Abstract: A liquid surfactant composition for cleaning a surface is provided. It comprises a cleansing surfactant, a polymeric cationic material and an anionic or non-ionic emulsion of a fragrance composition blended with a waxy silicone material. The composition is preferably a liquid detergent composition for fabric washing. It can provide a long-lasting fragrance to the washed fabric.
LIQUID LAUNDRY DETERGENT COMPOSITIONS

[0001] This invention relates to the incorporation of fragrance compositions in liquid cleansing surfactant compositions. The invention is particularly applicable to liquid laundry detergent compositions like fabric washing compositions, but can also be used in other surfactant-containing compositions including personal care cleansing compositions such as hair shampoo or shower gel.

[0002] Fragrances are frequently incorporated in detergents to give a pleasant odour during use of the cleaning product and to mask the inherent smell of the soap or other surfactant present in the cleaning product. The fragrances are generally complex mixtures of fragrant compounds of varying volatility. Upon storage in a detergent composition, perfumes and fragrances can be altered through interactions and/or reactions with the other components of the composition. Due to their volatile nature, the fragrant compounds tend to be dissipated with time, particularly the most volatile compounds which are often associated with perceived freshness.

[0003] Moreover, during washing of fabrics with a laundry detergent, much of the fragrance is lost in the aqueous phase during the washing cycle. It has been recognised as desirable that the fragrance should not only survive storage in the detergent composition but should also survive the washing process and should be deposited on the fabric, so that fabrics laundered with a detergent containing the fragrance should have the pleasant odour of the fragrance.

[0004] Furthermore, once adsorbed onto the fabric surface, the fragrance tends to be dissipated very quickly. There is thus a need to improve the storage stability of perfumes and fragrances in a liquid laundry detergent composition, the efficiency of their deposition on the fabric being washed and their long-lasting effect through sustained delayed release once applied on fabrics.

[0005] WO-A-01/25389 describes a domestic care product comprising a fragrance particle, where the particle comprises a fragrance composition and a silicone polymer having a melting point of at least 10°C, and at least 20% of the silicone atoms in the silicone polymer have a substituent of 16 carbon atoms or more.
WO-A-03/082356 describes an emulsion comprising a disperse phase which is a blend of a fragrance composition and a waxy hydrophobic material having a melting point in the range 0-200 C dispersed in a continuous phase comprising an aqueous solution of concentration at least 0.1 M of a salt capable of ionic disassociation in water. The protected fragrance composition can be produced in powdered form for blending with a solid cleaning product such as a powder detergent. To produce a fragrant liquid cleaning product, for example a liquid laundry detergent, a fragrance containing emulsion can be dispersed in the liquid cleaning product.

WO-A-2004/084844 describes the use of a waxy silicone material to control release of an active material, selected from fragrances, sunscreens, vitamins, drugs, biocides, pest repellents, catalysts and cooling agents, from a cleaning composition, personal care product, household care product or textile treatment composition, wherein the waxy silicone material is a cycopolysiloxane.

A liquid surfactant containing composition, such as a laundry detergent composition according to the present invention contains a polymeric cationic material and a fragrance composition blended with a waxy silicone material, whereby the polymeric cationic material improves the efficiency of deposition of the fragrance composition blend on the fabric being washed and the waxy silicone material improves the long lasting effect of the fragrance.

Usually, a material is said to be waxy when its melting point is within or close to the working temperature, for example a melting point in the range 10 to 200C. Preferably, a waxy material, even if formed of a mixture of different compounds such as a polymer usually is, has a true melting point i.e. a sharp melting point or melts in a low range of temperature instead of a melting zone through a wide range of temperature. Herein after, the melting point preferably refers to the temperature whereby the complete mixture has melted.

A waxy material can be formed of a mixture of a waxy compound with a liquid compound.

A silicone material is a material containing at least one silicon-containing compound, preferably a polysiloxane compound, preferably a polydiorganopolysiloxane compound. A waxy silicone compound can for example comprise a hydrophobic polysiloxane compound. Preferably, the polysiloxane compound contains at least one
substituent comprising at least 12 carbon atoms preferably at least 16 carbon atoms. The substituent preferably contains a hydrocarbon chain. Preferably, the polyorganosiloxane compound has at least one substituent which is a long chain containing an alkyl group.

[0012] A process according to one aspect of the invention for preparing a liquid detergent composition for fabric washing comprises adding to a liquid detergent surfactant composition a polymeric cationic material and an emulsion of a fragrance composition blended with a waxy silicone material.

