HARD SURFACE CLEANING COMPOSITION AND PROCESS

A hard surface cleaning composition comprising:

a) a microcapsule comprising:
   i) a perfume contained within;
   ii) a polymer shell; and fixed to the outside of the shell,
   iii) a nonionic polysaccharide deposition aid that causes the microcapsule to deposit from aqueous dispersion onto a cleaning implement comprising cotton,

b) at least an effective amount of surfactant for cleaning the hard surface; and
c) water.

Also, a hard surface cleaning process comprising the steps of: using a cleaning implement comprising cotton to apply to a hard surface and move around on the hard surface to remove soil from the hard surface an aliquot of aqueous cleaning composition according to the first aspect of the invention, rinsing the cleaning implement in water to remove surfactant and soil from the cotton and leaving the rinsed cotton cleaning implement to dry, whereby after rinsing at least 25 wt% of the microcapsules in the composition applied to the hard surface are deposited onto and retained by the cotton of the cleaning implement.
Description

Field of the Invention

[0001] The present invention relates to hard surface cleaning compositions designed to be applied to a hard surface using a cleaning implement comprising cotton; e.g. a mop. The compositions comprise surfactant to assist with cleaning the hard surface and microencapsulated perfume. The invention further relates to a hard surface cleaning method that deposits microencapsulated perfume benefit agent, preferably microencapsulated perfume onto a cleaning implement comprising cotton while using it to clean a hard surface with the composition.

Background and Prior Art

[0002] The deposition of a perfume onto a hard surface, for example a floor or a bath, is a well-known method of imparting fragrance to the hard surface.

[0003] Perfume may be delivered from a cleaning implement to a hard surface by means of a deposition aid, which itself has an affinity for the hard surface in question, thereby enabling delivery during the cleaning process. This approach is disclosed in many patent documents, particularly those directed to the field of polymeric microencapsulation of perfume and other benefit agents.

[0004] EP 2382907 A2 discloses a surface cleaning implement comprising elastic compressed foam with additives including microcapsules.

[0005] WO 2008/055787 A1 discloses a sponge holding particles for delivery of active ingredients, such as perfume, for cleaning hard surfaces.

[0006] US 2010/0059523 A1 discloses a container with multiple compartments to allow substrate specific perfumes to be added to an odour base cleaning liquid.

[0007] WO 2007/080552 A1 discloses a cleaning implement with layers of melamine foam and supporting material to which a perfume source is attached by permanent adhesive. The perfume source is selected from the group consisting of perfume microcapsules or perfume loaded carrier particles.


[0009] EP 1721963 A1 discloses a household cleaning liquid with perfume containing microcapsules that delivers better perfume than from liquid with perfume.


[0012] DE 29702433 U1 discloses a household cleaning cloth impregnated with a perfume oil. The perfume gives an indication of whether the cloth is fresh or not.

[0013] However, despite a scent effect from the free perfume in a typical product, consumers still experience smelly, unhygienic dishcloths after a dish wash process, smelly mops after a floor washing process, and so on.

[0014] A more detailed example of the problem experienced by a consumer is as follows: The consumer performing a hand dish wash process, uses a typical hand dish wash detergent, which contains benefit agents, such as fragrance, in a free form. During the hand wash process, the fragrance provides a pleasant smell to the consumer when the detergent is in the bottle and also when it is in the wash liquor. Some of the fragrance transfers to the cleaning implement (for example cloth) but is quickly removed by rinsing or evaporation.

Brief Description of the Invention

[0015] According to a first aspect of the present invention there is provided a hard surface cleaning composition comprising:

a) a microcapsule comprising:
   i) a perfume contained within;
   ii) a polymer shell; and fixed to the outside of the shell,
   iii) a nonionic polysaccharide deposition aid that causes the microcapsule to deposit from aqueous dispersion onto a cleaning implement comprising cotton,

b) at least an effective amount of surfactant for cleaning the hard surface; and
c) water.
By targeting cotton in the cleaning implement the microcapsules are deposited onto the cleaning implement at the same time as the hard surface is cleaned. We have found that using this composition it is possible to deliver long lasting consumer desirable fragrance to the cleaning implement whilst still delivering excellent hard surface cleaning.

Transfer is the process whereby the microcapsule is transferred to the cleaning implement during the cleaning process. Retention is the mechanism that prevents the microcapsule from being removed from the cleaning implement during rinsing. If either transfer or retention does not work efficiently then the magnitude of the benefit on the cleaning implement decreases. We have found that by using the nonionic polysaccharide deposition aid both transfer and retention are increased.

We have found that a particularly beneficial result is achieved by encapsulating perfume, in a polymeric shell and attaching to the shell a motif that recognizes the cotton material the cleaning implement is made from via a molecular recognition process. In this way, an increased level of perfume can be deposited onto the cleaning implement where it can then be released slowly or in response to shear, thus providing prolonged fragrance to the cleaning implement.

