supplemented with or replaced by a peroxycacid, examples of such peracids can be found in US 4 686 063 and US 5 397 501 (Unilever). A preferred example is the imido peroxycarboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phthalimido peroxycaproic acid (PAP). Such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

A bleach stabiliser (transition metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), diethylenetriamine pentaacetate (DTPA), the polyphosphonates such as Dequest (Trade Mark), ethylenediamine tetramethylene phosphonate (EDTMP) and diethylenetriamine pentamethylene phosphate (DETPMP) and non-phosphate stabilisers such as EDDS (ethylene diamine disuccinate). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.
An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

5

The compositions according to the invention may also contain one or more enzyme(s). Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions. Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilins which are obtained from particular strains of \textit{B. Subtilis}, \textit{B. licheniformis}, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark obtainable from Showa-Denko of Japan), Optimase (Trade Mark from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark obtainable from Pfizer of U.S.A.).
Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used.

The compositions of the invention may contain alkali metal, preferably sodium, carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate copolymer, or sodium silicate. One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%. The amount of sodium silicate may suitably range from 0.1 to 5 wt%.

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; soil release polymers; inorganic salts such as sodium sulfate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; fluorescers and decoupling polymers. This list is not intended to be exhaustive.

The detergent composition when diluted in the wash liquor (during a typical wash cycle) will typically give a pH of the wash liquor from 7 to 10.5 for a main wash detergent.

Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or post-dosing those ingredients unsuitable for processing via the slurry. The skilled detergent
formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/litre, more preferably at least 500 g/litre. Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251 A and EP 420 317 A (Unilever).

The micro-powders of the invention are particularly well suited to incorporation into detergent powders.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

The fabric treatment compositions of the invention can also contain adjuvants that are normal in the cosmetic, pharmaceutical and/or dermatological field, such as hydrophilic or lipophilic gelling agents, hydrophilic or lipophilic active agents, preserving agents, antioxidants, solvents, fragrances, fillers, screening agents, bactericides, odour absorbers, photobleaches (singlet oxygen or radical type) and dyestuffs. The amounts of these various adjuvants are those conventionally used in the field under consideration and are, for example, from 0.01 to 20% of the total weight of the composition. Examples of suitable biocides for use in the present
invention include Proxel (1,2-benzisothiazolin-3-one), available from, for example, Univar, Avecia and Uniqema; and Kathon CG (Methylchloroisothiazolinone and Methylisothiazolinone), available from Rhom and Haas.

5 **Treatment**

The treatment of the substrate with the composition of the invention can be made by any suitable method such as washing, soaking or rinsing of the substrate but also by direct application such as spraying, rubbing, spotting, smearing, etc. The treatment may involve contacting the substrate with an aqueous medium comprising the material of the invention.

The treatment may be provided as a spray composition e.g., for domestic (or industrial) application to fabric in a treatment separate from a conventional domestic laundering process. Suitable spray dispensing devices are disclosed in WO 96/15310 (Procter & Gamble) and are incorporated herein by reference.

**Shading Dyes**

Optional shading dyes can be used. Preferred dyes are violet or blue. Suitable and preferred classes of dyes are discussed below. Moreover the unsaturated quaternary ammonium compounds are subject to some degree of UV light and/or transition metal ion catalysed radical auto-oxidation, with an attendant risk of yellowing of fabric. The presence of a shading dye also reduces the risk of yellowing from this source.

Different shading dyes give different levels of colouring. The level of shading dye present in the compositions of the present invention depend, therefore, on the type of shading dye. Preferred overall ranges, suitable for the present invention are from 0.00001 to 0.1 wt %, more preferably 0.0001 to 0.01 wt %, most preferably 0.0005 to 0.005 wt % by weight of the total composition.
Direct Dyes

Direct dyes (otherwise known as substantive dyes) are the class of water soluble dyes which have an affinity for fibres and are taken up directly. Direct violet and direct blue dyes are preferred.

Preferably the dye are *bis-azo* or *tris-azo* dyes are used.