[0013] A detergent composition is a composition able to clean surfaces. It contains a surfactant compound, for example a cationic compound. A liquid detergent composition is typically based on one or more active organic detergent surfactant of the anionic, cationic, non-ionic or amphoteric type, or mixtures thereof. Suitable anionic organic detergent surfactants are alkali metal soaps of higher fatty acids, alkyl aryl sulphonates, for example sodium dodecyl benzene sulphonate, long chain (fatty) alcohol sulphates, olefin sulphates and sulphonates, sulphated monoglycerides, sulphated esters, sulphonated or sulphated ethoxylated alcohols, sulpho-succinates, alkane sulphonates, phosphate esters, alkyl isethionates, alkyl taurates and alkyl sarcosinates. Suitable cationic organic detergent surfactants are alkylamine salts, quaternary ammonium salts, sulphonium salts and phosphonium salts. Suitable non-ionic organic surfactants are condensates of ethylene oxide with a long chain (fatty) alcohol or fatty acid, condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxides, sucrose esters, fluorosurfactants, fatty acid alkylol amides and fatty amine oxides. Suitable amphoteric organic detergent surfactants are imidazoline compounds, alkylaminoacid salts and betaines. The liquid laundry detergent composition usually contains water as diluent.

[0014] The fragrance composition may be solid or liquid and may be a single fragrant compound, or a natural scented oil, or may be a mixture of fragrant compounds and/or natural oils. Examples of some natural oils and fragrant compounds particularly suitable for laundry detergent compositions are described in WO-A-01/25389. Further examples include the damascones, for example 1-2,6,6-trimethyl-3-cyclohexenyl-2-buten-1-one (delta-damascone), and 3-(4-t-butylphenyl)-2-methylpropanal (lilial).

[0015] The waxy silicone material is generally a polysiloxane containing at least one hydrocarbon substituent having 12 or more carbon atoms. Preferably the waxy silicone
material is a cyclopolysiloxane, although linear polysiloxane waxes can be used. We have found that the waxy cyclopolysiloxanes tend to be more miscible with fragrance compounds than linear polysiloxane waxes are. Therefore, waxy cyclopolysiloxanes are preferred.

[0016] The waxy polysiloxane preferably comprises methyl alkyl siloxane units \(((\text{CH}_3)(R')\text{SiO}_2/2)\), where \(R'\) is a long chain alkyl group having 12 or more, preferably 16 to 100 carbon atoms. The long chain alkyl group \(R'\) can optionally be substituted by polar substituents such as amino, amido, alcohol, alkoxy, or ester groups. All the siloxane units of the waxy polysiloxane may be such methyl alkyl siloxane units, (this may be preferred if the waxy polysiloxane is a cyclopolysiloxane) or the waxy polysiloxane may additionally contain dimethyl siloxane units or units of the formula \(((\text{CH}_3)(R^\prime')\text{SiO}_2/2)\) where \(R^\prime\) is an alkyl group having 1-11 carbon atoms, for example ethyl, a cycloalkyl group such as 2-cyclohexylethyl, a haloalkyl group or an aromatic group. The methyl group of the above siloxane units could be replaced by ethyl or another lower alkyl group if desired. Preferably at least 20% of the silicon atoms in the polysiloxane, and most preferably at least 50%, have an alkyl substituent having 16 to 100 carbon atoms, most preferably 20 to 45 carbon atoms. The cyclopolysiloxane is preferably a cyclotetrasiloxane or cyclopentasiloxane or a mixture thereof. The waxy polysiloxane preferably has a melting point in the range 10-200 °C, most preferably 30 to 80 °C.

[0017] One preferred type of waxy cyclopolydimethylsiloxane contains aromatic groups, for example aryl groups attached directly to Si such as phenyl, or aralkyl groups comprising phenyl or substituted phenyl groups attached to silicone through an alkyene linkage, in addition to long chain alkyl groups. Waxy cyclopolysiloxanes containing aralkyl groups, that is, silicon-bonded substituents of the formula X-Ph, wherein X denotes a divalent aliphatic organic group bonded to silicon through a carbon atom and Ph denotes an optionally substituted aromatic group, are particularly preferred, for example 2-phenylpropyl, benzyl, 2-phenylethyl or 2-(t-butylphenyl)ethyl. Such aralkyl groups may for example be present in 10 to 80%, preferably 20 to 50% of the siloxane units of the waxy cyclopolysiloxane, usually as methyl aralkyl siloxane units.