Also, according to the invention, there is provided a hard surface cleaning process comprising the steps of: using a cleaning implement comprising cotton to apply to a hard surface and move around on the hard surface to remove soil from the hard surface an aliquot of aqueous cleaning composition according to the first aspect of the invention, rinsing the cleaning implement in water to remove surfactant and soil from the cotton and leaving the rinsed cotton cleaning implement to dry, whereby after rinsing at least 25 wt% of the microcapsules in the composition applied to the hard surface are deposited onto and retained by the cotton of the cleaning implement.

Detailed Description of the Invention

The composition

The microcapsule

Any type of microcapsule that is suitable for use in compositions for the treatment of hard surfaces can be used. In the following passages, the microcapsule may also be described as "microcapsule(s)" "encap(s)" "particles" or "capsules".

The shell may be permeable to the benefit agent. In such an embodiment, the shell is comprised of materials including aminoplasts, proteins, polyurethanes, polysaccharides, gums and any other encapsulating material which may be used effectively in the present invention, such as polymethylmethacrylate.

Preferred encapsulating polymers include those formed from melamine formaldehyde or urea formaldehyde condensates, as well as similar types of aminoplasts. Most preferably the shell comprises melamine formaldehyde.

Additionally, microcapsules made via the simple or complex coacervation of gelatin are also preferred for use with the coating. Microcapsules having shell walls comprised of polyurea, polyurethane, polyamide, polylefins, polysaccharide, protein, silicone, lipid, gums, polyacrylate, polystyrene, and polyesters or combinations of these materials are also possible.

A representative process used for aminoplast encapsulation is disclosed in US 3,516,941 though it is recognized that many variations with regard to materials and process steps are possible. A representative process used for gelatin encapsulation is disclosed in US 2,800,457 though it is recognized that many variations with regard to materials and process steps are possible. Both of these processes are discussed in the context of fragrance encapsulation for use in consumer products in US 4,145,184 and US 5,112,688 respectively.

Encapsulation can provide pore vacancies or interstitial openings depending on the encapsulation techniques...
Fragrance microcapsules known in the art and suitable for use in the present invention comprise a wall or shell infrastructure, for example a "sponge" type encaps. The capsules may have a hollow nature. Alternatively, the capsules may be solid porous structures, or a solid infrastructure, for example a "sponge" type encaps.

Microcapsule formation using mechanisms similar to the foregoing mechanism, using (i) melamine-formaldehyde or urea-formaldehyde pre-condensates and (ii) polymers containing substituted vinyl monomeric units having proton-donating functional group moieties (e.g. sulfonic acid groups or carboxylic acid anhydride groups) bonded thereto is disclosed in US 4,406,816, US 4,406,816 (2-acrylamido-2-methyl-propane sulfonic acid groups), GB 2,062,570A (styrene sulfonic acid groups) and GB 2,006,709A (carboxylic acid anhydride groups).

For liquid compositions, the microcapsules may be used in the form of a slurry, which preferably comprises about 40% solids. The amount of such a 40% capsule slurry to be used in a composition is up to 10%, preferably from 0.1 to 5%, more preferably from 1 to 2% by weight of the total composition.

Particle size and average diameter of the microcapsules can vary from about 10 nanometres to about 1000 microns, preferably from about 50 nanometres to about 100 microns, more preferably from about 2 to about 40 microns, even more preferably from about 4 to 15 microns. A particularly preferred range is from about 5 to 10 microns, for example 6 to 7 microns. The microcapsule size distribution can be narrow, broad or multimodal. Multimodal distributions may be composed of different types of capsule chemistries.

The microcapsules for use in the compositions of the invention may be prepared by a miniemulsion polymerisation process substantially as described in WO2005/121185.

The term "latex" or "latex particle" as used herein is defined as a stable colloidal dispersion of a polymeric substance in an aqueous medium. The polymer microcapsule particles are usually approximately spherical and of typical colloidal dimensions. Particle diameters may range from about 30 to 500 nm (The Encyclopaedia of Polymer Science and Engineering, Second Edition, Volume 8, Page 647, John Wiley and Sons Inc. (1987)).

The Deposition Aid

The microcapsule comprises a deposition aid. Deposition aids modify the properties of the exterior of the particle. One particular benefit which can be obtained with these materials is to make the particle more substantive to a desired substrate, in this case cotton. Deposition aids are preferably selected from non-hydrolysable polymers.

