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# (54) Title: IMPROVEMENTS RELATING TO SURFACE TREATMENT COMPOSITIONS

**(57) Abstract**: A benefit agent delivery particle, comprising a benefit agent, and having at the outer surface of the particle one or more delivery aids which include a chitosan salt, which comprises a chitosan component and an anion, wherein the anion of said salt is an organic anion with a molecular weight of greater than 60, and wherein the chitosan component comprises a backbone which comprises amine groups provides a deposition benefit on a substrate such as skin, fabric and particularly hair.

WO 2014/064121 A2

# IMPROVEMENTS RELATING TO SURFACE TREATMENT COMPOSITIONS

## Technical Field

The present invention relates to treatment compositions and, more specifically, to compositions comprising particles which comprise a benefit agent and a deposition aid. The invention also relates to delivery of the benefit agent to skin or fabrics and especially to hair.

## Background of the Invention

The present invention will be described with particular reference to perfume although the technology is applicable to other benefit agents used in skin, hair or fabric treatment processes and compositions, and most especially in hair treatment compositions and treatment processes.

In laundry applications deposition of a perfume is used, for example, during fabric treatment processes such as fabric washing and conditioning. Methods of deposition are diverse and include deposition during the wash or rinse stages of the laundry process or direct deposition before or after the wash, such as by spraying or rubbing or by use of impregnated sheets during tumble drying or water additives during steam ironing. The perfume is often incorporated into a carrier or delivery system. Carrier systems have also been suggested for hair and skin applications, for example in hair shampoos, conditioners and other treatment compositions.

After deposition onto a surface, a problem exists in that longevity of adherence to that surface of the benefit agent, in a surfactant and/or detergent polymer containing environment, is inherently poor. For example, a perfume carrier which has been deposited onto a surface may be removed again, or the perfume may be leached from its carrier. Protection of the perfume is, therefore, required before and after it has been deposited onto a surface. Much the same problems are encountered with other benefit agents, which are, like perfume, typically relatively expensive and present in compositions at relatively low levels.

WO 07/62833 relates to compositions which comprise core-shell encapsulated perfume particles decorated with a polysaccharide which is substantive to cellulose. Preferred polysaccharides disclosed therein are locust bean gum, tamarind xyloglucan, guar gum or mixtures thereof. Thus it is known to have particles comprising a benefit agent (perfume) which use cellulose-substantive polysaccharide as a delivery aid to assist the particles in binding to a specific substrate.

Chitosan is a linear polysaccharide composed of randomly distributed • -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is known to have a number of commercial uses in agriculture and horticulture, water treatment, chemical industry, pharmaceuticals and biomedical applications.

Latex particles having a shell of chitosan in the form of an organic salt (acetate) are known from US 2006/0171999 (published August 3rd 2006). These are applied to cloth by padding then cured. Padding maximises the deposition of the particles on the cloth. This curing step is believed to film-form the latex particles (by melting) and leave the chitosan adhered to the surface of the fabric where it functions as an antimicrobial.

## Brief Description of the Invention

We have determined that, compared to unmodified particles, deposition of the modified particle of the invention onto hair, both undamaged and damaged, is improved, particularly undamaged hair.

We have now further determined that, compared to a chitosan acetate salt deposition aid, organic acid salts of chitosan wherein the anion has a higher molecular weight than acetate show improved deposition, including on damaged substrates, for example, and in particular, on damaged hair, as well as virgin substrates.

Accordingly, a first aspect of the present invention provides a benefit agent delivery particle, comprising a benefit agent, and having at the outer surface of the particle one or more delivery aids which include a chitosan salt, which comprises a chitosan component and an anion, wherein the anion of said salt is an organic anion with a molecular weight of greater than 60, and wherein the chitosan component comprises a backbone which comprises amine groups.

Preferably, said amine groups comprise a mole fraction in salt form, of from 5 mol % to 30 mol %, preferably from 10 mol % to 30 mol %,by total number of mols of amine groups.

Preferred organic anions may be selected from the list consisting of arginine, creatinine, 3,5-dihydroxybenzoic acid, guanidineacetic acid, protocatechuic acid, pyroglutamic acid, and mixtures thereof, most preferably arginine.

Preferably the zeta potential of the particles as measured using a Malvern Nano ZS90 apparatus, in DI water at a solid content of 50ppm and around pH of 7 is above 15 mV, more preferably above 20 mV.

Advantageously the particle comprises a hydrophobic benefit agent. Further and more particular examples of benefit agents are given below.

Preferably the chitosan component of the salt (as a protonated material) has a molecular weight in excess of 10kDa, more preferably in the range 30-1000kDa. This latter material is referred to in the art as “Chitosan Short Chain”. These weights are equivalent to a degree of polymerisation of around 200 to around 500.

The particle preferably further comprises a non-polysaccharide polymer, more preferably an aminoplast polymer. Typically, the non-polysaccharide polymer is cross linked in the form of relatively large water-insoluble macromolecules.

Typically, the particle has an average diameter of less than 10 micron, and preferably an average diameter in the range 1-10 micron. One benefit of small particles is that they are less visible in clear products. However, if the particles are too small then can become difficult to break thereby releasing the benefit agent.

Highly preferred particles comprise a core which comprises the benefit agent and a shell which comprises the water insoluble non-polysaccharide polymer, with the chitosan salt attached at the outer surface of the shell.

Such particles have an inner region, typically forming a “core” which contains the benefit agent and a water-insoluble “shell” which protects the benefit agent and regulates the flow of benefit agent into and out of the core. The core may comprise a droplet of the benefit agent or may comprise a polymer matrix into which the benefit agent is adsorbed.

The particle can be a carrier which controls thermodynamic (rather than kinetic) partition of the benefit agent between the interior region and elsewhere. This is particularly advantageous where late-stage addition of perfume or other benefit agent is required as the particles and the benefit agent may therefore be dosed into the product separately. In the alternative, the shell is largely impermeable to the benefit agent and the benefit agent is released on breakage of the shell.

A further aspect of the present invention provides a hair, skin or laundry treatment composition comprising

a) a particle according to the first aspect of the invention, and,
b) at least one surfactant.

Advantageously, where the benefit agent is hydrophobic, the core shell particles will prevent or reduce the extraction of the benefit agent by the surfactant.

Preferably the surfactant comprises at least 3%wt on total composition of an alkyl ether sulphate, in for example, a shampoo. When the composition is a conditioner a cationic surfactant is preferably included such as an alkyl ammonium material.

A yet further aspect of the present invention subsists in a process for the production of benefit agent delivery particles, in which:

a) a core is encapsulated using emulsion polymerization to form core-shell particles, and,

b) a further polymer layer is formed on the outer surface of the core shell-particles in the presence of the chitosan salt,

wherein the benefit agent is either present in or as the core during step (a) of the process or adsorbed into the core in a subsequent step.

Advantageously, this multi-step process provides that the chitosan salt deposition aid is entrapped at the surface of the particle, in such a manner that it is not removed by exposure to water.

In the alternative the chitosan salt can be attached to the particle by means of the reaction of a linking group with the particle, for example by the use of 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrogen chloride (EDAC).

## Detailed Description of the Invention

In order that the present invention may be further and better understood it will be further described below with reference to specific embodiments of the invention and further preferred and/or optional features. All amounts quoted are wt.% of total composition unless otherwise stated.

Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts or ratios of material or conditions of reaction, physical properties of materials and/or use are to be understood as modified by the word “about”.

### Benefit Agents

Benefit agents provide a range of benefits to, as the case may be, skin or fabrics, and most preferably to hair

Various benefit agents can be incorporated into the particles. Where the end use of the particles is in connection with the preferred surfactant-containing formulations, any compatible benefit agent which can provide a benefit to a substrate which is treated with a preferably surfactant-containing composition can be used. Advantages of the particles of the invention in the presence of surfactant are a good retention of the benefit agent on storage of a formulation and controllable release of the benefit agent during and after product usage.

Benefits include, for laundry applications, benefits of softening, conditioning, lubricating, crease reducing, ease of ironing, moisturising, colour preserving and/or anti-pilling, quick drying, UV protecting, shape retaining, soil releasing, texturising, insect repelling, fungicidal, dyeing and/or fluorescent benefit to the fabric.

A highly preferred benefit is the delivery of fragrance (whether free and/or encapsulated), or pro-fragrance.

Other preferred benefit agents are flavours and fragrances, profragrance, clays, enzymes, antifoams, fluorescers, bleaching agents and precursors thereof (including photo-bleach), dyes and/or pigments, conditioning agents (for example cationic surfactants including water-insoluble quaternary ammonium materials, fatty alcohols and/or silicones), lubricants (e.g. sugar polyesters), colour and photo-protective agents (including sunscreens), antioxidants, ceramides, reducing agents, sequesterants, colour care additives (including dye fixing agents), unsaturated oil, emollients, moisturisers, insect repellents and/or pheromones, drape modifiers (e.g. polymer latex particles such as PVAc) and anti-microbial and microbe control agents. Mixtures of two or more of these may be employed. Particular benefit agents are described in further detail below.

For skin compositions the preferred benefit agents include one or more of fragrances, moisturisers, sunscreens, skin lightening agents, antimicrobials, oils and insect repellents. For hair compositions the list of preferred benefit agents is the same with the addition of colour protection agents and dyes.

Preferred antimicrobials include Triclosan™, climbazole, octapyrox, ketoconizole, zinc pyrithione, and quaternary ammonium compounds.

Antidandruff agents are benefit agents suitable for use in hair treatment compositions that are active against dandruff and are typically antimicrobial agents and preferably antifungal agents. Antifungal agents typically display a minimum inhibitory concentration of about 50 mg/ml or less against Malassezia spp.

Suitable antidandruff benefit agents include compounds selected from ketoconazole, climbazole, octopirox, metal pyrithione salts, and mixtures thereof. The preferred azole based antifungal agents are ketoconazole and climbazole.

Preferred metal pyrithione salts are zinc, copper, silver and zirconium pyrithione. The most preferred is zinc pyrithione.

Preferably, the antidandruff active is present at from 0.01 to 5% wt. of the composition, more preferably from 0.1 to 2.5% wt. of the composition.