[0018] The waxy polysiloxane can be mixed with a liquid silicone, for example a polydiorganosiloxane, a branched liquid polysiloxane, a silicone polyether copolymer or an aminopolysiloxane. Particularly preferred liquid polysiloxanes are those containing aryl, for example phenyl, or aralkyl, for example benzyl, 2-phenylethyl or 2-phenylpropyl groups in
addition to alkyl groups such as methyl. The liquid polydiorganosiloxane can be linear or cyclic; cyclic siloxanes such as tetra(2-phenylpropyl)tetramethylcyclotetrasiloxane may be preferred. The liquid polysiloxane can contain functional groups, for example it can contain hydroxyl groups such as terminal silanol groups in a linear polydiorganosiloxane such as polydimethylsiloxane, alkoxy groups such as methoxy, ethoxy or propoxy bonded to silicon, or amino, amido, alcohol or alkoxy groups substituted in an organic group bonded to silicon. The waxy hydrophobic mixture of the waxy polysiloxane and the liquid silicone is preferably a solid, for example it preferably has a melting point in the range 10-200°C, but can alternatively be a viscous liquid. The liquid silicone can for example be used at up to 100% or even higher based on the weight of the wax, such as up to 200 or 300%, particularly if the blend of wax and liquid silicone is solid at 10°C, although the liquid silicone if used is preferably present at 1 to 60%, most preferably 10 to 30%, based on the weight of wax. An organic liquid, for example liquid paraffin or a naphthenic oil, can be used alternatively or additionally if it is compatible with the blend of fragrance and waxy polysiloxane.

[0019] The polymeric cationic material can be a natural or synthetic polymer substituted by cationic groups such as quaternary ammonium groups, or can be an addition polymer or condensation polymer of a polymerisable material containing cationic groups. For example the polymeric cationic material can be a polysaccharide such as cellulose or a cellulose ether, guar, starch or xanthan gum substituted by quaternary ammonium groups. Examples include the polymers sold under the Trade Marks ‘Jaguar C13-S’, which is a guar hydroxypropyltrimethylammonium chloride, ‘Jaguar C14-S’, which is another quaternary ammonium derivative of guar, ‘Cosmedia C261’, which is a guar hydroxypropyltrimethylammonium chloride, and ‘JR-400’, which is a cellulose ether with a [2-hydroxy-3-(trimethylammonio)propyl]-ω-hydroxy-polyoxyethylene chloride.

[0020] Preferred examples of cationic addition polymers include polymers of a diallyl dimethyl ammonium salt, for example a halide such as the chloride, which generally contain N,N-dimethylimidazolinium salt units, for example homopolymers of diallyl dimethyl ammonium chloride or the copolymers with acrylamide sold under the Trade Marks ‘Merquat 550’, ‘Merquat S’, ‘Merquat 740’ and ‘Merquat 2200’. Further examples of cationic addition polymers are polymers of methacrylamidopropyl trimethyl ammonium salts or methacryloyethyl trimethyl ammonium salts, such as polymers of a halide salt such as chloride or of a methylsulphate salt, for example copolymers with acrylic esters such as methyl acrylate, methyl methacrylate or ethyl acrylate.
[0021] The polymeric cationic material can be premixed with the blend of fragrance composition and waxy silicone material but is preferably added separately to the liquid laundry detergent composition. The polymeric cationic material is generally present at 0.01 to 1% by weight of the liquid laundry detergent composition, for example at 0.02 to 0.5%.

[0022] The blend of fragrance and waxy polysiloxane is preferably added as an emulsion to the liquid laundry detergent composition. An emulsion can conveniently be formed by melting the blend of fragrance and waxy polysiloxane, and liquid silicone if used, and emulsifying it in the continuous phase using at least one surfactant. The surfactant is preferably immiscible with the said blend. The surfactant is preferably an anionic surfactant. Examples of suitable anionic organic surfactants include alkali metal soaps of higher fatty acids, alkyl aryl sulphonates, long chain (fatty) alcohol sulphates, olefin sulphates and sulphonates, sulphated monoglycerides, sulphated esters, sulphonated ethoxylated alcohols, sulphasuccinates, alkane sulphonates, phosphate esters, alkyl isethionates, alkyl taurates and/or alkyl sarcosinates. We have found that when the blend of fragrance and waxy polysiloxane is added as an anionic emulsion, the deposition of the fragrance blend on the fabric is particularly improved, perhaps through interaction of the polymeric cationic material with the negative charge of the anionic emulsion.

[0023] Deposition of the fragrance blend on the fabric is also improved when the blend of fragrance and waxy polysiloxane is added as a nonionic emulsion. Examples of nonionic organic surfactants include condensates of ethylene oxide with a long chain (fatty) alcohol or fatty acid, condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxides, and sucrose esters. Mixtures of anionic and non-ionic surfactants can be used.