Preferred polysaccharide polymers, may be derived from a broad range of polysaccharides. Preferably, the polysaccharide is selected from the group consisting of: tamarind gum (preferably consisting of xyloglucan polymers), guar gum, locust bean gum (preferably consisting of galactomannan polymers), and other industrial gums and polymers, which include, but are not limited to, Tara, Fenugreek, Aloe, Chia, Flaxseed, Psyllium seed, quince seed, xanthan, gellan, welan, rhamnans, dextran, curdlan, pullulan, scleroglucan, schizophyllan, chitin, hydroxyalkyl cellulose, arabinan (preferably from sugar beets), de- branched arabinan (preferably from sugar beets), arabinoxylan (preferably from rye and wheat flour), galactan (preferably from lupin and potatoes), pectic galactan (preferably from potatoes), galactomannan (preferably from carob, and including both low and high viscosities), glucomannan, lichenan (preferably from Icelandic moss), mannan (preferably from ivory nuts), pachyman, rhamnogalacturonan, acacia gum, agar, alginate, carrageenan, chitosan, clavan, hyaluronic acid, heparin, inulin, cellodextrins, cellulose, cellulose derivatives and mixtures thereof.

Preferred non-hydrolysable substrate-substantive deposition aids include non-hydrolysable polysaccharides. The polysaccharides preferred for cotton substantivity for example have a B-1,4-linked backbone.

Preferably the polysaccharide is a cellulose, a cellulose derivative, or another B-1,4-linked polysaccharide having an affinity for cellulose, such as polymannan, polyglucan, polyglucomannan, polyxylglucan and polygalactomannan or a mixture thereof. More preferably, the polysaccharide is selected from the group consisting of polyxylglucan and polygalactomannan. Most preferably, the deposition aid is locust bean gum, xyloligucan, guar gum or mixtures thereof.

The preferred molecular weight of the polymeric deposition aid is in the range of from about 5 kDa to about 500 kDa, preferably 10 kDa to 500 kDa, more preferably 20 kDa to 300 kDa.

Preferably, the deposition-aid polymer is present at levels such that the ratio polymer:particle solids is in the range 1:500 to 3:1, preferably 1:200 to 1:3.

Perfume

An essential component of the microcapsule is the perfume. In addition to the perfume the composition may further comprise free oil perfume. Mixtures of different microcapsules may be used in combination in the composition.

Throughout this specification, unless the context demand otherwise, the term perfume includes all perfume raw materials, fragrance materials and pro-fragrances.
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, retinoic acid and provitamin A are capable of being converted into fragrant species including the ionones, damascones and damascenes. 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.

The perfume is typically present in an amount of from 10 to 85 % by total weight of the microcapsule, preferably from 15 to 75 % by total weight of the microcapsule. The perfume suitably is comprised of components with a molecular weight of from 50 to 500 Da. Pro-fragrances can be of higher molecular weight, being typically 1 to 10 kDa.

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 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. A. Cantander 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 taste to a consumer product traditionally perfumed or flavoured, or of modifying the odour and/or taste of said consumer product.

By perfume in this context is not only meant a fully formulated product fragrance, but also selected components of that fragrance, particularly those which are prone to loss, such as the so-called ‘top notes’.

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

Typical perfume components which it is advantageous to employ in the embodiments of the present invention include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100 to 250 °C.

It is also advantageous to microcapsule 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, Benzylic Aceton, Benzyl Alcohol, Benzyl Formate, Benzyl Isovalerate, Benzyl Propionate, Beta Gamma Hexenol, Camphor Gum, Laevo-Carvone, d-Carvone, Cinnamic Alcohol, Cinamyl Formate, Cis-Jasmone, cis-3-Hexyl Acetate, Cumic Alcohol, Cyclic C, Dimethyl Benzyl Carbinol, Dimethyl Benzyl Carbonil 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 (tricyclo Decenyl Propionate), Geranial, Hexenol, Hexenyl Acetate, Hexyl Acetate, Hexyl Formate, Hydrotropic Alcohol, Hydroxy citronellal, Indone, Isoumaryl Alcohol, Iso Menthone, Isopulegyl Acetate, Isoquinolone, Liguoster, Linalool, Linalool Oxide, Linalyl Formate, Menthone, Menthyl Acetphenone, Methy Amyl Ketone, Methyl Anthranilate, Methyl Benzoate, Methyl Benzyl 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, Phenoxo Ethanol, Phenyl Acetaldehyde, Phenyl Ethyl Acetate, Phenyl Ethyl Alcohol, Phenyl Ethyl Dimethyl Carbinol, Phenyl Acetate, Propyl Bornate, Pulegone, Rose Oxide, Saffrole, 4-Terpinenol, Alpha-Terpinienol, and/or Vinidine.

It is commonplace for a plurality of perfume components to be present in a formulation. In preferred microcapsules it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components from the list given of delayed blooming perfumes given above present in the particles.

Aromatherapy

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.
Insect Repellents

[0053] Perfumes 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). Some of these materials are odourless to humans. 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 flexuosus), 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. cinerarifolium and C. coccin- neum), 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.

Optional carrier oil

[0054] The capsules for use in the invention may comprise a carrier oil core. The oil must be compatible with the perfume such that the perfume can migrate into the oil core from a surrounding composition. It will be clear to a skilled person which oils are suitable for use with a certain perfume composition. The carrier oils are hydrophobic materials that are miscible in the perfume materials used in the present invention. Suitable oils are those having reasonable affinity for the fragrance chemicals. Suitable materials include, but are not limited to triglyceride oil, mono and diglycerides, mineral oil, silicone oil, diethyl phthalate, polyalphaolefins, castor oil and isopropyl myristate. Preferably, the oil is a triglyceride oil, most preferably a capric/caprylic triglyceride oil.

