



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 7/00, 7/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/26585</b> <b>(43) International Publication Date:</b> 3 June 1999 (03.06.99)
<b>(21) International Application Number:</b> PCT/EP98/07536 <b>(22) International Filing Date:</b> 18 November 1998 (18.11.98) <b>(30) Priority Data:</b> 9725013.8 26 November 1997 (26.11.97) GB <b>(71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW):</b> UNILEVER NV [GB/GB]; Weena 455, NL-3013 AL Rotterdam (GB).	<b>(72) Inventors:</b> CAREW, Peter, Simon; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). GALLAGHER, Peter; HPC Deutschland GmbH, Werk Buxtehude Factory, Alter Postweg 25, NL-21614 Buxtehude (DE). KONIDARIS, Peter, Christopher; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). LAM, Stanley; Unilever Thai Holdings Ltd., Lever House, 80/2 Srinakarin Road, Suanlaung, Bangkok 10250 (TH). REID, Euan, Stuart; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). WALTON, Ian, Berkeley; Unilever Thai Holdings Ltd., Lever House, 80/2 Srinakarin Road, Suanlaung, Bangkok 10250 (TH). <b>(74) Agent:</b> MOLE, Peter, Geoffrey; Unilever plc, Patent Dept., Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> WASHING COMPOSITION <b>(57) Abstract</b> <p>The invention provides a washing composition for washing a surface to deposit thereon a solid active agent, the washing composition comprising an emulsion of silicone droplets, the silicone droplets comprising: (a) a continuous silicone phase, and; (b) a dispersed phase of solid particulate active agent. Preferably the solid active agent is a solid antimicrobial such as zinc pyridinethione.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

- 1 -

**WASHING COMPOSITION****FIELD OF THE INVENTION**

5

The present invention relates to washing compositions, more particularly to washing compositions for washing a surface to deposit thereon a solid active agent, such as particles of a solid antimicrobial substance. Such washing

10 compositions include compositions for washing hair or skin, such as hair shampoos, conditioners, body shampoos, shower gels, facial washing compositions, bar soaps and bath foams. They may also include compositions for household cleaning, such as hard surface cleaners.

15

**BACKGROUND AND PRIOR ART**

Difficulties arise in achieving effective deposition of solid active agents onto a surface such as skin or hair when

20 the solid active agent is delivered by means of incorporation into rinse-off compositions, typically hair and body shampoos, conditioners and the like. Frequently, such active agents are preferentially rinsed away from the intended site of deposition, rather than being deposited

25 thereat.

US 5,037,818 describes that the presence of certain cationic polymers in aqueous washing compositions can enhance the deposition of water-insoluble particles such as solid

30 antimicrobials.

- 2 -

There remains the problem, however, that the typical, preferred types of antimicrobial (such as sulphur, selenium disulphide and heavy metal salts of pyridinethione) are relatively dense materials and have a tendency to settle out on storage, from compositions into which they are incorporated. Therefore, in order for compositions containing these types of active agent to be aesthetically acceptable in the package and to provide a consistent, effective level of performance, without requiring vigorous shaking of the package in which they are contained, it is conventional practice to suspend them in the composition with a suspending agent. Examples of commonly used suspending agents include crystalline suspending agents (such as ethylene glycol distearate), inorganic structurants (such as swelling clays) and hydrophilic polymeric thickening agents (such as carbomers). Although these materials are effective for suspending particulate matter, they can adversely affect lathering performance, impart an undesirable cloudy appearance to the composition, and, in particular, mitigate against effective deposition of the active agent on the desired site, thereby reducing performance.

The present invention seeks to solve the above problems and to facilitate and/or enhance deposition of solid active agents, such as particulate antimicrobials, from washing compositions, particularly rinse-off compositions.

EP 0 552 024 describes a rinse-off cleaning composition including an emulsion comprising an internal oil phase of a

- 3 -

silicone-type oil, in which the internal phase contains a surfactant soluble cosmetic agent, preferably dissolved therein. Phenylsilicones are particularly preferred silicone-type oils. Other alkyl-silicones are said to be less preferred owing to their inability to dissolve the hydrophobic materials which are the preferred cosmetic agents. The compositions are said to be particularly useful for enhancing deposition of surfactant soluble sunscreen materials from cleansing compositions such as shampoos.