Preferred sunscreens and/or skin lightening agents are vitamin B3 compounds. Suitable vitamin B3 compounds are selected from niacin, niacinamide, nicotinyl alcohol, or derivatives or salts thereof. Other vitamins which act as skin lightening agents can be advantageously included in the skin lightening composition to provide for additional skin lightening effects. These include vitamin B6, vitamin C, vitamin A or their precursors. Mixtures of the vitamins can also be employed in the composition of the invention. An especially preferred additional vitamin is vitamin B6. Other non-limiting examples of skin lightening agents useful herein include adapalene, aloe extract, ammonium lactate, arbutin, azelaic acid, butyl hydroxy anisole, butyl hydroxy toluene, citrate esters, deoxyarbutin, 1,3 diphenyl propane derivatives, 2, 5 di hydroxyl benzoic acid a nd its derivatives, 2-(4-

acetoxyphenyl)-1 ,3 d itha ne, 2-(4- Hydroxylphenyl)-1,3 dithane, ellagic acid, gluco pyranosyl-1-ascorbate, gluconic acid, glycolic acid, green tea extract, 4-Hydroxy-5-methyl-3[2H]-furanone, hydroquinone, 4 hydroxyanisole and its derivatives, 4-hydroxy benzoic acid derivatives, hydroxycaprylic acid, inositol ascorbate, kojic acid, lactic acid, lemon extract, linoleic acid, magnesium ascorbyl phosphate, 5-octanoyl salicylic acid, 2,4 resorcinol derivatives, 3,5 resorcinol derivatives, salicylic acid, 3,4,5 trihydroxybenzyl derivatives, and mixtures thereof. Preferred sunscreens useful in the present invention are 2-ethylhexyl-p-methoxycinnamate, butyl methoxy dibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyl dimethyl-p-aminobenzoic acid and mixtures thereof. Particularly preferred sunscreen is chosen from 2-ethyl hexyl-p-methoxycinnamate, 4,- t-butyl-4'- methoxydibenzoyl-methane or mixtures thereof. Other conventional sunscreen agents that are suitable for use in the skin lightening composition of the invention include 2-hydroxy-4-methoxybenzophenone, octyldimethyl- p-a mi nobenzoic acid, digalloyltrioleate, 2,2-dihydroxy-4- methoxybenzophenone, ethyl-4-(bis(hydroxypropyl)) aminobenzoate, 2- ethylhexyl-2- cyano-3,3-diphenylacrylate, 2-ethylhexylsalicylate, glyceryl- p-aminobenzoate, 3,3,5- trimethylcyclohexyl-salicylate, methylanthranilate, p-dimethyl-aminobenzoic acid or aminobenzoate, 2-ethylhexyl-p-dimethyl- amino-benzoate, 2-phenylbenzimidazole-5- sulfonic acid, 2-(p- dimethylaminophenyl)-5-sulfonic benzoxazoic acid and mixtures of these compounds.

Preferred anti-oxidants include vitamin E, retinol, antioxiants based on hydroxytoluene such as Irganox™ or commercially available antioxidants such as the Trollox™ series.

Benefit Agent Association and Carriers

The delivery aid is attached to a particle which either comprises the benefit agent per-se or which is itself a carrier for the benefit agent. An example of the latter would be a perfume, antidandruff agent, insect repellent or other benefit agent carrying particle with the delivery aid attached at the surface of the particle. While it is preferred to use polymer particles, preferably core-shell encapsulates, many other types of particle can be envisaged as the benefit agent carrier.

Perfumes have been adsorbed onto a clay or zeolite material that is then admixed into particulate detergent compositions: U.S. Pat. No. 4,539,135 discloses particulate laundry compounds comprising a clay or zeolite material carrying perfume. Combinations of perfumes generally with larger pore size zeolites such as zeolite X and Y are also taught in the art. East German Patent Publication No. 248,508, relates to perfume dispensers containing a faujasite-type zeolite (e.g., zeolite X and Y) loaded with perfume. Also, East German Patent Publication No. 137,599, published Sep. 12, 1979 teaches compositions for use in powdered washing agents to provide thermo-regulated release of perfume. Zeolites A, X and Y are taught for use in these compositions. Other perfume delivery systems are taught by WO 97/34982 and WO 98/41607, published by The Procter & Gamble. WO 97/34982 discloses particles comprising perfume loaded zeolite and a release barrier, which is an agent derived from a wax and having a size (i.e., a cross-sectional area) larger than the size of the pore openings of the zeolite carrier. WO 98/41607 discloses glassy particles comprising agents useful for laundry or cleaning compositions and a glass derived from one or more of at least partially-water-soluble hydroxylic compounds.

Silicas, amorphous silicates, crystalline nonlayer silicates, layer silicates, calcium carbonates, calcium/sodium carbonate double salts, sodium carbonates, sodalites, alkali metal phosphates, pectin, carboxyalkylcelluloses, gums, resins, gelatin, gum arabic, porous starches, modified starches, carboxyalkyl starches, cyclodextrins, maltodextrins, synthetic polymers such as polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), cellulose ethers, polystyrene, polyacrylates, polymethacrylates, polyolefins, aminoplast polymers, crosslinkers and mixtures thereof can all provide a basis for perfume particles.

Polymer particles are however preferred, especially polymer particles which comprise an aminoplast polymer.

Suitable particles in the micron range include known types of melamine/urea-formaldehyde encapsulates, silica, clays starch and zeolite particles and coacervates with a typical size range of 1-10 microns.

In one particularly preferred aspect of the invention the chitosan salt, as deposition aid, is attached to at least partially pre-formed particles.

The delivery aid is bound 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 delivery aid is adsorbed onto the particle as the polymerisation proceeds and the particle grows in size. It is believed that under such circumstances part of the adsorbed delivery aid becomes buried within the interior of the particle. Hence at the end of the polymerisation, part of the delivery aid is entrapped and bound in the polymer matrix of the particle, whilst the remainder is free to extend into the aqueous phase.

The delivery aid is preferably mainly attached to the particle surface and is preferably not, to any significant extent, distributed throughout the internal bulk of the particle. Thus the particle which is produced when using a delivery aid according to the preferred process of the invention can be thought of as a "hairy ball". As noted above, it is important that the chitosan salt is not removed by water as it cannot then function effectively as a delivery aid. Thus, for example spray-drier coating of chitosan onto particles would not result in chitosan being an effective delivery aid as the chitosan would be removed from the particles on exposure to water.

The polymer carrier particles of the invention can comprise a wide selection of monomer units. By "monomer units" as used herein is meant the monomer units of the polymer chain, thus references to "a polymer particle comprising water-insoluble monomer units" as used herein means that the polymer particle is derived from water-insoluble monomers.

As noted above aminoplast (for example melamine/formaldehyde or urea/formaldehyde) core/shell particles with benefit agent present in the core and the chitosan salt attached to the outer surface of the shell are particularly preferred.

Where the particle itself is not the benefit agent, the benefit agent is typically present in an amount of from 10-85% by total weight of the carrier particle, preferably from 20 to 75 % by total weight of the particle.

While it is essential for the present invention that the delivery aid comprises a chitosan salt, additional delivery aids may be present at the surface of the particle. These can advantageously be selected from cellulose derivatives and polyesters, so give better substantivity to a plurality of substrates. Particularly preferred polysaccharide additional deposition aids include dextran, hydroxy-propyl methyl cellulose, hydroxy-ethyl methyl cellulose, hydroxy-propyl guar, hydroxy-ethyl ethyl cellulose, methyl cellulose, locust bean gum, xyloglucan, guar gum. Particularly preferred polyester additional deposition aids include polymers having one or more nonionic hydrophilic components comprising oxyethylene, polyoxyethylene, oxypropylene or polyoxypropylene segments, and, one or more hydrophobic components comprising terephthalate segments.

## Volatile Benefit Agents

Perfume is one example of a volatile benefit agent. Typical volatile benefit agents have a molecular weight of from 50 to 500. Where pro-fragrances are used the molecular weight will generally be higher.

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 Flavour Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavour 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’. The perfume component could also be in the form of a pro-fragrance. WO 2002/038120 (P&G), for example, relates to photo-labile pro-fragrance conjugates which upon exposure to electromagnetic radiation are capable of releasing a fragrant species.

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.

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.

It is also advantageous to encapsulate perfume components which have a low LogP (i.e. those which will be partitioned into water), preferably with a LogP of less than 3.0. These materials, of relatively low boiling point and relatively low LogP 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, Cinamyl 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 Heptenone, 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 Acetophenone, 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.

It is commonplace for a plurality of perfume components to be present in a formulation. In the encapsulates 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 of delayed blooming perfumes given above present in the encapsulated perfume.

Part or all of the perfume may be in the form of a pro-fragrance. For the purposes of the present invention a pro-fragrance is any material which comprises a fragrance precursor that can be converted into a fragrance. The pro-fragrance can, for example, be a food lipid. Food lipids typically contain structural units with pronounced hydrophobicity. The majority of lipids are derived from fatty acids. In these ‘acyl’ lipids the fatty acids are predominantly present as esters and include mono-, di-, triacyl glycerols, phospholipids, glycolipids, diol lipids, waxes, sterol esters and tocopherols. In their natural state, plant lipids comprise antioxidants to prevent their oxidation. While these may be at least in part removed during the isolation of oils from plants some antioxidants may remain. These antioxidants can be pro-fragrances. In particular, the carotenoids and related compounds including vitamin A, retinol, retinal, retinoic acid and provitamin A are capable of being converted into fragrant species including the ionones, damascones and damscenones. Preferred pro-fragrance food lipids include olive oil, palm oil, canola oil, squalene, sunflower seed oil, wheat germ oil, almond oil, coconut oil, grape seed oil, rapeseed oil, castor oil, corn oil, cottonseed oil, safflower oil, groundnut oil, poppy seed oil, palm kernel oil, rice bran oil, sesame oil, soybean oil, pumpkin seed oil, jojoba oil and mustard seed oil.

Suitable pro-fragrances are those that generate perfume components which are aldehydes.