Optional further microencapsulated benefit agents

[0055] In addition to the essential perfume the microcapsules may also comprise other benefit agents.


[0057] Preferred further benefit agents are selected from the group comprising antimicrobial agents and antioxidants.

Antimicrobials

[0058] Preferred antimicrobials include Triclosan™, climbazole, octapyrox, ketoconazole, zinc pyrithione, and quater- nary ammonium compounds.

Antioxidants

[0059] Preferred anti-oxidants include vitamin E, retinol, antioxidants based on hydroxytoluene such as Irganox™ or commercially available antioxidants such as the Troiox™ series.

Surfactant

[0060] The composition comprises surfactant. The surfactant preferably comprises both anionic surfactant and nonionic
surfactant. Preferably the composition comprises from 0.1 to 50 wt% surfactant. More preferably, the amount of surfactant is at least 0.5 wt%, most preferably at least 1 wt%. The maximum amount of surfactant is more preferably at most 30 wt%, even more preferably at most 20 wt%, and most preferably at most 10 wt%.

Anionic surfactant

[0061] Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid mono-esters and sulphonic acids which have in the molecular structure a branched or straight chain alkyl or alkylene group containing from 6 to 22 carbon atoms.

[0062] The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkyl-benzenesulfonates and mixtures with olefin-sulfonates and alkyl sulfates, and the fatty acid mono-glyceride sulfates.

[0063] The most preferred anionic surfactants are alkyl-aromatic sulfonates such as alkylbenzenesulfonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of alkylbenzenesulfonates or of alkyl-toluene-, -xylene- or -phenolsulfonates, alkylnapthalene-sulfonates, ammonium diaminonaphthalene-sulfonate, and sodium dinonyl-naphthalene-sulfonate.

Nonionic surfactant

[0064] A suitable class of nonionic surfactants is compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB.

[0065] Other suitable classes of nonionic surfactants are:

- alkyl polyglycosides, which are condensation products of long chain aliphatic alcohols and saccharides;
- tertiary amine oxides of structure R₁R₂R₃N-O, where R₁ is an alkyl group of 8 to 20 carbon atoms and R₂ and R₃ are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure R₁R₂R₃P-O, where R₁ is an alkyl group of 8 to 20 carbon atoms and R₂ and R₃ are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure R₁R₂S=O, where R₁ is an alkyl group from 10 to 18 carbon atoms and R₂ is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- fatty acid alkylolamides, such as the ethanol amides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans.

[0066] The concentration of nonionic surfactant to be employed in a hard surface cleaning composition of the invention may be at least 0.1 %, preferably at least 0.5%, most preferably at least 1%. The amount is suitably at most 20%, preferably not more than 15% and most preferably not more than 10%.

[0067] In a preferred embodiment the surfactant comprises anionic and nonionic surfactants in a ratio between 20:1 and 1:10, more preferably from 15:1 to 1:5, and ideally above 10:1 to 1:2.

Optional further surfactant

[0068] The compositions may optionally further comprise amphoteric, cationic or zwitterionic surfactants.

[0069] Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate.

[0070] Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium chloride.

[0071] A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide with long chain aliphatic amines. The compounds behave like nonionic surfactants in alkaline medium and like cationic surfactants in acid medium.

[0072] Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group
substituted by an anionic water-solubilising group, for instance betaine and betaine derivatives such as alkyl betaine, in particular C_{12}-C_{16} alkyl betaine, 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecyl-methyl-sulphonium)-propane-1-sulphonate betaine, 3-(cetyltrimethyl-phosphonium)-propane-1-sulphonate betaine and N,N-dimethyl-N-dodecyl-glycine. Other well-known betaines are the alkylamidopropyl betaines e.g. those wherein the alkylamido group is derived from coconut oil fatty acids.

Further Optional Ingredients

[0073] The compositions may contain one or more other ingredients. Such ingredients include preservatives (e.g. bactericides) (for example 1,2-benzisothiazolin-3-one), pH buffering agents, pH modifiers such as hydrochloric acid or lactic acid, anti-redeposition agents, soil-release agents, polyelectrolytes, anti-shrinkage agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, pearlisers and/or opacifiers, natural oils/extracts, processing aids, e.g. electrolytes, hygiene agents, e.g. anti-bacterial and antifungal, thickeners, colorants, whiteners, optical brighteners, soil suspending agents, detergae agents, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), gel-control agents, freeze-thaw stabilisers, hydrotropes, free oil perfumes and mixtures thereof.

Product Form

[0074] The compositions of the present invention are aqueous liquids. They may be supplied in any known form of packaging such as bottles, spray applicators and unit dose forms; e.g. sachets. The composition is preferably used for domestic hard surface cleaning.