[0024] An emulsion can alternatively be made by emulsifying the waxy polysiloxane in the absence of the fragrance. The fragrance can be post-added to the emulsion, which is then heated above the melting point of the waxy polysiloxane and left standing at this temperature, allowing the fragrance to diffuse within the hydrophobic waxy polysiloxane droplet.
Deposition of the fragrance blend on other substrates is also improved when the blend of fragrance and waxy polysiloxane is added as an anionic or nonionic emulsion, for example deposition on hair from a shampoo or deposition on skin from a shower gel.

The invention thus includes a liquid surfactant composition comprising a cleansing surfactant, a polymeric cationic material and an anionic or non-ionic emulsion of a fragrance composition blended with a waxy silicone material.

A process for preparing a liquid surfactant composition according to this aspect of the invention comprises adding to a liquid cleansing surfactant composition a polymeric cationic material and an anionic or nonionic emulsion of a fragrance composition blended with a waxy silicone material.

The polymeric cationic material can be added to the emulsion of the fragrance composition with waxy silicone but preferably, the polymeric cationic material is added to the liquid cleansing surfactant.

Preferably, in a first step, a polymeric cationic material is added to the liquid cleansing surfactant composition. Then, in a second step, the anionic or nonionic emulsion of a fragrance composition blended with a waxy silicone material is added to the liquid cleansing composition obtained in the first step. We have found this is beneficial to the emulsion stability.

In addition to the detergent surfactant, water, polymeric cationic material and wax fragrance blend, the liquid laundry detergent compositions of the invention may contain one or more additional ingredients selected from solvents, alkanolamines, pH adjusting agents, opacifiers, perfumes, dyes, colour stabilisers, bactericides, brighteners, soil release agents and softening agents.

The liquid laundry detergent compositions of the invention, as well as washing fabrics clean, deliver fragrance to the fabrics with longevity of fragrance effect. The polymeric cationic material helps the blend of fragrance composition and waxy silicone material to deposit effectively on fabrics being washed, for example fabrics made of textile fibers such as cotton, wool, silk, nylon, and the like. The waxy silicone material can also provide fabric softening benefits.
The invention is illustrated by the following Examples, in which parts and percentages are by weight.

**Examples 1 to 4**

An aqueous thickening solution was prepared by dispersing 8.9 g xanthan gum (sold under the trade mark Keltrol RD) and 24.5 g hydroxyethylcellulose (sold under the trade mark Natrosol 250 LR) in 962.3 g of demineralised water. 4.2 g Kathon CG (Trade Mark) biocide was then added.

A cyclopolsiloxane wax was made by reacting an olefin mixture of C26-C45 chain length with tetramethylcyclotetrasiloxane. 84.6 g of the above thickening solution, 28.8 g of Maranil Paste A 55 (trade mark) sodium C\textsubscript{12-18}n-alkylenzenesulphonate, 108.7 g of the cyclopolsiloxane wax, and 5.4 g of Dow Corning BF20+ (trade mark) antifoam emulsion were loaded in a stirred reactor and heated to 80°C. 28.4 g of damascone fragrance was then added. After 20 minutes, the heating was stopped. During the cooling, 231.9 g of soft water were added, followed by 1.29 g of Proxel BD20 biocide, forming an emulsion of fragrance particles comprising damascone "encapsulated" in cyclopolsiloxane wax. The damascone concentration in the emulsion was 5.88%.

A liquid detergent composition was made from 75% water, 17.7% Maranil Paste A, 55, 7.3% Dehydol LT7 (trade mark) ethoxylated C\textsubscript{12-18} alcohols and 0.1% of a polymeric cationic material as deposition aid polymer. The polymers used were:

- **Example 1**: Jaguar C14-S: Guar Hydroxypropyl Trimonium Chloride, a quaternary ammonium derivative of guar (from Rhodia), CAS Number: 65497-29-2
- **Example 2**: Merquat 550 diallyl dimethyl ammonium chloride acrylamide copolymer (from Nalco)
- **Example 3**: JR-30M quaternary ammonium derivative of cellulose ether (from Dow Chemical)
- **Example 4**: Cosmedia guar hydroxypropyl trimethyl ammonium chloride (from Cognis)
- **Example 5**: Jaguar C13-S quaternary ammonium derivative of guar (from Rhodia), similar to Jaguar C-14-S.
In examples 1 to 4, 12.8% of the emulsion of encapsulated fragrance particles was added to each detergent composition to give a concentration of 0.75% damascone fragrance in each composition. In a comparative test a liquid detergent composition containing 0.75% non-encapsulated damascone with no polymeric cationic material was used.