We have now surprisingly found that solid active agents, such as particulate antimicrobials, can be successfully incorporated as a dispersed phase into the silicone phase of a silicone emulsion. Incorporation of the solid active agent into the silicone phase in this way enhances deposition and delivery of the solid active agent from a rinse-off washing composition, particularly in conjunction with a cationic polymer. Careful control of the silicone particle size may also, advantageously, enhance targeting of the active agent to the hair follicle.

#### SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a washing composition for washing a surface to deposit thereon a solid active agent, the washing composition comprising an emulsion of silicone droplets, the silicone droplets comprising:

(a) a continuous silicone phase, and;

(b) a dispersed phase of solid particulate active agent.

- 4 -

In a second aspect, the invention provides a method of making an emulsion of silicone droplets comprising:

- 5 (a) a continuous silicone phase, and;
- (b) a dispersed phase of solid particulate active agent,

for incorporation into a washing composition, the method  
10 comprising the steps of:

- (a) dispersing the solid active agent into silicone fluid,  
and
- 15 (b) emulsifying the dispersion so obtained, thereby forming  
an emulsion of silicone droplets comprising:
- (a) a continuous silicone phase, and;
- 20 (b) a dispersed phase of solid particulate active agent.

#### DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

##### The Emulsion

25

Washing compositions in accordance with this invention comprise an emulsion of silicone droplets, the silicone droplets comprising a continuous silicone phase, and a dispersed phase of solid particulate active agent.

30

- 5 -

The emulsion itself has a continuous phase (in which the silicone droplets are emulsified), which comprises one or more surfactants, at least as emulsifying agents for the silicone droplets, which may be present in an amount of from  
5 0.1 to 50%, preferably 0.5 to 30%, typically 1 to 10% by weight of the emulsion.

Suitable emulsifiers are well known in the art and include anionic and nonionic emulsifiers. Examples of anionic  
10 emulsifiers are alkylarylsulphonates, e.g., sodium dodecylbenzene sulphonate, alkyl sulphates e.g., sodium, lauryl sulphate, alkyl ether sulphates, e.g., sodium lauryl ether sulphate nEO, where n is from 1 to 20 alkylphenol  
ether sulphates, e.g., octylphenol ether sulphate nEO where  
15 n is from 1 to 20, and sulphosuccinates, e.g., sodium dioctylsulphosuccinate.

Examples of nonionic emulsifiers are alkylphenol ethoxylates, e.g., nonylphenol ethoxylate nEO, where n is  
20 from 1 to 50, alcohol ethoxylates, e.g., lauryl alcohol nEO, where n is from 1 to 50, ester ethoxylates, e.g., polyoxyethylene monostearate where the number of oxyethylene units is from 1 to 30.

25 The continuous phase of the emulsion may, and preferably does, comprise water, preferably in an amount of from 0.1 to 70% by weight, typically 0.5 to 50% by weight of the emulsion.

- 6 -

Silicone Phase

Suitable silicones for the silicone phase are non-volatile silicone fluids, which may be one or more polyalkyl siloxanes, one or more polyalkylaryl siloxanes, or mixtures thereof. The silicone is present in an emulsified form, as dispersed droplets.

Suitable polyalkyl siloxanes include polydimethyl siloxanes which have the CTFA designation dimethicone, having a viscosity of from 5 to 1,000,000 centistokes at 25°C. These siloxanes are available commercially from the General Electric Company as the Viscasil series and from Dow Corning as the DC 200 series. The viscosity can be measured by means of a glass capillary viscometer as set out further in Dow Corning Corporate Test Method CTM004 July 20 1970.

Also suitable is polydiethyl siloxane.

Also suitable are silicone gums, such as those described in US Pat. No. 4,152,416 (Spitzer), and on General Electric Silicone Rubber product Data Sheet SE 30, SE 33, SE 54 and SE 76. "Silicone gum" denotes polydiorganosiloxanes having a molecular weight of from 200,000 to 1,000,000 and specific examples include polydimethyl siloxane polymers, polydimethyl siloxane/diphenyl/methylvinylsiloxane copolymers, polydimethylsiloxane/methylvinylsiloxane copolymers and mixtures thereof.