The hard surface cleaning process

[0075] The hard surface cleaning process comprises the steps of: using a cleaning implement comprising cotton to apply to the hard surface and move around on the hard surface to remove soil from the hard surface an aqueous cleaning composition according to the invention comprising surfactant and microcapsules comprising perfume, rinsing the cleaning implement in water to remove surfactant and soil from the cotton and leaving the rinsed cotton cleaning implement to dry, whereby after rinsing at least 25 wt%, preferably at least 40 wt% and more preferably at least 60 wt% of the microcapsules in the composition applied to the hard surface are transferred onto and retained by the cotton of the cleaning implement.

[0076] During the stage of the process when the composition is being moved around on the hard surface by the cleaning implement the microcapsules are transferred to the cotton. They are at this stage of the process in aqueous medium and thus deformable and not easily ruptured by shear forces. When they dry out they become easily ruptured and rupture to release fragrance during storage and also next time the cleaning implement is used. The hard surface and the cleaning implement are chemically different. For example, the hard surface is a stone material and the cleaning implement is polyester cotton. Preferably the hard surface comprises no polysaccharide based materials.

[0077] The hard surface is preferably any household surface such as found in kitchens and bathrooms, including cooker tops, extractor fans, tiles, floors, baths, toilets, wash basins, showers, dishwashers, taps, sinks, work surfaces, etc. These surfaces may, for example, be made of plastics, glass, enamel, ceramic, wood (painted, lacquered or otherwise) or metal (e.g. stainless steel or chrome) and include, for example: kitchen work surfaces, cabinets, cooker tops, extractor fans, tiles, sinks, etc. Examples of kitchen surfaces are stainless steel, chrome, vitreous enamel, vitrocramic, or ceramic tile.

[0078] The hard surface is preferably selected from the group consisting of ceramic (for example sink, toilet, bath, shower), pottery (for example plates, cups, bowls), metal, wood, enamel, glass, plastic, natural stone, and man-made stone.

[0079] Where the hard surface is a floor, the cleaning implement is preferably an applicator. For example a mop, a cloth or a sponge.

[0080] Where the hard surface is a dish, the cleaning implement is preferably selected from a cloth, a towel, a sponge, a scourer, and a brush.

[0081] The cleaning implement comprising cotton is preferably selected from the group consisting of: mop and cloth.

[0082] Many suitable treatment hard surface cleaning processes may be adapted for use with the invention. For example, floor and tile cleaning, hand dish washing.

EXAMPLES

[0083] The invention will now be further described with reference to the following non-limiting examples. Examples of
the invention are represented by a number. Comparative examples are represented by a letter.

[0084] Unless otherwise stated, amounts of components are expressed as a percentage of the total weight of the composition.

Example 1 - Release of perfume from a dried cloth - panel data

[0085] Hard surface cleaning Composition 1 and Comparative Composition A were prepared with the ingredients shown in Table 1. The level and type of perfume in each composition was the same.

1. 5 ml of Composition 1 (or A) was applied to a melamine work surface and wiped with a cotton cloth for 10 seconds.
2. The cloth was then rinsed under cold running water for 10 seconds.
3. Steps 1 & 2 were performed a further four times using a new cloth and surface each time.
4. The cloths were air dried at room temperature overnight.
5. Panellists then assessed the dry cloths for perfume intensity pre- and post-rub on a scale of 1 to 5 where 1 is the weakest intensity.

The results of the panel test are given in Table 2. It will be seen that compared to Comparative Composition A, containing only free perfume, Composition 1, containing a microcapsule with a deposition aid, gives significantly higher perfume scores on the cotton cleaning cloth, especially after rubbing, as would occur to some extent the next time the cloth were used.

Tables 1 and 2 also show that when two formulations, one containing free fragrance and one containing a microcapsule containing fragrance, are wiped from a surface, then rinsed, very little free fragrance is left (low results for composition A). The presence of the microcapsule can be seen by the higher pre- and post-rub results, which shows that the microcapsule has successfully transferred to the cloth from the surface.

Table 1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Supplier trade name</th>
<th>Supplier</th>
<th>1 (wt%)</th>
<th>A (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary alcohol ethoxylate</td>
<td>Neodol 91-8</td>
<td>Shell</td>
<td>5.000</td>
<td>5.000</td>
</tr>
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<td>Acusol 190</td>
<td>Dow Chemicals</td>
<td>0.500</td>
<td>0.500</td>
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<td>Monoethanolamine</td>
<td>-</td>
<td>BP Chemicals</td>
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<td>1.000</td>
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<td>Dipropylene glycol n-butyl ether</td>
<td>-</td>
<td>Dow Chemicals</td>
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<td>0.016</td>
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<td>1,2-benzisothiazoline-3-one</td>
<td>Nipacide Bit 20</td>
<td>Clariant</td>
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<td>0.180</td>
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<td>Palm kernel fatty acid</td>
<td>Prifac 7907</td>
<td>Croda</td>
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<td>0.900</td>
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<tr>
<td>Sodium Hydroxide</td>
<td>-</td>
<td>-</td>
<td>0.400</td>
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<tr>
<td>Free perfume</td>
<td>-</td>
<td>Givaudan</td>
<td>-</td>
<td></td>
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<tr>
<td>Microencapsulated perfume (with xyloglucan deposition aid)</td>
<td>-</td>
<td>Givaudan</td>
<td>1.000</td>
<td>-</td>
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<tr>
<td>Water and minors</td>
<td>-</td>
<td>-</td>
<td>To 100</td>
<td>To 100</td>
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</table>