A 1kg wash load of 4 terry towels and 5 pillowcases was washed using the above detergent compositions in a Miele washing machine W934, Short Program at 40°C and 600rpm. 12 litres of de-ionized water has been added into the washing machine at the beginning of the wash cycle. In each wash 55g of the liquid detergent plus 5g of soda ash and 2g of a silicone antifoam have been placed in the drum of the washing machine before starting the wash. The perfume delivery (perceived fresh fragrance) was assessed on the wet fabrics directly after washing and on the subsequently dried fabrics 1, 2 and 3 days after washing. There was no marked difference in perfume delivery of the wet fabrics, but the perceived freshness of the fabrics of Example 1 in particular, and also Examples 2, 3 and 4, was substantially greater than those of the comparative example 1, 2 or 3 days after washing and drying. The fabrics of Examples 1, 2, 3 and 4 were also softer than the fabric of the comparative example.

Example 5

The same procedure was followed but the perceived fresh fragrance was evaluated towards two comparatives, one with the pure perfume as above and another with towels treated with a detergent containing encapsulated perfume but no cationic polymer. There was no marked difference between the 3 types of towels when wet. After 1 day, example 5 was clearly better than the 2 comparatives and this good result was confirmed at day 2, day 3 and day 7. The results with the encapsulated fragrance were only slightly better than the pure perfume, while the results of example 5 were clearly improved towards both comparatives.
CLAIMS

1. A liquid surfactant composition for cleaning a surface comprising:
a. a cleansing surfactant
b. a polymeric cationic material and
c. an anionic or non-ionic emulsion of a fragrance composition blended with a waxy silicone material.

2. A composition according to claim 1, wherein the cleansing surfactant comprises a detergent compound.

3. A composition according to any preceding claim, wherein the composition is a liquid detergent composition for fabric washing.

4. A composition according to any preceding claim, wherein the polymeric cationic material improves the efficiency of deposition of the fragrance composition blend on the surface being cleaned.

5. A composition according to any preceding claim, wherein the polymeric cationic material is a polysaccharide substituted by quaternary ammonium groups.

6. A composition according to any preceding claim, wherein the polymeric cationic material contains N,N-dialkylimidazolinium salt units.

7. A composition according to any preceding claim, wherein the polymeric cationic material is a polymer of a dialkyl diallyl ammonium salt.

8. A composition according to any preceding claim, wherein the polymeric cationic material contains methacrylamidopropyl trialkyl ammonium salt units or methacyrloyoxyethyl trimethyl ammonium salt units.

9. A composition according to any preceding claim, wherein the waxy silicone material is a cycopolysiloxane substituted by hydrocarbon substituents having 12 or more carbon atoms.

10. A composition according to Claim 9 wherein at least 20% of the silicon atoms in the cycopolysiloxane have an alkyl substituent having 16 to 100 carbon atoms.

11. A composition according to Claim 9 or 10 wherein the cycopolysiloxane also contains aryl or aralkyl substituents.

12. A composition according to any preceding claim wherein the waxy silicone material and the fragrance composition are blended with a liquid silicone compatible with the waxy silicone material.
13. A composition according to any preceding claim wherein the waxy silicone material and the fragrance composition are emulsified in an anionic oil-in-water emulsion or a nonionic oil-in-water emulsion.

14. A process for preparing a liquid surfactant composition such as a liquid detergent composition, comprising adding to a liquid surfactant composition a polymeric cationic material and an emulsion of a fragrance composition blended with a waxy silicone material.

15. A process according to claim 11, wherein the blend of fragrance composition and waxy silicone material is added to the liquid composition as an anionic oil-in-water emulsion or as a nonionic oil-in-water emulsion.

16. A process for preparing a liquid detergent composition for fabric washing, comprising adding an emulsion of a fragrance composition blended with a waxy silicone material to a liquid detergent composition which contains a polymeric cationic material.

17. A process for preparing a liquid surfactant composition, especially a liquid detergent composition for fabric washing, comprising adding to a liquid cleansing surfactant composition, first a polymeric cationic material then an anionic or nonionic emulsion of a fragrance composition blended with a waxy silicone material.
INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/052978

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/37 C11B3/50 CH D17/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

EPO=Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>NO 03/082356 A (DOW CORNING [US]; CREUTZ SERGE [BE]; SEGHIR HOURIA [BE]; NACHON GUZMAN) 9 October 2003 (2003-10-09) cited in the application paragraph [0003]; claims 1-19; examples 1-7</td>
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X Further documents are listed in the continuation of Box C.

X See patent family annex.

* Special categories of cited documents
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Date of the actual completion of the international search 12 June 2008

Date of mailing of the international search report 26/06/2008

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
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