Aldehydes useful in perfumery include but are not limited to phenylacetaldehyde, p-methyl phenylacetaldehyde, p-isopropyl phenylacetaldehyde, methyinonyl acetaldehyde, phenylpropanal, 3- (4-t-butylphenyl)-2-methyl propanal, 3- (4-t-butylphenyl)- propanal, 3- (4-methoxyphenyl)-2-methylpropanal, 3- (4-isopropylphenyl)-2- methylpropanal, 3- (3, 4-methylenedioxyphenyl)-2-methyl propanal, 3- (4- ethylpheny)-2, 2-dimethylpropanal, phenylbutanal, 3-methyl-5-phenylpentanal, hexanal, trans-2-hexenal, cis-hex-3-enal, heptanal, cis-4-heptenal, 2-ethyl-2- heptenal, 2,6-dimethyl-5-heptenal, 2,4-heptadienal, octanal, 2-octenal, 3,7- dimethyloctanal, 3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-1,6-octadien-3-al, 3,7-dimethyl-6-octenal, 3,7-dimethyl-7-hydroxyoctan-1-al, nonanal, 6-nonenal, 2,4-nonadienal, 2, 6-nonadienal, decanal, 2-methyl decanal, 4-decenal, 9- decenal, 2,4-decadienal, undecanal, 2-methyldecanal, 2-methylundecanal, 2,6,10-trimethyl-9-undecenal, undec-10-enyl aldehyde, undec-8-enanal, dodecanal, tridecanal, tetradecanal, anisaldehyde, bourgenonal, cinnamic aldehyde, a-amylcinnam-aldehyde, a-hexyl cinnamaldehyde, methoxy-cinnamaldehyde, citronellal, hydroxy-citronellal, isocyclocitral, citronellyl oxyacet-aldehyde, cortexaldehyde, cumminic aldehyde, cyclamen aldehyde, florhydral, heliotropin, hydrotropic aldehyde, lilial, vanillin, ethyl vanillin, benzaldehyde, p-methyl benzaldehyde, 3,4-dimethoxybenzaldehyde, 3-and 4- (4-hydroxy-4-methyl-pentyl)-3-cyclohexene-1-carboxaldehyde, 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde, 1-methyl-3- (4-methylpentyl)-3-cyclohexen-carboxaldehyde, p-methylphenoxyacetaldehyde, and mixtures thereof.

Another group of perfumes with which the present invention can be applied are the so-called ‘aromatherapy’ materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian. By means of the present invention these materials can be transferred to textile articles that will be worn or otherwise come into contact with the human body (such as handkerchiefs and bed-linen).

The volatile benefit agents also include insect repellent materials (where insect should be read broadly to include other pests which are arthropods but not strictly hexapods – for example ticks). Many of these materials overlap with the class of perfume components and some are odourless to humans or have a non-perfume odour. Commonly used 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), Marigolds (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.

The benefit agent may be encapsulated alone or co-encapsulated with carrier materials, further deposition aids and/or fixatives. Preferred materials to be co-encapsulated in carrier particles with the benefit agent include waxes, paraffins, stabilizers and fixatives.

An optional yet preferred component of carrier particles is a formaldehyde scavenger. This is particularly advantageous in carrier particles which may comprise formaldehyde as a consequence of their manufacturing process or components. formaldehyde scavenger is chosen from: sodium bisulfite, urea, cysteine, cysteamine, lysine, glycine, serine, carnosine, histidine, glutathione, 3,4-diaminobenzoic acid, allantoin, glycouril, anthranilic acid, methyl anthranilate, methyl 4-aminobenzoate, ethyl acetoacetate, acetoacetamide, malonamide, ascorbic acid, 1,3-dihydroxyacetone dimer, biuret, oxamide, benzoguanamine, pyroglutamic acid, pyrogallol, methyl gallate, ethyl gallate, propyl gallate, triethanol amine, succinamide, thiabendazole, benzotriazol, triazole, indoline, sulfanilic acid, oxamide, sorbitol, glucose, cellulose, poly(vinyl alcohol), poly(vinyl amine), hexane diol, ethylenediamine-N,N'-bisacetoacetamide, N-(2-ethylhexyl)acetoacetamide, N-(3-phenylpropyl)acetoacetamide, lilial, helional, melonal, triplal, 5,5-dimethyl-1,3-cyclohexanedione, 2,4-dimethyl-3-cyclohexenecarboxaldehyde, 2,2-dimethyl-1,3-dioxan-4,6-dione, 2-pentanone, dibutyl amine, triethylenetetramine, benzylamine, hydroxycitronellol, cyclohexanone, 2-butanone, pentane dione, dehydroacetic acid, chitosan, or a mixture thereof. Preferred formaldehyde scavengers are sodium bisulfite, ethyl acetoacetate, acetoacetamide, ethylenediamine-N,N'-bisacetoacetamide, ascorbic acid, 2,2-dimethyl-1,3-dioxan-4,6-dione, helional, triplal, lilial and mixtures thereof.

## Process Details

In the highly preferred embodiments in which the particles have a distinct core and shell, a typical process for the production of the particles will involve at least one emulsion polymerisation step.

For those embodiments where the core essentially comprises a hydrophobic benefit agent, the emulsion polymerisation can take the form of dispersing the benefit agent in an aqueous system with appropriate materials to form the required polymer shell present either in the benefit agent or the aqueous system. Polymerisation then proceeds at the surface of the dispersed droplets of benefit agent (or benefit agent plus fixative or carrier) to form a shell around a core comprising the benefit agent. Such methods are well known, for example to produce aminoplast perfume encapsulates.

In those embodiments of the invention which have a polymer-containing core polymerisation may occur in at least two phases, in which the shell and the core are formed sequentially. The shell can be polymerised after the core or the order of polymerisation can be reversed.

Core First: In this approach the core is formed first and the shell is deposited onto the core.

Core Second: In this approach polymerisation occurs in at least two phases. In an earlier of these phases a shell is formed by a step-growth polymerisation. This shell encloses and contains the reagents for the chain-growth reaction which occurs in a later phase. Temporal separation of these phases is accomplished by control of the reagents present and the reaction conditions. Typically, at least one of the components of the shell-forming reaction is withheld from the initial reaction mixture and added gradually to control the progress of the reaction in the shell-forming phase. Advantageously, the first phase of the reaction is performed under conditions in which the chain-growth reaction is inhibited. These conditions include a sufficiently low temperature (for a thermally activated reaction) or conditions of sufficiently low light (for a photo-activated reaction). Once the shell-forming reaction has proceeded sufficiently, the conditions are modified (for example, by raising the temperature or exposing the reaction mixture to light) to cause the reaction to form the inner region to start. A preferred method is one in which an emulsion is formed comprising the chain-growth polymer components in a non-aqueous dispersed phase and the step-growth polymer components are at the interface between the dispersed phase and the continuous aqueous phase.

Typically the aqueous phase comprises an emulsifying agent, and one of the co-monomers for the step-growth polymer. Depending on the polymer chemistry chosen it may also contain any diol, alcohol or amine cross-linking agent. The disperse phase comprises the chain-growth monomer, the initiator, any isocyanate or vinyl cross-linking agents, the other co-monomer for the step growth polymer and any optional benefit agent.

The benefit agent may be present in the reaction mixture, at a level to give the benefit agent levels in the resulting particles at the levels disclosed above, although it is also possible to form “empty” particles and subsequently expose them to a benefit agent which can be adsorbed into the core of the particle.

Surface modification materials are generally added to the aqueous phase towards the end of the process, where, for example, further monomer(s) can be added to form further shell material and bind additional materials to the outside of the particle.

For simple core-shell particles, the core including benefit agent is preferably less than or equal to 95 % wt of mass, and the shell generally 5 %wt or greater of the mass of the particle, more preferably 80 % wt and 20 % wt respectively.

In a preferred embodiment the emulsion polymerisation step is a so-called “mini-emulsion” polymerisation, performed with a dispersed phase droplet size of below one micron.  Sufficiently fine emulsions can be obtained by a range of methods, including sonication, and/or via high shear dynamic mixers or static mixers.  Mini-emulsion products have excellent suspending properties.

## Emulsifying Agents

Many emulsifying agents are known for use in emulsion polymerisation.  Suitable emulsifying agents for use in the polymerisation process may comprise, but are not limited to, non-ionic surfactants such as polyvinylpyrrolidone (PVP), polyethylene glycol sorbitan monolaurate (Tween 20), polyethylene glycol sorbitan monopalmitate (tween 40), polyethylene glycol sorbitan monooleate (Tween 80), polyvinyl alcohol (PVA), and poly(ethoxy)nonyl phenol, ethylene maleic anhydride (EMA) copolymer, Easy-Sperse™ (from ISP Technologies Inc.), ionic surfactants such as partially neutralized salts of polyacrylic acids such as sodium or potassium polyacrylate or sodium or potassium polymethacrylate. Brij™-35, Hypermer™ A 60, or sodium lignosulphate, and mixtures thereof.

Emulsifiers may also include, but are not limited to, acrylic acid-alkyl acrylate copolymer, poly(acrylic acid), polyoxyalkylene sorbitan fatty esters, polyalkylene co-carboxy anhydrides, polyalkylene co-maleic anhydrides, poly(methyl vinyl ether-co-maleic anhydride), poly(propylene-co-maleic anhydride), poly(butadiene co-maleic anhydride), and poly(vinyl acetate-co-maleic anhydride), polyvinyl alcohols, polyalkylene glycols, polyoxyalkylene glycols, and mixtures thereof.

Preferred emulsifying agents are fatty alcohol exthoylates (particularly of the Brij™ class), salts of ether sulphates (including SLES), alkyl and alkaryl sulphonates and sulphates (including LAS and SDS) and cationic quaternary salts (including CTAC and CTAB).

The nature of the emulsifying agent can be selected to ensure that the finished particle is compatible with the environment in which it will be used.

In particular, cores which are formed in the presence of anionic surfactant systems (for example SLES 1-4 EO, preferably 1-3 EO and the others mentioned above) are compatible with products in which the environment comprises an anionic surfactant, such as, for example body-wash products and shampoos.

Cores which are formed in the presence of cationic surfactant (for example a cationic quaternary salt as mentioned above and in particular one of the alkyl trimethyl ammonium halides) are compatible with products in which the environment comprises a cationic surfactant, for example a hair conditioner.

It is particularly preferred that the emulsifying agent further comprises a nonionic surfactant. This is believed to produce a particle which deposits better on skin or hair than one produced solely with a charged surfactant emulsifier. It is also preferred that the non-ionic surfactant is hydrophilic, so as to promote the formation of a stable mini-emulsion. The alcohol ethoxylates with more than ten moles of ethoxylation, for example Synperonic A20 (C1320EO), yield good results.