1Melamine formaldehyde microcapsule, particle size 10 to 30 micron. 40 wt% fragrance.

1.5 ml of Composition 1 (or A) was applied to a melamine work surface and wiped with a cotton cloth for 10 seconds.
2. The cloth was then rinsed under cold running water for 10 seconds.
3. Steps 1 & 2 were performed a further four times using a new cloth and surface each time.
4. The cloths were air dried at room temperature overnight.
5. Panellists then assessed the dry cloths for perfume intensity pre- and post-rub on a scale of 1 to 5 where 1 is the weakest intensity.

Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pre-rub</th>
<th>Post-rub</th>
</tr>
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<tr>
<td>1</td>
<td>2.89</td>
<td>3.72</td>
</tr>
<tr>
<td>A</td>
<td>1.17</td>
<td>0.86</td>
</tr>
<tr>
<td>Least significant differences</td>
<td>-0.53</td>
<td>-0.41</td>
</tr>
<tr>
<td>Least significant differences/2</td>
<td>-0.27</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

[0087] It will be seen that compared to Comparative Composition A, containing only free perfume, Composition 1, containing a microcapsule with a deposition aid, gives significantly higher perfume scores on the cotton cleaning cloth, especially after rubbing, as would occur to some extent the next time the cloth were used.

[0088] Tables 1 and 2 also show that when two formulations, one containing free fragrance and one containing a microcapsule containing fragrance, are wiped from a surface, then rinsed, very little free fragrance is left (low results for composition A). The presence of the microcapsule can be seen by the higher pre- and post-rub results, which shows that the microcapsule has successfully transferred to the cloth from the surface.
Example 2: Retention of perfume after rinsing: instrument measurement

Four compositions were prepared based on the formulation given in Table 1 (but without free perfume or microencapsulated perfume), and designated Compositions 2, 3, 4 and B. Different perfume microcapsules were added to Compositions 2 to 4 and free perfume oil was added to Comparative Composition B. The perfume levels of each example were the same. The ingredients are given in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard surface cleaner composition (as in table 1 but without free perfume or microencapsulated benefit agent)</td>
<td>1.2 1.2 1.2 1.2</td>
</tr>
<tr>
<td>Water</td>
<td>98.3 98.3 98.0 98.6</td>
</tr>
<tr>
<td>Unmodified perfume microcapsule (43% solids, 40% fragrance)¹</td>
<td>0.5 - - -</td>
</tr>
<tr>
<td>Xyloglucan-modified microcapsule (43% solids, 40% fragrance)²</td>
<td>- 0.5 - -</td>
</tr>
<tr>
<td>Cationic polymer-modified microcapsule (26% solids, 23% fragrance)³</td>
<td>- - 0.8 -</td>
</tr>
<tr>
<td>Free fragrance</td>
<td>- - 0.2 -</td>
</tr>
</tbody>
</table>

¹Melamine formaldehyde microcapsule, particle size 10 to 30 micron, supplied by Givaudan.
²Melamine formaldehyde microcapsule with xyloglucan surface modification, particle size 10 to 30 micron, supplied by Givaudan.
³Melamine formaldehyde microcapsule, with cationic polymer surface modification; particle size 10 to 30 micron, supplied by IFF.

Measurement of fragrance intensity

The amount of fragrance on a cloth was determined using a gas chromatograph-mass spectrometer (GC-MS) (Agilent 6890N GC + 5973 Inert MSD). The column used was a SGE HP5ms (30 m, 0.32 mm dia., 0.25 μm film thickness), column flow was set at 2.0 ml/min. GC temperature profile was:

- 50°C to 100°C @ 4°C/min
- 100°C to 150°C @ 5°C/min
- 150°C to 200°C at 6°C/min
- 200°C to 280°C @ 10°C /min
- Hold at 280°C for 2 minutes

Mass spectrometer was used in SCAN mode. The 15 most intense peaks detected in the first 30 minutes of the run were used.