Aminofunctional silicones which have the CTFA designation amodimethicone, are also suitable for use in the



- 7 -

compositions of the invention, as are polydimethyl siloxanes having hydroxyl end groups (which have the CTFA designation dimethiconol).

5 The optimum viscosity for the silicone phase will depend on the physical properties of the solid active agent to be dispersed therein. In cases where the solid active agent is an antimicrobial such as a heavy metal (typically zinc) pyridinethione, it is generally advisable that the viscosity  
10 of the silicone phase is at least 10,000, preferably at least 50,000 centistokes, e.g 60,000 centistokes. We have found that this facilitates adequate retention of the dispersed phase of solid active agent within the droplets of the continuous silicone phase. If the viscosity of the  
15 continuous silicone phase is too low, then the dispersed particles of, e.g. zinc pyridinethione may tend to migrate towards the exterior surfaces of the droplets of silicone in which they are contained. If the viscosity is too high, then the washing composition may become difficult to  
20 process.

The average particle size of the silicone droplets in washing compositions according to this invention is suitably from 1 to 100 microns, preferably from 2 to 30 microns, more  
25 preferably 3 to 10 microns. A silicone particle size of from 3 to 10 microns is particularly preferred when the composition is intended for application to hair, since this size is believed to give optimum targeting of the silicone particles to the hair follicle, thereby optimising targeting  
30 of the solid active agent, e.g. an antimicrobial, to the hair follicle. Particle size may be measured by means of a

- 8 -

laser light scattering technique, using a 2600D Particle Sizer from Malvern Instruments.

Washing compositions of the invention generally contain from  
5 0.01 to 10%, preferably from 0.5 to 5% by weight based on  
the total washing composition, of silicone (the silicone *per se* and not the emulsion of silicone droplets). Particularly  
where the washing composition is a rinse-off cleansing  
shampoo composition for the hair or the body, if less than  
10 0.01% by weight is present in the composition, little  
conditioning benefit will be attributable to the silicone,  
and if more than 10% by weight is present, the skin and/or  
hair may appear or feel greasy.

15 Solid Particulate Active Agent Phase

The nature of the solid particulate active agent employed in  
washing compositions of the invention is not critical and a  
wide variety of materials can be deposited onto various  
20 substrates from washing compositions in accordance with the  
invention. Materials which it is of practical benefit to  
deposit on substrates are mentioned in US 3,489,686 and  
these can also be employed in the washing compositions of  
this invention. These include substances having an average  
25 particle diameter of from about 0.2 to about 50 microns,  
preferably from about 0.4 to about 10 microns, and they may  
be anti-microbial agents, sunscreens, fabric brighteners,  
and various substances that create a favourable skin feel  
after washing. One class of solid active agent that is of  
30 special interest are the heavy metal salts of  
pyridinethione, especially zinc pyridinethione.

- 9 -

Where the solid active agent is an antimicrobial agent, such as zinc pyridinethione, this may be suitably be employed in the washing composition in an amount of from 0.001% to about 1% by weight of the total composition.

5

Other suitable solid active agents include other antimicrobials such as climbazole, piroctone olamine, selenium sulphide and ketoconazole, pigment particles such as solid dyes or colorants suitable for application to hair and metal colloids.

10

#### Formulations

It is most preferred that the emulsion is formulated with additional components to form the final washing composition of the invention. Preferably, the emulsion constitutes from 1 to 100% by weight, typically from 1 to 70%, preferably from 5 to 60% by weight of the total washing composition.

15

Additional components which may be formulated with the emulsion into the final composition include surfactants, conditioning agents, polyols, thickening agents, deposition aids, pearlescers, buffers, as well as other optional adjunct materials such as foam boosters, perfumes, dyes, colouring agents, preservatives, proteins, polymers, moisturising agents, natural skin and hair nutrients (such as amino acids), hair fibre benefit agents (such as ceramides and lipids), fruit and herb extracts.