DLS data for samples shows that as the level of surfactant increases the particle size becomes smaller, which is also advantageous.

Preferably, the ratio of non-ionic to anionic emulsifier should be greater than 1:1 (i.e. non-ionic is present in excess) and the total surfactant level should be >3%wt of the polymerisation mixture.

Co-surfactant:

Typically a co-surfactant will be present in the dispersed phase during polymerisation and some of this will remain in the resulting particle. Suitable co-surfactants for use in the present invention include hexadecane, cetyl alcohol, lauroyl peroxide, n-dodecyl mercaptan, dodecyl methacrylate, stearyl methacrylate, polystyrene, polydecene, mineral oils, isopropyl myristate $C_{13}$-$C_{15}$ alkyl benzoate and polymethyl methacrylate.

The preferred cosurfactants comprise hexadecane, polydecene and isopropyl myristate.

As a wt% of oil phase as a total, the co-surfactant is typically 0–20%, preferably 1-15%, more pref 2-12.5%.

Catalyst

Depending on the reactants present, optional catalyst may be present in the dispersed phase of the emulsion. For example in isocyanate/diol reactions a catalyst can advantageously minimises the hydrolysis of isocyanate to primary amine, which can react with further isocyanate to form polyurea. This unwanted reaction can result in an excess of diol being left at the end of the process which can potentially lead to the formation of malodour and interfere with cross-linking reactions.

Suitable catalysts may comprise amino or organo-metalic compounds such as N,N'-dimethylaminoethanol, N,N'-dimethylcyclohexylamine, bis-(2-dimethylaminoethyl) ether, N,N'-dimethylacetylamine, diaminobicyclooctane, stannous octoate and dibutyl tin dilaurate, 1,3-bis(dimethylamino) butane, pentamethyldiethylenetriamine and mixtures thereof.

When required, the level of catalyst is typically 0.1-2%with respect to chain-growth monomer.

Deposition Aid Attachment

As noted above, polymerisation may occur in at least two phases. In one method during the earlier phase the shell is formed by a reaction which, in preferred embodiments occurs at less than about 60 Celsius, typically 15-55 Celsius. In the later phase the core is polymerised at a preferred temperature of more than about 70 Celsius, typically 70-95 Celsius. Both reactions are allowed to proceed for sufficiently long for polymerisation to be essentially complete, 1-3 hours being typical for each stage.

Deposition aid is typically added at or towards the end of shell formation when for example, further shell forming material (for example further isocyanate and co-momomer) are also added to bind the deposition aid to the outer surface of the particle by the formation of further shell material which entraps a portion of the deposition aid and leads to a “hairy” particle in which the “hair” comprises the deposition aid. In the alternative the particles can be essentially fully formed and the deposition aid attached by means of a chemical linkage.

In addition to the chitosan salts other deposition aid may be present. These are preferably nonionic materials and suitable deposition aids include

Preferred Formulations:

In one embodiment of the invention the core of the particle comprises a rubbery polymeric material, i.e. one which has a Tg such that it is rubbery under conditions of storage. Suitable materials for the formation of cores with this property are the C2-C30, preferably C3-C18, more preferably C3-C12 acylates or methacrylates, with the butyl and methyl derivatives being particularly preferred. The core is intended to be a good solvent for the benefit agent.

Preferably the shell of the particle is a glassy material, i.e. one which has a Tg such that it is glassy under the conditions of storage. Suitable materials for the formation of shells with this property include the methyl methacrylates. The shell is intended to be a kinetic barrier for the benefit agent as well as maintaining capsule integrity. Typically the shell is 10-100 nm thick, preferably 20-40 nm.

The particles are typically included in compositions at levels of from 0.001% to 10%, preferably from 0.005% to 5%, most preferably from 0.01% to 3% by weight of the total composition.

Laundry Treatment Compositions

The delivery aid linked particles of the invention may be incorporated into laundry compositions. This may be done by mixing a slurry/dispersion product with some or all of the other components of the composition, for powders preferably by spraying onto the components. Advantageously, the slurry/dispersion need not be dried extensively (if at all) and this reduces benefit agent losses.

The active ingredient in the compositions for these laundry compositions is preferably a surface active agent or a fabric conditioning agent. More than one active ingredient may be included. For some applications a mixture of active ingredients may be used.

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, especially, an aqueous based liquid. In particular the compositions may be used in laundry compositions, especially in liquid, powder or tablet laundry composition. Liquids are particularly preferred as the problems of hydrolysis and enzyme attack on the deposition aid are more marked in liquid compositions.

The laundry compositions are preferably main wash (fabric washing) compositions or rinse-added softening compositions. The main wash compositions may include a fabric softening agent and the rinse-added fabric softening compositions may include surface-active compounds, particularly non-ionic surface-active compounds.

It is preferred that laundry compositions according to the invention comprise one or more enzymes. When present in a composition, the aforementioned enzymes may be present at levels from about 0.00001 wt.% to about 2 wt.%, from about 0.0001 wt.% to about 1 wt.% or even from about 0.001 wt.% to about 0.5 wt.% enzyme protein by weight of the composition.

Hair Treatment Compositions:

It is especially preferred that compositions of the present invention are hair treatment compositions and in particular are either hair shampoo compositions and/or hair conditioning compositions. As noted above the preferred benefit agents for delivery are one or more of fragrances, moisturisers, sunscreens, skin lightening agents, antimicrobials (especially anti-dandruff agents), oils, insect repellents, colour protection agents and dyes.

While the surfactants suitable for use in hair treatment compositions are described in further detail below, a particularly preferred hair treatment (shampoo) composition comprises a solution of 3-18%wt alkyl ether sulphate, 1-4% of a zwitterionic or amphoteric surfactant and 0.1-5% inorganic salt.

## Use in Products

The end-product compositions of the invention may be in any physical form e.g., a solid bar, a paste, gel or liquid, or especially, an aqueous-based liquid. The particles are typically included in said compositions at levels of from 0.001% to 10%, preferably from 0.005% to 7.55%, most preferably from 0.01% to 5% by weight of the total composition.

Depending on the end-use compositions according to the present invention will typically contain one or more of surfactants (which may be anionic, cationic, non-ionic, zwitterionic and ampphoteric), surfactant and/or non-surfactant conditioning agents, fatty alcohols, suspending agents and thickeners, polymers, silicones and shading agents.

## Surfactants

The particles of the invention may be advantageously incorporated into surfactant-containing compositions, especially for use in the treatment of hair or laundry.

Formulated compositions comprising the particles of the invention may contain a surface-active compound (surfactant) which may be chosen from soap and non soap anionic, cationic, non-ionic, amphoteric and zwitterionic surface active compounds and mixtures thereof. Many suitable surface active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred surface-active compounds that can be used are soaps and synthetic non soap anionic, and non-ionic compounds.

Surfactants: anionic

Suitable anionic surfactants for laundry compositions are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly $C_8$ to $C_{18}$ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred. Sodium alkyl sulphates generally make up the bulk of the anionic surfactant present in laundry compositions due to their low cost.

For hair treatment compositions examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, alkyl ether sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, and alkyl ether carboxylic acids and salts thereof, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The surfactant blends used in skin and hair compositions are generally milder than those used in laundry compositions.

The alkyl and acyl groups generally contain from 8 to 18, preferably from 10 to 16 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether sulphosuccinates, alkyl ether phosphates and alkyl ether carboxylic acids and salts thereof may contain from 1 to 20 ethylene oxide or propylene oxide units per molecule.

Typical anionic cleansing surfactants for use in hair shampoo compositions of the invention include one or more of sodium oleyl succinate, ammonium lauryl sulphosuccinate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium lauryl ether sulphosuccinate, ammonium lauryl sulphate, ammonium lauryl ether sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate, lauryl ether carboxylic acid and sodium N-lauryl sarcosinate.

Preferred anionic surfactants for use in hair treatment compositions are the alkyl sulfates and alkyl ether sulfates. These materials have the respective formulae $R^2OSO_3M$ and $R^1O\ (C_2H_4O)\ _xSO_3M$, wherein $R^2$ is alkyl or alkenyl of from 8 to 18 carbon atoms, x is an integer having a value of from about 1 to about 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. Most preferably for hair compositions $R^2$ has 12 to 14 carbon atoms, in a linear rather than branched chain.

Preferred anionic surfactants for use in hair treatment compositions are selected from sodium lauryl sulphate and sodium lauryl ether sulphate(n)EO, (where n is from 1 to 3); more preferably sodium lauryl ether sulphate(n)EO, (where n is from 1 to 3); most preferably sodium lauryl ether sulphate(n)EO where n=1.

Preferably the level of alkyl ether sulphate in a hair treatment composition according to the invention is from 0.5 wt% to 25 wt% of the total composition, more preferably from 3 wt% to 18 wt%, most preferably from 6 wt% to 15 wt% of the total composition.

The total amount of anionic cleansing surfactant in hair treatment (shampoo) compositions of the invention generally ranges from 0.5 wt% to 45 wt%, more preferably from 1.5 wt% to 20 wt%.

Surfactants: nonionic

Compositions according to the present invention may contain non-ionic surfactant. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C8 to 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 to Cl5 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 if the level of non-ionic surfactant is from 0 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%, by weight of a fully formulated laundry composition comprising the particles of the invention.

Hair treatment compositions of the invention may contain non-ionic surfactant. Most preferably non-ionic surfactants are present in hair treatment compositions in the range 0 to 5wt%.

Nonionic surfactants that can be included in hair treatment compositions of the invention include condensation products of aliphatic (C8 - C18) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups. Alkyl ethoxylates are particularly preferred. Most preferred are alkyl ethoxylates having the formula R-(OCH2CH2)nOH, where R is an alkyl chain of C12 to C15, and n is 5 to 9.

Other suitable nonionic surfactants for use in hair treatment compositions include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:

$$RO - (G)n$$

wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about C5 to about C20. Preferably R represents a mean alkyl chain length of from about C8 to about C12. Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C5 or C6 monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

The degree of polymerisation of the APG, n, may have a value of from about 1 to about 10 or more. Preferably, the value of n lies from about 1.1 to about 2. Most preferably the value of n lies from about 1.3 to about 1.5.

Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

Other sugar-derived nonionic surfactants which can be included in compositions of the invention include the C10-C18 N-alkyl (Cl-C6) polyhydroxy fatty acid amides, such as the C12-C18 N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide.

Surfactants: amphoteric or zwitterionic

Amphoteric or zwitterionic surfactant can be included in an amount ranging from 0.5 wt% to about 8 wt%, preferably from 1 wt% to 4 wt% of a composition according to the invention, particularly a hair treatment composition.

Examples of amphoteric or zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphoacetates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in hair treatment compositions of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine, lauryl betaine, cocamidopropyl betaine and sodium cocoamphoacetate.

A particularly preferred amphoteric or zwitterionic surfactant is cocamidopropyl betaine.

Mixtures of any of the foregoing amphoteric or zwitterionic surfactants may also be suitable. Preferred mixtures are those of cocamidopropyl betaine with further amphoteric or zwitterionic surfactants as described above. A preferred further amphoteric or zwitterionic surfactant is sodium cocoamphoacetate.

Surfactants: cationic

Compositions of the invention for hair treatment or laundry use may be so-called conditioners, and typically contain a conditioning surfactant. Hair conditioner compositions will typically comprise one or more conditioning surfactants which are cosmetically acceptable and suitable for topical application to hair.

Suitable conditioning surfactants include those selected from cationic surfactants, used singly or in admixture. Preferably, the cationic surfactants have the formula $N^+R^1R^2R^3R^4$ wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently ($C_1$ to $C_{30}$) alkyl or benzyl. Preferably, one, two or three of $R^1$, $R^2$, $R^3$ and $R^4$ are independently ($C_4$ to $C_{30}$) alkyl and the other $R^1$, $R^2$, $R^3$ and $R^4$ group or groups are ($C_1$-$C_6$) alkyl or benzyl. More preferably, one or two of $R^1$, $R^2$, $R^3$ and $R^4$ are independently ($C_6$ to $C_{30}$) alkyl and the other $R^1$, $R^2$, $R^3$ and $R^4$ groups are ($C_1$-$C_6$) alkyl or benzyl groups. Optionally, the alkyl groups may comprise one or more ester (-OCO- or –COO-) and/or ether (-O-) linkages within the alkyl chain. Alkyl groups may optionally be substituted with one or more hydroxyl groups. Alkyl groups may be straight chain or branched and, for alkyl groups having 3 or more carbon atoms, cyclic. The alkyl groups may be saturated or may contain one or more carbon-carbon double bonds (e.g., oleyl). Alkyl groups are optionally ethoxylated on the alkyl chain with one or more ethyleneoxy groups.

Suitable cationic surfactants for use in conditioner compositions according to the invention include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride, cetylpyridinium chloride, tetramethylammonium chloride, tetraethylammonium chloride, octyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, tallowtrimethylammonium chloride, dihydrogenated tallow dimethyl ammonium chloride (e.g., Arquad 2HT/75 from Akzo Nobel), cocotrimethylammonium chloride, PEG-2-oleammonium chloride and the corresponding hydroxides thereof. Further suitable cationic surfactants include those materials having the CTFA designations Quaternium-5, Quaternium-31 and Quaternium-18. Mixtures of any of the foregoing materials may also be suitable. A particularly useful cationic surfactant for use in conditioners according to the invention is cetyltrimethylammonium chloride, available commercially, for example as GENAMIN CTAC, ex Hoechst Celanese. Another particularly useful cationic surfactant for use in conditioners according to the invention is behenyltrimethylammonium chloride, available commercially, for example as GENAMIN KDMP, ex Clariant.

Another example of a class of suitable cationic surfactants for use in the invention, especially in hair treatment compositions, either alone or together with one or more other cationic surfactants, is a combination of (i) and (ii) below:

(i) an amidoamine corresponding to the general formula (I):

$$R^1CONH(CH_2)_mN(R^2)R^3$$

in which $R^1$ is a hydrocarbyl chain having 10 or more carbon atoms, $R^2$ and $R^3$ are independently selected from hydrocarbyl chains of from 1 to 10 carbon atoms, and m is an integer from 1 to about 10; and

(ii) an acid.

As used herein, the term hydrocarbyl chain means an alkyl or alkenyl chain.

Preferred amidoamine compounds are those corresponding to formula (I) in which

$R^1$ is a hydrocarbyl residue having from about 11 to about 24 carbon atoms, $R^2$ and $R^3$ are each independently hydrocarbyl residues, preferably alkyl groups, having from 1 to about 4 carbon atoms, and m is an integer from 1 to about 4.

Preferably, $R^2$ and $R^3$ are methyl or ethyl groups.

Preferably, m is 2 or 3, i.e. an ethylene or propylene group.

Preferred amidoamines useful herein include stearamido-propyldimethylamine, stearamidopropyl-diethylamine, stearamidoethyl-diethylamine, stearamidoethyl-dimethylamine, palmitamidopropyl-dimethylamine, palmitamidopropyl-diethylamine, palmitamidoethyl-diethylamine, palmitamidoethyl-dimethylamine, behenamidopropyl-dimethylamine, behenamidopropyl-diethylmine, behenamidoethyl-diethylamine, behenamidoethyl-dimethylamine, arachidamidopropyl-dimethylamine, arachidamidopropyl-diethylamine, arachid-amidoethyl-diethylamine, arachidamidoethyl-dimethylamine, and mixtures thereof.

Particularly preferred amidoamines useful herein are stearamidopropyl-dimethylamine, stearamidoethyl-diethylamine, and mixtures thereof.

Commercially available amidoamines useful herein include: stearamidopropyldimethylamine with tradenames LEXAMINE S-13 available from Inolex (Philadelphia Pennsylvania, USA) and AMIDOAMINE MSP available from Nikko (Tokyo, Japan), stearamidoethyldiethylamine with a tradename AMIDOAMINE S available from Nikko, behenamidopropyldimethylamine with a tradename INCROMINE BB available from Croda (North Humberside, England), and various amidoamines with tradenames SCHERCODINE series available from Scher (Clifton New Jersey, USA).

A protonating acid may be present. Acid may be any organic or mineral acid which is capable of protonating the amidoamine in the conditioner composition. Suitable acids useful herein include hydrochloric acid, acetic acid, tartaric acid, fumaric acid, lactic acid, malic acid, succinic acid, and mixtures thereof. Preferably, the acid is selected from the group consisting of acetic acid, tartaric acid, hydrochloric acid, fumaric acid, lactic acid and mixtures thereof.

The primary role of the acid is to protonate the amidoamine in hair treatment composition thus forming a tertiary amine salt (TAS) in situ in the hair treatment composition. The TAS in effect is a non-permanent quaternary ammonium or pseudo-quaternary ammonium cationic surfactant.

Suitably, the acid is included in a sufficient amount to protonate more than 95 mole% (293 K) of the amidoamine present.

In hair conditioners of the invention, the level of cationic surfactant will generally range from 0.01 % to 10%, more preferably 0.05 % to 7.5%, most preferably 0.1 % to 5% by weight of the composition.

For laundry conditioners Dilute products typically contain up to about 8 %, preferably from 2 to 8 % by weight of softening active, whereas concentrated products may contain from about 8 to about 50 %, preferably from 8 to 25 % by weight active. Compositions of more than about 25 % by weight of active are defined as "super concentrated", depending on the active system, and are also intended to be covered by the present invention. The fabric conditioning agent may, for example, be used in amounts of preferably from 2 % to 30 % more preferably from 5 % to 25 % and most preferably from 8 % to 20 % by weight of the composition. The fabric softening active, for use in fabric conditioner compositions of the present invention typically comprises an ester-linked triethanolamine quaternary ammonium compound (QAC).

Preferably, the QAC is derived from palm or tallow feed stocks. These feed stocks may be pure or predominantly palm or tallow based. Blends of different feed stocks may be used. The fatty acid chains of the QAC preferably comprise from 20 to 35 wt % of saturated C18 chains and from 20 to 35 wt % of monounsaturated C18 chains by weight of total fatty acid chains. In a preferred embodiment as a laundry conditioner, the fatty acid chains of the QAC comprise from 25 to 30 wt %, preferably from 26 to 28 wt % of saturated C18 chains and from 25 to 30 wt %, preferably from 26 to 28 wt % of monounsaturated C18 chains, by weight of total fatty acid chains. In a further preferred embodiment, the fatty acid chains of the QAC comprise from 30 to 35 wt %, preferably from 33 to 35 wt % of saturated C18 chains and from 24 to 35 wt %, preferably from 27 to 32 wt % of monounsaturated C18 chains, by weight of total fatty acid chains. The preferred quaternary ammonium materials for use in the present invention can be derived from feedstock having an overall iodine value of from 30 to 45, preferably from 30 to 42 and most preferably 36.

Commercial examples of suitable laundry conditioning agents include Stepantex™ UL85, ex Stepan, Prapagen™ TQL, ex Clariant, and Tetranyl™ AHT-1, ex Kao, (both di-[hardened tallow ester] of triethanolammonium methylsulphate), AT-1 (di-[tallow ester] of triethano-lammonium methylsulphate), and L5/90 (di-[palm ester] of triethanolammonium methylsulphate), both ex Kao, and Rewoquat™ WE15 (a di-ester of triethanol-ammonium methylsulphate having fatty acyl residues deriving from C10-C20 and C16-C18 unsaturated fatty acids), ex Witco Corporation. Also, quaternary ammonium actives such as Stepantex VK90, Stepantex VT90, SP88 (ex-Stepan), Ceca Noramine, Prapagen TQ (ex-Clariant), Dehyquart AU-57 (ex-Cognis), Rewoquat WE18 (ex-Degussa) and Tetranyl L190 P, Tetranyl L190 SP and Tetranyl L190 S (all ex-Kao) are suitable.

In laundry conditioners the presence of non-ionic as a floc-prevention agent, enables the formation of a thick "dilute" fabric conditioner composition, which does not flocculate upon use. Lutensol™ AT25 (BASF) based on coco chain and 25 EO groups is an example of a suitable nonoionic surfactant. Other suitable surfactants include Renex 36 (Trideceth-6), ex Uniqema; Tergitol 15-S3, ex Dow Chemical Co.; Dihydrol LT7, ex Thai Ethoxylate ltd; Cremophor CO40, ex BASF and Neodol 91-8, ex Shell.