Calibration and perfume extraction

Sixteen 10 x 10 cm pieces of woven cotton sheeting were taken for each of Compositions 2, 3 and 4. Four different volumes of each microcapsule containing diluted hard surface cleaning composition were applied (0.25, 0.50, 0.75 and 1.00 ml) to four replicate cloths. The cloths were then dried overnight. The cloths were then placed in individual 28 ml glass vials and 5 ml of tert-buty1 methyl ether (tBME) added. The vials were then placed on a bottle roller for 90 minutes. The free tBME was then transferred to a 2 ml GC vial and analysed on the GC-MS as detailed above. The total ion counts (TICs) for the selected peaks was then summed for each composition, then the average taken across the three compositions to give a total fragrance level. The results are shown in Table 4. The results indicate that all three microcapsule containing compositions gave a linear dose response.

Table 4

<table>
<thead>
<tr>
<th>Amount applied (ml)</th>
<th>Average Sum of Total Ion Counts</th>
<th>95% Confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>1,308,776,047</td>
<td>30,228,998</td>
</tr>
</tbody>
</table>
The data plotted produces a straight-line fit with an $R^2 = 0.974$ and a gradient of $y = 4.538 \times 10^9 x$. Thus the amount of fragrance measured by the GC-MS can be directly correlated to the amount of fragrance/microcapsule on the cotton fabric.

Free fragrance

1 ml of Comparative Composition B was applied to twelve 10x10 cm woven cotton cloths. Four of these were allowed to dry overnight. Four were dried for 2 hours, then rinsed for 30 minutes (2 cloths in 150 ml demin water, Reax mixer, speed setting no. 4). Four were left for 10 minutes before being rinsed for 30 minutes as previously described. The fragrance level was then determined by GC-MS as previously described. The percentage of fragrance retained compared to the retention of the same quantity of fragrance contained in a microcapsule was then calculated using the 1 ml data from Table 4. The results are given in Table 5. It can be seen that rinsing removes most of the free perfume.

<table>
<thead>
<tr>
<th>Preparation Route</th>
<th>Average sum TICs</th>
<th>% Fragrance retained vs encaps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dried overnight</td>
<td>1126812087</td>
<td>24.37</td>
</tr>
<tr>
<td>Dried before rinsing</td>
<td>44346999.5</td>
<td>0.96</td>
</tr>
<tr>
<td>Wet rinsed</td>
<td>124661458</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Example 3 - Effect of drying

1 ml of Composition 2 was applied to ten 10x10cm pieces of woven cotton sheeting. The samples were then dried for 2, 3, 4, 5 or 24 hours at room temperature, then extracted and analysed as before. The results are shown in Table 6.

<table>
<thead>
<tr>
<th>Drying Time (h)</th>
<th>Sum of TICs</th>
<th>95% Confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4,651,402,850</td>
<td>312,039,445.1</td>
</tr>
<tr>
<td>3</td>
<td>5,065,926,548</td>
<td>432,456,660.4</td>
</tr>
<tr>
<td>4</td>
<td>4,475,656,966</td>
<td>599,343,339.5</td>
</tr>
<tr>
<td>5</td>
<td>4,685,026,948</td>
<td>830,632,226.3</td>
</tr>
<tr>
<td>24</td>
<td>4,650,993,139</td>
<td>1,151,176,379</td>
</tr>
</tbody>
</table>

This shows that no significant fragrance loss occurs over time when the composition comprises a perfume microcapsule. Table 6 shows that the encaps, when they have transferred onto the cloth, do not lose fragrance as they dry, only when they are subjected to shear (as demonstrated in Table 1).

Example 4

This example investigated the transfer of melamine formaldehyde microcapsules from a hard surface to a cotton cloth during treatment of the hard surface with Compositions 2 to 4 & B. Four hard surfaces, representative of those needing to be cleaned in a domestic hard surface cleaning process, were selected. These were: a melamine formaldehyde worktop, a glazed tile, an unglazed tile and a stainless steel surface.
Woven cotton was used as the cleaning cloth.

1 ml of Composition 2, 3, 4 or B was pipetted onto each surface. The surface was then wiped with the cloth until the surface was visibly free of liquid. Some cloths were allowed to dry overnight so that the quantity of microcapsule transferred to the cloth could be measured. Other cloths were left for 10 minutes after wiping then rinsed for 30 minutes as described in Example 2. These cloths were then dried overnight so that the propensity of the microcapsule to remain on the cotton fabric could be determined.

Using the values obtained from the 1 ml data in Table 4, the percentage transfer and retention onto the cloth (based on amount in product) were calculated for each surface and each microcapsule (the results are given in Table 7 for transfer and Table 8 for retention after rinsing). Free fragrance (B) is as already recorded in Table 5. Table 7 shows how much microcapsule is transferred from the surface onto the cloth during the cleaning stage. Table 8 shows how much microcapsule is left when the cloths used to generate the data in table 7 are rinsed.

Using the values obtained from the 1 ml data in Table 4, the percentage transfer and retention onto the cloth (based on amount in product) were calculated for each surface and each microcapsule (the results are given in Table 7 for transfer and Table 8 for retention after rinsing). Free fragrance (B) is as already recorded in Table 5. Table 7 shows how much microcapsule is transferred from the surface onto the cloth during the cleaning stage. Table 8 shows how much microcapsule is left when the cloths used to generate the data in table 7 are rinsed.