Most preferably, the direct dye is a direct violet of the following structures:

![Chemical structure](image)

wherein:
- ring D and E may be independently naphthyl or phenyl as shown;
- $R_1$ is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;
- $R_2$ is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;
R₃ and R₄ are independently selected from: hydrogen and C1-C4-alkyl, preferably hydrogen or methyl;
X and Y are independently selected from: hydrogen, C₁-C₄-alkyl and C₁-C₄-alkoxy; preferably the dye has X = methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

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. Bis-azo copper containing dyes such as direct violet 66 may be used.

The benzidene based dyes are less preferred.

Preferably the direct dye is present at 0.00001 wt% to 0.0010 wt% of the formulation.

In another embodiment the direct dye may be covalently linked to the photo-bleach, 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 $SO_3^-$ 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.

Other preferred non-azine acid dyes are acid violet 17, acid black 1 and acid blue 29.

Preferably the acid dye is present at 0.0005 wt% to 0.01 wt% of the formulation.

Hydrophobic dyes

The composition of the invention may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, naphthalimides, 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.

Preferably the hydrophobic dye is present at 0.0001 wt% to 0.005 wt% of the formulation.
Basic dyes

Basic dyes are organic dyes which 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 International.

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.

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 reactive group of the dyes 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 International.

Preferred examples include 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 are not preferred.

Particularly 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, direct violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77 and mixtures thereof.

10 Further Optional Ingredients

The compositions of the invention may contain one or more other ingredients. Such ingredients include further preservatives (e.g. bactericides), pH buffering agents, perfume carriers, hydrotropes, anti-redeposition agents, soil-release agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, silicones, antifoams, colourants, pearlisers and/or opacifiers, natural oils/extracts, processing aids, e.g. electrolytes, hygiene agents, e.g. anti-bacterials and antifungals, thickeners and skin benefit agents.

20 Examples

Embodiments of the invention will now be illustrated by the following non-limiting examples. Further modifications will be apparent to the person skilled in the art.

Examples of the invention are represented by a number. Comparative examples are represented by a letter.

Unless otherwise stated, amounts of components are expressed as a percentage of the total weight of the composition.
Example 1: Preparation and composition of Laundry Liquid Detergent 1, in accordance with the invention, and Comparative Example A.

Detergent 1 and Comparative Example A had the following compositions.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>1</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic 7EO, branched (100%)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Fatty acid (100%)</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Anionic surfactant</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Organic acid</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>NaOH solution (50%) + Triethanolamine</td>
<td>To pH 8.25</td>
<td>To pH 8.25</td>
</tr>
<tr>
<td>Encapsulated Perfume slurry</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Encapsulated Phase Change Material</td>
<td>0.30</td>
<td>-</td>
</tr>
<tr>
<td>Perfume oil</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Water and minors (dyes etc)</td>
<td>To 100</td>
<td>To 100</td>
</tr>
</tbody>
</table>

Detergent 1 is based on a commercially available laundry detergent liquid composition, containing encapsulated perfume and free perfume.

Encapsulated phase change material, Lurapret TX PMC 28, available from BASF was post dosed into Detergent 1.

Example 2: Treatment of Fabric using Detergent 1 and Comparative Example A

100 % cotton terry towelling monitors were washed with Detergent 1 and Comparative Example A using a method that simulated a domestic machine wash, as follows:-

1. 40 g of fabric was treated in 1000 ml of water containing 5.5 g of Liquid Detergent (Detergent 1 or Comparative Example A)
2. The fabric was then washed in a Tergotometer at 30°C for 30 minutes
3. The fabric wash then spun in a Creda Debonair Autopump spin drier for 15 seconds and allowed to dry in air at ambient temperature.

An untreated monitor was used as a control.

**Example 3:- Perfume intensity arising from fabric treated with Detergent 1 and Comparative Example A**

The dry monitors were then assessed using a standard perfume test (blind sequential monadic, randomised, using 8 expert assessors). Assessments were made both prior to rubbing and after rubbing.

Table 2: Perfume intensity of washed-only fabric (control), and fabric treated with comparative example A and Detergent 1.