Oily conditioning agents:

Compositions according to the present invention, especially hair treatment compositions may also comprise a dispersed, non-volatile, water-insoluble oily conditioning agent. Preferably such non-silicone conditioning oily conditioning agents are present in hair conditioner compositions.

By "insoluble" is meant that the conditioning agent is not soluble in water (distilled or equivalent) at a concentration of 0.1% (w/w), at 25°C.

Suitable oily or fatty conditioning agents are selected from hydrocarbon oils, fatty esters and mixtures thereof. Straight chain hydrocarbon oils will preferably contain from about 12 to about 30 carbon atoms. Also suitable are polymeric hydrocarbons of alkenyl monomers, such as C2-C6 alkenyl monomers.

Specific examples of suitable hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used.

Suitable fatty esters are characterised by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, Monocarboxylic acid esters include esters of alcohols and/or acids of the formula R'COOR in which R' and R independently denote alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20. Di- and trialkyl and alkenyl esters of carboxylic acids can also be used.

Particularly preferred fatty esters are mono-, di- and triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C1-C22 carboxylic acids. Preferred materials include cocoa butter, palm stearin, sunflower oil, soyabean oil and coconut oil.

The oily or fatty material is suitably present at a level of from 0.05 wt% to 10 wt%, preferably from 0.2 wt% to 5 wt%, more preferably from about 0.5 wt% to 3 wt%. “Oils” as used in this specification are distinguished from perfume materials in that perfume materials are listed as odiferous materials in Arctander’s “Perfume and Flavor Materials of Natural Origin” ( ISBN-10: 0-931710-36-7), or listed as odiferous materials in various databases including Flavourbase 2010, ESO 2000 (2006 update) and PMP 2001. Perfume materials are generally present as part of a complex mixture of components where each odiferous component is present at a level of below 0.5%wt of the composition as a whole. Oils present for other purposes are generally present at levels above 0.5%wt of the composition as a whole.

The laundry compositions of the invention may contain a non-cationic softening material, which is preferably an oil and more preferably an oily sugar derivative.

Fatty alcohol:

Hair conditioners of the invention will typically also incorporate a fatty alcohol. The combined use of fatty alcohols and cationic surfactants in compositions is believed to be especially advantageous, because this leads to the formation of a lamellar phase, in which the cationic surfactant is dispersed.

Representative fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 22. Fatty alcohols are typically compounds containing straight chain alkyl groups. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials in conditioner compositions is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

The level of fatty alcohol in hair conditioners of the invention will generally range from 0.01 to 10%, preferably from 0.1 % to 8%, more preferably from 0.2 % to 7 %, most preferably from 0.3 % to 6 % by weight of the composition. The weight ratio of cationic surfactant to fatty alcohol is suitably from 1:1 to 1:10, preferably from 1:1.5 to 1:8, optimally from 1:2 to 1:5. If the weight ratio of cationic surfactant to fatty alcohol in hair treatment compositions is too high, this can lead to eye irritancy from the composition. If it is too low, it can make the hair feel squeaky for some consumers.

The fatty alcohol may be present in laundry conditioners as a fatty complexing agent and is preferably present in an amount greater than 0.3 to 5% by weight based on the total weight of the composition. More preferably, the fatty component is present in an amount of from 0.4 to 4%. The weight ratio of the mono-ester component of the quaternary ammonium fabric softening material to the fatty complexing agent is preferably from 5:1 to 1:5, more preferably 4:1 to 1:4, most preferably 3:1 to 1:3, e.g. 2:1 to 1:2.

Suspending agent:

Preferably an aqueous composition of the invention further comprises a suspending agent and/or viscosity enhancer.

Examples of suitable materials include: natural gums such as carrageenan, xanthan gum, gum arabic, gum tragacanth and guar gum and derivatives thereof such as hydroxypropyl guar and guar hydroxypropyl trimoniumchloride; inorganic thickeners such as colloidal magnesium aluminium silicate (Veegum), finely divided silica, natural clays such as bentonite and synthetic clays such as the synthetic hectorite available as Laponite (ex Laporte Industries Ltd);

Perferred are materials selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof.

Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives, since these impart pearlescence to the composition.

Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493.

Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used; they are available commercially as Carbopol 910, Carbopol 934, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trademark) materials are available from Goodrich.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

Mixtures of any of the above suspending agents may be used. Preferred is a mixture of cross-linked polymer of acrylic acid and crystalline long chain acyl derivative.

Suspending agent will generally be present in a hair treatment composition of the invention at levels of from 0.1 % to 10%, preferably from 0.5 % to 6 %, more preferably from 0.9 % to 4 % by total weight of suspending agent based on the total weight of the composition.

<u>Silicone</u>:

The compositions of the invention can contain emulsified droplets of a silicone. In hair treatment composition these give enhancing conditioning performance.

Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188.

The viscosity of the emulsified silicone itself (not the emulsion or the final composition) is typically at least 10,000 cst at 25 oC the viscosity of the silicone itself is preferably at least 60,000 cst, most preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed 109 cst for ease of formulation.

Emulsified silicones for use in the compositions of the invention will typically have an average silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10 micron, ideally from 0.01 to 1 micron. Silicone emulsions having an average silicone droplet size of £ 0.15 micron are generally termed microemulsions.

Emulsified silicones for use in the compositions of the invention will typically have an size in the composition of less than 30, preferably less than 20, more preferably less than 15. Preferably the average silicone droplet is greater than 0.5 micron, more preferably greater than 1 micron, ideally from 2 to 8 micron.

Silicone particle size may be measured by means of a laser light scattering technique, for example using a 2600D Particle Sizer from Malvern Instruments.

Examples of suitable pre-formed emulsions include Xiameter MEM 1785 and microemulsion DC2-1865 available from Dow Corning. These are emulsions /microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation.

A further preferred class of silicones for inclusion in compositions of the invention, especially hair treatment compositions are amino functional silicones. By "amino functional silicone" is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group. Examples of suitable amino functional silicones include: polysiloxanes having the CTFA designation "amodimethicone".

Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166 and DC2-8566 (all ex Dow Corning).

Suitable quaternary silicone polymers are described in EP-A-0 530 974. A preferred quaternary silicone polymer is K3474, ex Goldschmidt.

Also suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant.

Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC939 Cationic Emulsion and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

The total amount of silicone is preferably from 0.01 wt% to 10 %wt of the total composition more preferably from 0.1 wt% to 5 wt%, most preferably 0.5 wt% to 3 wt% is a suitable level.

Cationic polymers:

Cationic polymers are preferred ingredients in hair-treatment compositions of the invention for enhancing performance.

Suitable cationic polymers may be homopolymers which are cationically substituted or may be formed from two or more types of monomers. The weight average ($M_w$) molecular weight of the polymers will generally be between 100 000 and 2 million daltons. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof. If the molecular weight of the polymer is too low, then the conditioning effect is poor. If too high, then there may be problems of high extensional viscosity leading to stringiness of the composition when it is poured.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic to non-cationic monomer units is selected to give polymers having a cationic charge density in the required range, which is generally from 0.2 to 3.0 meq/gm. The cationic charge density of the polymer is suitably determined via the Kjeldahl method as described in the US Pharmacopoeia under chemical tests for nitrogen determination.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

The cationic polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic polymers include, for example:

- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;
- mineral acid salts of amino-alkyl esters of homo-and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, (as described in U.S. Patent 4,009,256);
- cationic polyacrylamides(as described in WO95/22311).

Other cationic polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives.

Cationic polysaccharide polymers suitable for use in compositions of the invention include monomers of the formula:

$A\text{-}O\text{-}[R\text{-}N^{+}(R^{1})(R^{2})(R^{3})X^{-}]$,

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof. $R^1$, $R^2$ and $R^3$ independently represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in $R^1$, $R^2$ and $R^3$) is preferably about 20 or less, and X is an anionic counterion.

Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from the Amerchol Corporation, for instance under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimethylammonium chloride (commercially available from Rhodia in their JAGUAR trademark series). Examples of such materials are JAGUAR C13S, JAGUAR C14, JAGUAR C15, JAGUAR C17 and JAGUAR C16 Jaguar CHT and JAGUAR C162.

Mixtures of any of the above cationic polymers may be used.

Cationic polymer will generally be present in a hair shampoo composition of the invention at levels of from 0.01 to 5%, preferably from 0.05 to 1%, more preferably from 0.08 to 0.5% by total weight of cationic polymer based on the total weight of the composition.

The amount of polymer used in the laundry compositions of the invention is suitably from 0.001 to 0.5 wt %, preferably from 0.005 to 0.4 wt %, more preferably from 0.05 to 0.35 wt % and most preferably from 0.1 to 0.25 wt %, by weight of the total composition. An example of a preferred polymer is Flosoft 270LS ex SNF.

Minors:

As further optional components for inclusion in compositions according to the invention may be mentioned the following conventional adjunct materials known for use in cosmetic compositions: emulsifiers, humectants, suspending agents, rheology modifiers, pearlescing agents, opacifiers, salts, perfumes, buffering agents, colouring agents, emollients, moisturisers, foam stabilisers, sunscreen materials, antimicrobial agents, preservatives, antioxidants, and natural oils and extracts. Some or all of these may be present in the bulk of the composition as well as some being present as a benefit agent in the befit agent delivery particles.

Shading dye:

Optional shading dyes can be used in the hair and laundry compositions of the present invention. Preferred dyes appear violet or blue. The shading dyes can perform a variety of functions relating to the yellowing of the substrate. For example in laundry compositions any 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 and shading dye 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 depends, 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.

In order that the present invention may be further understood and carried forth into practice it will be further described with reference to the following examples. In the examples, as in the rest of the specification, all percentages are by weight unless otherwise specified.

## Examples

### Example 1: Chitosan complex preparation

Chitosan (cat. # 448877), 3,5-dihydroxybenzoic acid and guanidineacetic acid were obtained from Aldrich. Acetic acid and arginine were purchased from Sinopharm Chemical. Creatine monohydrate was from Acros. Protocatechuic acid and pyroglutamic acid were from J & K Chemica.