It will be seen that the microcapsules from the compositions in accordance with the invention, have a dramatically higher deposition affinity for the cloth than the hard surface, across the whole range of hard surfaces.

Compared to the free fragrance (composition B) the microcapsules show much higher retention on the cotton cloth.

Table 5 shows how poorly free fragrance is retained, particularly when rinsed. Table 8 shows greater than 76% fragrance retention whereas, under the same conditions, only 2.7% of free fragrance would be left (wet rinsed result).

**Claims**

1. A hard surface cleaning composition comprising:

   a) a microcapsule comprising:

      i) perfume contained within;
      ii) a polymer shell; and fixed to the outside of the shell,
      iii) a nonionic polysaccharide deposition aid that causes the microcapsule to deposit from aqueous dispersion onto a cotton cleaning implement,

   b) surfactant for cleaning the hard surface; and
   c) water.

2. A composition as claimed in claim 1, wherein the microcapsule further comprises a benefit agent is selected from an antimicrobial agent, a conditioning agent and an anti-malodour active.
3. A composition according to any preceding claim wherein the polymer shell is susceptible to rupture when it dries and comprises aminoplasts, proteins, polyurethanes, polysaccharides, gums and polyacrylates or polymethylmethacrylate.

4. A composition according to claim 4 wherein the polymer shell is formed from melamine formaldehyde or urea formaldehyde condensates, preferably the shell comprises melamine formaldehyde.

5. A composition according to any preceding claim wherein the nonionic polysaccharide is selected from the group consisting of: polymannan, polyglucan, polyglucosan, polyxyloglucan and polygalactomannan and mixtures thereof, preferably from the group consisting of polyxyloglucan and polygalactomannan, more preferably from the group consisting of locust bean gum, xyloglucan, guar gum and mixtures thereof.

6. A hard surface cleaning process comprising the steps of: using a cleaning implement comprising cotton to apply to a hard surface and move around on the hard surface to remove soil from the hard surface an aliquot of aqueous cleaning composition according to the first aspect of the invention, rinsing the cleaning implement in water to remove surfactant and soil from the cotton and leaving the rinsed cotton cleaning implement to dry, whereby after rinsing at least 25 wt% of the microcapsules in the composition applied to the hard surface are deposited onto and retained by the cotton of the cleaning implement.

7. A process according to claim 6 wherein more than 30 wt% of the microcapsules applied in the aliquot is retained on the cotton.

8. A process according to claim 6 or 7 wherein the hard surface being cleaned is selected from the group consisting of ceramic, pottery, metal, wood, enamel, glass, plastic, natural stone, and man-made stone.
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<td>WO 2011/054389 A1 (UNILEVER PLC [GB]); UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; FERGUSON) 12 May 2011 (2011-05-12) A * claims * * see the experimental part of the citation *</td>
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<td>WO 2013/026656 A1 (UNILEVER PLC [GB]); UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; CHEN HON) 28 February 2013 (2013-02-28) * claims * * example 3 * * The Model Shampoo Formulation * * The list of benefit agents; page 8 - page 11 *</td>
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The present search report has been drawn up for all claims.

Place of search: Munich
Date of completion of the search: 18 January 2016
Examiner: Culmann, J

CATEGORY OF CITED DOCUMENTS

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18-01-2016

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<td>BR P10619080 A2</td>
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<td>CA 2630581 A1</td>
<td>07-06-2007</td>
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<td>CN 101336287 A</td>
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<td>EP 1954796 A1</td>
<td>13-08-2008</td>
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<td>EP 2319910 A2</td>
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<td>ES 2380376 T3</td>
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<td>US 2009275494 A1</td>
<td>05-11-2009</td>
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<td>WO 2007062833 A1</td>
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<td>ZA 200804678 A</td>
<td>27-01-2010</td>
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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82.
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 2382907 A2 [0004]
- WO 2008055787 A1 [0005]
- US 20100059523 A1 [0006]
- WO 2007080552 A1 [0007]
- AU 2011232788 A1 [0008]
- EP 1721963 A1 [0009]
- WO 200027271 A2 [0011]
- DE 29702433 U1 [0012]
- WO 2009121682 A [0020]
- US 3516941 A [0027]
- US 2800457 A [0027]
- US 4145184 A [0027]
- US 5112688 A [0027]
- US 4406816 A [0030]
- US 4406816 B [0030]
- GB 2062570 A [0030]
- GB 2006709 A [0030]
- WO 2005121185 A [0033]

Non-patent literature cited in the description

- Fenaroli’s Handbook of Flavour Ingredients. CRC Press, 1975 [0045]
- Synthetic Food Adjuncts. 1947 [0045]
- Perfume and Flavour Chemicals. Montclair, 1969 [0045]
- POUCHER. Journal of the Society of Cosmetic Chemists, 1955, vol. 6 (2), 80 [0047]