<table>
<thead>
<tr>
<th>No Treatment (control)</th>
<th>Perfume intensity difference upon Shear$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.03571</td>
</tr>
<tr>
<td>A</td>
<td>0.7857</td>
</tr>
<tr>
<td>1</td>
<td>0.9642</td>
</tr>
</tbody>
</table>

| Increased in intensity express as a percentage benefit | 18.51% |

$^1$Perfume intensity upon shear = difference in perfume intensity between un-rubbed and rubbed fabric.

The higher the number, the higher the perfume intensity.

It will be seen that fabric treated in accordance with the invention provided improved perfume boost.
The boost on rubbing for 1 is 18.5% larger than that for comparative example A. This is a surprising effect given the low level of encapsulated phase change material used in the composition.
CLAIMS

1. A laundry detergent composition, which comprises:
   (i) an encapsulated volatile benefit agent;
   (ii) an encapsulated phase change active having a phase transition temperature of from 24 to 39°C;
   (iii) at least one anionic surfactant; and
   (iv) at least one non-ionic surfactant;
   wherein the composition further comprises a non-encapsulated volatile benefit agent.

2. A composition according to claim 1, which further comprises a sugar polyester.

3. A composition according to any preceding claim, wherein the volatile benefit agent is selected from a perfume, insect repellent, aromatherapy oil, sensates such as menthol and an essential oil.

4. A composition according to claim 3, wherein the volatile benefit agent is a perfume.

5. A composition according to any preceding claim, wherein the volatile benefit agent is present in an amount of from 0.01 to 10 % by weight, based on the total weight of the composition.

6. A composition according to any preceding claim, wherein the encapsulated phase change material is present in an amount of from 0.01 to 15 wt % by total weight of the composition.
7. A composition according to any preceding claim, wherein the phase change active comprises hydrocarbon materials comprising a linear or branched alkyl chain comprising an average of from 12 to 50 carbon atoms per molecule.

8. A composition according to claim 7, wherein the phase change active is selected from mineral oil, liquid paraffins, cracked hydrocarbons and mixtures thereof.

9. A composition according to claim 8, wherein the phase change active is n-octadecane.

10. A composition according to claim 7, wherein the phase change active comprises a mixture of mineral oil and petroleum jelly.

11. A composition according to any preceding claim, wherein the encapsulated phase change material has a particle size of from 10 nm to 1000 microns.

12. A composition according to any preceding claim, which is an aqueous composition.

**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C11D/83 C11D3/18 C11D3/50 C11D17/00

ADD.

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 practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<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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<tbody>
<tr>
<td>Y</td>
<td>WO 2010/060677 AI (HENKEL AG &amp; CO KGAA [DE]; BAUER ANDREAS [DE]; FABER WERNER [DE]; LAHN) 3 June 2010 (2010-06-03) page 9, paragraph 1-4; claims 1-14 page 1, paragraphs 1, 4 page 2, paragraph 2 page 8, paragraph 4 page 14, paragraph 5 page 21, paragraph 3 - page 22, paragraph 2</td>
<td>1-3, 5-13</td>
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<td>Y</td>
<td>WO 95/33817 AI (UNI LEVER NV [NL]; UNI LEVER PLC [GB]) 14 December 1995 (1995-12-14) page 1, lines 5-9; claims 1-14; examples 1-3 page 3, line 28 - page 4, line 19 page 5, line 1 - page 11, line 14 page 25, lines 1-10</td>
<td>1-3, 5-13</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

**A** document defining the general state of the art which is not considered to be of particular relevance

**E** earlier application or patent but published on or after the international filing date

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**O** document referring to an oral disclosure, use, exhibition or other means

**P** document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"A" document member of the same patent family

Date of the actual completion of the international search: 3 April 2013

Date of mailing of the international search report: 11/04/2013

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: Kliewer, Erich

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<td>WO 2009/083941 A2 (PROCTER &amp; GAMBLE [US] ; SMETS JOHAN [BE] ; GANAPATHYSUNDARAM RAMANAN VEN) 9 July 2009 (2009-07-09) page 1, lines 8-28; claims 1-12; examples 1-4</td>
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