### 1a) Preparation of chitosan-acetic acid complex (Ac)

To 20 ml of 0.5% acetic acid aqueous solution was added 200 mg of chitosan and the mixture was stirred until chitosan dissolved completely. Then the liquid was filtered and lyophilized for 48 hours to afford a white solid and this is denoted **Ac**.

### 1b) Preparation of chitosan complexes with other acids

Taking arginine as an example, a typical procedure for chitosan complex preparation is shown as follows. To 20 ml of 0.5% acetic acid aqueous solution was added 200 mg of chitosan and the mixture was stirred until chitosan dissolved completely. Then 10.8 mg of arginine was added (the feeding ratio was 5 molar% relative to the calculated number of chitosan repeating unit) and the mixture was stirred for 24 hours and then filtered and lyophilized for 48 hours to afford a white solid. The product is denoted **A5** (5 molar% arginine). Similarly **A10, A15 and A25** (10, 15 and 25 molar% respectively arginine) and other complexes were prepared and the sample information for all chitosan complexes is shown in

Table 1.

Table 1. chitosan complex samples

| Sample code | Complexing acid | molar ratio of complexing acid to chitosan |
|---|---|---|
| Ac | Acetic acid | -- |
| A5 | Arginine | 5 % |
| A10 | Arginine | 10 % |
| A15 | Arginine | 15 % |
| A25 | Arginine | 25 % |
| C5 | Creatinine | 5 % |
| C10 | Creatinine | 10 % |
| D5 | 3,5-Dihydroxybenzoic acid | 5 % |
| D10 | 3,5-Dihydroxybenzoic acid | 10 % |
| G5 | Guanidineacetic acid | 5 % |
| G10 | Guanidineacetic acid | 10 % |
| Pr5 | Protocatechuic acid | 5 % |
| Pr10 | Protocatechuic acid | 10 % |
| Py5 | Pyroglutamic acid | 5 % |
| Py10 | Pyroglutamic acid | 10 % |

## <u>Example 2</u>: Surface Attachment of chitosan complex onto latex particles (1 μm) *via* EDAC Coupling

1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrogen chloride (EDAC) was from TCI. Aqueous latex (solid content 2.5%) of Fluoresbrite® yellow green (YG) microspheres (1 micron) was from Polysciences, USA.

### <u>2a) Purification of latex particles</u>

The fluoresbrite YG microspheres latex (1 • m) was purified through the following procedure. Two 2.0 ml centrifuge tubes, each containing 1.5 g of the latex were centrifuged at 9000 rpm for 7 minutes. The supernatant was removed and 1.0 ml of pH 7.0 phosphate buffer was added to each tube and the mixtures were agitated through vortex mixing to re-disperse the pellets. Then the latex was centrifuged at 9000 rpm for 7 minutes. The supernatant was removed and the buffer wash was repeated once. Then 1.0 ml of de-ionized water was added to each tube containing the centrifuge pellets and the mixtures were agitated using the aforementioned method for re-dispersion. The obtained latex was centrifuged again at 10000 rpm for 7 minutes and the supernatant was removed. The wash in de-ionized water was also repeated once. The obtained pellets were combined and re-dispersed in 0.5 ml of DI water to obtain a solids level of 15%.

### 2b) Latex particles activation using EDAC

120 mg of EDAC in 0.5 ml of DI water was added dropwise to the obtained latex from 2a and the latex was stirred at room temperature for three hours. The latex was then centrifuged at 9000 rpm for 7 minutes and the supernatant was removed. 1.0 ml of pH 7.0 buffer was added and the mixture was agitated for good dispersion and the mixture was then subjected to centrifugation at 9000 rpm for 7 minutes. The supernatant was removed and the buffer wash was repeated once. The obtained pellet was then subjected to centrifugal wash with DI water (twice, 1.0 ml of water each) at the same speed for the same duration. The obtained pellet was re-dispersed in 2.0 ml of DI water and homogenised through vortex and sonication for 5 minutes.

### 2c) Grafting of chitosan complex onto latex particles

Taking chitosan complex A5 as an example, the grafting was carried out as follows to generate A5-grafted polystyrene latex (PS-*graft*-A5). 1% A5 aqueous solution was prepared by dissolving 10 mg of the chitosan complex in 1 ml of DI water. 300 mg of the solution was added to a 2 ml centrifuge tube containing 700 microliters of DI water. To the solution was added 133 microliters of the EDAC activated latex and the mixture was agitated at 40 °C for 24 hours. Then the latex was centrifuged at 9000 rpm for 7 minutes and the supernatant was removed.

The obtained pellet was re-dispersed in 1.0 ml of DI water and centrifuged. The supernatant was removed and the centrifugal wash was repeated three times and the obtained pellet was dispersed in 1.0 ml of DI water. The final solid content of latex was around 0.4% (w/w).

### 2d) Preparation of comparative example (polystyrene latex without surface attached chitosan complex)

A comparative (control) sample without any addition of chitosan complex was prepared by diluting 160 microliters of the original latex with 850 microliters of DI water to get final solid content of latex 0.4% (w/w).

### 2e) Characterization of chitosan complex modified polystyrene latex particle

The sizes and zeta potentials of the modified polystyrene particles were measured on Malvern Nano ZS90 dynamic light scattering and compared with original particles. Each latex sample was diluted with DI water before measurement. The final solid content and pH of latex sample is 50ppm and around 7, respectively. The results shown in Table 2 indicates that the grafting were successful.

**Table 2. Characterization of polystyrene (PS) latex particle before and after grafting**

| Code of latex particles | Size (micron) | Zeta potential (mV) |
|---|---|---|
| PS (control) | 1.6 | -37.9 |
| PS-*graft*-Ac | 2.0 | 14.4 |
| PS-*graft*-A5 | 2.1 | 23.4 |
| PS-*graft*-A10 | 1.3 | 23.6 |
| PS-*graft*-A15 | 2.1 | 28.0 |
| PS-*graft*-A25 | 1.6 | 36.0 |
| PS-*graft*-C5 | 1.7 | 26.7 |
| PS-*graft*-C10 | 4.6 | 24.0 |
| PS-*graft*-D5 | 1.6 | 21.5 |
| PS-*graft*-D10 | 1.2 | 16.6 |
| PS-*graft*-G5 | 3.0 | 23.5 |
| PS-*graft*-G10 | 2.5 | 22.3 |
| PS-*graft*-Pr5 | 1.5 | 21.5 |
| PS-*graft*-Pr10 | 1.4 | 24.9 |
| PS-*graft*-Py5 | 2.2 | 18.6 |
| PS-*graft*-Py10 | 2.1 | 22.2 |

## Example 3: Deposition performance of polystyrene latex particles on hair

Deposition of polystyrene latex particles (1 µm, with or without chitosan complex) on hair was investigated through hair wash using shampoo base composed of sodium laurethsulfate (SLES), cocamidopropyl betaine (CAPB) and sodium chloride or conditioner base mainly composed of behenyltrimethylammonium chloride (BTAC), cetearyl alcohol and hydroxyethyl cellulose (HEC) (details shown in Table 2a below). The fluorescence measurement was carried out using a TECAN SAFIRE 2 microplate reader.

**Table 2a: Composition of the hair conditioner base**

| **INCI name** | **Trade name** | **% content** |
|---|---|---|
| Behenyltrimethylammonium Chloride (BTAC) | Genamin BTLF | 3.18 |
| Cetearyl Alcohol | Lanette S3 | 4.44 |
| Hydroxyethyl cellulose (HEC) | Natrosol 250HHR | 0.22 |
| DMDM hydantoin | Glydant | 0.11 |
| Methylchloroisothaizolinone<br>Methylisothiazolinone | Kathon CG | 0.04 |
| Water | - | 92.0 |

## 3a) Preparation of shampoo base and conditioner base

The shampoo base was prepared by dissolving SLES (70% aqueous solution), CAPB and sodium chloride in water to afford a solution of 12% SLES, 1.6% CAPB and 1.0% sodium chloride.

The conditioner base was prepared by the following procedure.

(1) HEC (2.0 g) was mixed with DI water (650.0g) and heated to 80°C with stirring (150 rpm). Then BTAC (28.6 g) was added and mixed well.
(2) In a separate vessel, cetearyl alcohol (40.0g) was melted at around 80 °C.
(3) The molten cetearyl alcohol was added slowly to the HEC mixture under high shear (7,000 rpm for 15 min at 80°C). Then agitation was stopped and the mixture was cooled down to 60°C.
(4) DI water (169.0 g) was added while the mixture was maintained at 60°C.
(5) The obtained mixture was cooled to 35 °C and preservatives (DMDM hydantoin and Methylchloroisothaizolinone Methylisothiazolinone) were added. The product at was finally sheared at 7,000 rpm for 2 min.

### 3b) Hair wash procedure

Hair switches (5.5 cm length, around 750mg weight, virgin or damaged hair) were pretreated by soaking in a bottle containing 14% SLES solution at 40 °C with continuous shaking for 30 minutes and then rinsing with tap water thoroughly. The switches were dried in air at room temperature overnight before use.

A typical hair wash procedure is shown as follows. Three hair switches were wetted with tap water and swung to remove excess water. 70 mg of the shampoo base (or conditioner base) was added to a Petri dish together with 20 microliters of the polystyrene latex and the first switch was gently rubbed with the mixture for 1 minute and then rinsed with 500 ml of tap water. The switch was swung dry and then immersed in a vial containing 20 milliliters of ethyl acetate for 30 minutes. 200 microliters of the extraction liquid was withdrawn from the vial and added to a 96-well microplate for fluorescence measurement (excitation 441 nm, emission 486 nm) to afford a reading of $E_1$.

The second switch was wetted with tap water and swung dry, to which 20 microliters of the latex was added. The switch was also extracted with 20 milliliters of ethyl acetate for 30 minutes. 200 microliters of the extraction liquid was withdrawn and added to the microplate and subjected to measurement using the aformentioned method and afforded a reading of $E_0$.

The third switch was extracted without added latex in 20 millilitres of ethyl acetate for 30 minutes. 200 microliters of the extraction liquid was taken to the microplate and afforded a reading $E_b$ upon fluorescence measurement. The percent deposition (%deposition) was calculated according to the following equation:

$$\%Deposition = \frac{E_1 - E_b}{E_0 - E_b} \times 100 .$$

### 3c) Hair deposition performance

The deposition performances of polystyrene latex particles with and without grafted chitosan complex on virgin or damaged hair are shown in Table 3.

Table 3. Deposition performances of polystyrene latex particles on hair

| Code of latex particles | Depostion from Shampoo base | | Depostion from Conditioner base | |
|---|---|---|---|---|
| | Deposition on virgin hair (%) | Deposition on damaged hair (%) | Deposition on virgin hair (%) | Deposition on damaged hair (%) |
| PS (control) | 2±1 | 0±0 | 16±4 | 14±1 |
| PS-*graft*-Ac | 16±6 | 3±2 | 16±2 | 14±1 |
| PS-*graft*-A5 | 7±1 | 4±1 | 11±1 | 19±1 |
| PS-*graft*-A10 | 21±7 | 10±5 | 13±3 | 21±1 |
| PS-*graft*-A15 | 25±4 | 15±2 | 23±1 | 20±5 |
| PS-*graft*-A25 | 27±4 | 20±3 | 37±8 | 28±2 |
| PS-*graft*-C5 | 7±3 | 6±2 | 13±8 | 15±1 |
| PS-*graft*-C10 | 12±2 | 9±1 | 7±1 | 15±3 |
| PS-*graft*-D5 | 5±1 | 4±1 | 7±1 | 9±1 |
| PS-*graft*-D10 | 11±3 | 6±1 | 9±2 | 15±1 |
| PS-*graft*-G5 | 6±1 | 8±2 | 5±1 | 12±1 |
| PS-*graft*-G10 | 11±2 | 5±1 | 8±2 | 13±2 |
| PS-*graft*-Pr5 | 27±6 | 6±2 | 18±3 | 16±1 |
| PS-*graft*-Pr10 | 14±2 | 12±4 | 14±1 | 15±3 |
| PS-*graft*-Py5 | 7±1 | 5±1 | 8±2 | 10±1 |
| PS-*graft*-Py10 | 16±2 | 10±3 | 12±4 | 21±1 |

## Example 4: Surface attachment of chitosan complex onto Melamine Formaldehyde (MF) capsule (8 µm) *via* shell forming process

Melamine (CP), formaldehyde (37% aqueous solution, AR), formic acid (98%, AR) acetic acid (AR), sodium carbonate (AR), and sodium chloride (AR) were purchased from Sinopharm Chemical. Melamine Formaldehyde (MF) fluorescent capsules latex (particle size 8 µm, particle solid content 45.5%, perfume solid content 43.0%) was obtained from Givaudan.

### 4a) Mixing MF latex with chitosan

2.5 g of chitosan was added to 500 ml of 0.25% aqueous acetic acid solution and the mixture was agitated overnight to yield a 0.5% chitosan solution. 100 g of the above solution was then homogenized at 14,000 rpm. 1.82 g of MF latex was diluted with 20 ml of DI water and the obtained latex was added dropwise to the chitosan solution while the homogenization was maintained. The obtained mixture (pH 4.3) was used for the further reaction.

### 4b) Grafting of chitosan onto MF capsules

4.85 g of formaldehyde was dissolved in 11 g of DI water in a 20 ml vial and the pH of the solution was adjusted to 8.9 with 5.0% sodium carbonate solution. 2.5 g of melamine and 0.15 g of sodium chloride were then added. The mixture was first stirred for 10 minutes at room temperature and then heated and stirred at 62 °C until it turned into a clear solution (melamine-formaldehyde prepolymer solution).

110 ml of the mixture prepared in 4a was transferred to a 250 ml three neck round-bottom flask fitted with overhead stirrer and condenser. After the temperature of the mixture was raised to 75 °C, 0.53 g of the above melamine-formaldehyde prepolymer solution was added and the pH of the final mixture was

adjusted to 3.9 using 10% aqueous formic acid solution. The mixture was then stirred at 75 °C for 2 hours and then cooled to room temperature. This sample was denoted MF-*graft*-Ac with final solid content around 0.7% (w/w).

### 4c) Acid complexing on chitosan-*grafted*-MF capsules

Taking arginine as an example, the preparation of MF capsules grafted with chitosan-arginine complex with 10% arginine feeding ratio (MF-*graft*-A10) is as follows. Aqueous solution of arginine (21.4 mg/ml) was prepared and 126 microliters of the solution was added to 5 ml of the obtained MF-*graft*-Ac sample and the mixture was agitated on a roller overnight The final solid content was around 0.7% (w/w). Similarly, MF capsules grafted with chitosan-protocatechuic acid complex (MF-*graft*-Pr10) and chitosan-pyroglutamic acid complex (MF-*graft*-Py10) were prepared.

### 4d) Preparation of comparative example (MF capsule without surface attached chitosan complex)

A comparative (control) sample without any addition of chitosan complex was prepared by diluting 16 microliters of the MF capsule as supplied with 984 microliters of DI water to get final solid content of MF capsule 0.7% (w/w).

### 4e) Characterization of chitosan complex modified MF capsule

The sizes of the MF capsules were estimated from microscopic images. The zeta potentials of the MF capsules were measured on a Malvern ZETASIZER NANO-ZS (ZEN3600) with 633nm He-Ne laser. Each capsule sample was diluted with DI water before measurement. The final solid content and pH of latex sample is 50ppm and around 5, respectively. The results shown in Table 4 indicate that the grafting were successful.

Table 4. Characterization of MF capsule before/after grafting

| Code of MF capsules | Size* (micron) | Zeta potential (mV) |
|---|---|---|
| MF (control) | 8 | -48 |
| MF-*graft*-Ac | 8 | 7 |

* Note: size data were estimated from microscopic images

## <u>Example 5:</u> Deposition performance of MF capsules on hair

Deposition of MF particles (as above, supplied by Givaudan, with or without chitosan complex) on hair was investigated through hair wash using shampoo base composed of sodium laurethsulfate (SLES), cocamidopropyl betaine (CAPB) and sodium chloride or conditioner base composed of or conditioner base mainly composed of behenyltrimethylammonium chloride (BTAC), cetearyl alcohol and hydroxyethyl cellulose (HEC) (details shown in **Appendix 1**) The fluorescence measurement was carried out using a TECAN SAFIRE 2 microplate reader.

### <u>5a) Preparation of shampoo base and conditioner base</u>

The preparation of shampoo base and conditioner base were both the same as described in Example 3a.

### <u>5b) Hair wash procedure</u>

The hair wash and calculation procedure were the same as described in Example 3b, except that ethanol and 40 minutes were used as extraction solvent and extraction time, respectively, instead of ethyl acetate and 30 minutes for hair switch extraction. In addition, the fluorescence measurement conditions were excitation wavelength 468 nm and emission wavelength 520 nm.

## 5c) Hair deposition performance

The deposition performances of MF capsule with and without grafted chitosan complex on virgin or damaged hair were shown in Table 5.

Table 5. Deposition performances of MF capsules on hair

| Code of latex particles | Depostion from Shampoo base | | Depostion from Conditioner base | |
|---|---|---|---|---|
| | Deposition on virgin hair (%) | Deposition on damaged hair (%) | Deposition on virgin hair (%) | Deposition on damaged hair (%) |
| MF (control) | 50±5 | 54±4 | 60±6 | 56±7 |
| MF-*graft*-Ac | 81±4 | 52±11 | 78±6 | 69±8 |
| MF-*graft*-A10 | 84±10 | 75±8 | 78±5 | 63±5 |
| MF-*graft*-Pr10 | 76±8 | 66±6 | 93±4 | 58±7 |
| MF-*graft*-Py10 | 80±7 | 72±7 | 89±4 | 66±8 |

## CLAIMS

1. A benefit agent delivery particle, comprising a benefit agent, and having at the outer surface of the particle one or more delivery aids which include a chitosan salt, which comprises a chitosan component and an anion, wherein the anion of said salt is an organic anion with a molecular weight of greater than 60, and wherein the chitosan component comprises a backbone which comprises amine groups.

2. A benefit agent delivery particle according to claim 1, wherein the amine groups comprise a mole fraction in salt form, of from 5% to 30%, preferably from 10% to 30%.

3. A benefit agent delivery particle according to claim 1 or claim 2, wherein the particles have a zeta potential as measured using a Malvern Nano ZS90 apparatus in DI water at a solid content of 50ppm and around pH of 7 is above 15 mV, more preferably above 20 mV.

4. A benefit agent delivery particle according to any preceding claim wherein the chitosan component of the salt, as a protonated material, has a molecular weight in excess of 10kDa.

5. A benefit agent delivery particle according to any preceding claim which comprises a non-polysaccharide polymer, more preferably an aminoplast polymer.

6. A benefit agent delivery particle according to any preceding claim which has an average diameter of less than 10 micron, preferably an average diameter in the range 1-10 micron.

7. A benefit agent delivery particle according to any preceding claim comprising a core which comprises the benefit agent and a shell which comprises the water insoluble non-polysaccharide polymer, with the chitosan salt attached at the outer surface of the shell.

8. A benefit agent delivery particle according to any preceding claim wherein the benefit agent is selected from flavours and fragrances, profragrance, clays, enzymes, antifoams, fluorescers, bleaching agents and precursors thereof, dyes and/or pigments, conditioning agents, lubricants, colour and photo-protective agents, antioxidants, ceramides, reducing agents, sequestrants, colour care additives, unsaturated oil, emollients, moisturisers, insect repellents and/or pheromones, drape modifiers, anti-microbial and microbe control agents and mixtures thereof.

9. A benefit agent delivery particle according to any preceding claim wherein the benefit agent is selected from fragrances, moisturisers, sunscreens, skin lightening agents, anti-dandruff agents, oils, insect repellents, colour protection agents and dyes.

10. A composition comprising

    a) a particle according to any of the preceding claims, and
    b) at least one surfactant.

11. A composition according to claim 10 comprising at least 3% wt on total composition of an alkyl ether sulphate.

12. A process for the production of benefit agent delivery particle according to any one of claims 1 to 9, in which:

a) a core is encapsulated using emulsion polymerization to form core-shell particles, and,

b) a further polymer layer is formed on the outer surface of the core shell-particles in the presence of the chitosan salt,

wherein the benefit agent is either present in or as the core during step (a) of the process or adsorbed into the core in a subsequent step.