25

In preferred embodiments, the washing composition of the invention may take the form of a rinse-off cleansing shampoo

30

- 10 -

composition for the hair or the body, comprising one or more surfactants.

Further surfactants may be present as an additional  
5 ingredient if sufficient for cleansing purposes is not provided as the emulsifier for the emulsion of silicone droplets containing the dispersed solid active agent. Such further surfactants are typically selected from anionic, nonionic, zwitterionic and amphoteric surfactants or  
10 mixtures thereof.

In particularly preferred embodiments the washing composition of the invention may take the form of a rinse-off cleansing shampoo composition for the hair or the body,  
15 as described above, and in which the solid active agent is an antimicrobial agent, especially zinc pyridinethione or zirconium pyridinethione.

#### Surfactant

20 Suitable anionic surfactants for rinse-off cleansing shampoo compositions of the invention include the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-  
25 alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may  
30 be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from one

- 11 -

to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

5 Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauroyl isethionate and sodium N-lauryl  
10 sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

15 Nonionic surfactants suitable for use in shampoo compositions of the invention may include condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides,  
20 usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups. Other suitable nonionics include mono- or di-alkyl alkanolamides. Example include coco mono- or di- ethanolamide and coco mono-isopropanolamide.

25 Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycines, alkyl carboxyglycines, alkyl amphopropionates,  
30 alkylamphoglycines alkyl amidopropyl hydroxysultaines,

- 12 -

acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl  
5 betaine and sodium cocamphopropionate.

The total amount of surfactant (including that used as emulsifier for the silicone droplets) in shampoo compositions of the invention is generally from 0.1 to 50%  
10 by weight, preferably from 5 to 30%, more preferably from 10% to 25% by weight of the total shampoo composition.

#### Deposition Polymer

15 A particularly preferred further component in shampoo compositions of the invention is a deposition polymer. This further enhances deposition of the silicone particles, and therefore the solid active agent contained therein, from the composition. This improves performance of the composition,  
20 and also cost-effectiveness, since enhanced deposition means that less of the solid active agent needs to be incorporated into the composition.

The deposition polymer may be a homopolymer or be formed  
25 from two or more types of monomers. The molecular weight of the polymer will generally be between 5 000 and 10 000 000, typically at least 10 000 and preferably in the range 100 000 to about 2 000 000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or  
30 protonated amino groups, or a mixture thereof.

- 13 -

The cationic charge density is suitably at least 0.1 meq/g, preferably above 0.8 or higher. The cationic charge density should not exceed 3 meq/g. It is preferably less than 2 meq/g. The charge density can be measured using the  
5 Kjeldahl method and should be within the above limits at the desired pH of use, which will in general be from about 3 to 9 and preferably between 4 and 8.

The cationic nitrogen-containing group will generally be  
10 present as a substituent on a fraction of the total monomer units of the cationic deposition 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.

15 Suitable cationic deposition 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  
20 (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  
25 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,  
30 especially tertiary, are preferred.

- 14 -

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

5    Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkyl aminoalkyl acrylate, dialkylamino alkylmethacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt,  
10   trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidine, e.g., alkyl vinyl imidazolium, and quaternized pyrrolidine, e.g.,  
15   alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidine salts. The alkyl portions of these monomers are preferably lower alkyls such as the C<sub>1</sub>-C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls.

20   Suitable amine-substituted vinyl monomers include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C<sub>1</sub>-C<sub>7</sub> hydrocarbyls, more preferably C<sub>1</sub>-C<sub>3</sub>, alkyls.

25

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

30



- 15 -

Suitable cationic deposition polymers include, for example: copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g., Chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance

5 Association, "CTFA". as Polyquaternium-16) such as those commercially available from BASF Wyandotte Corp.

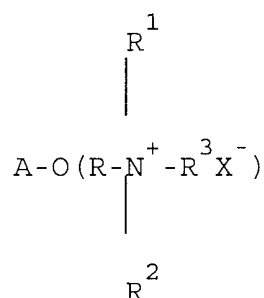
(Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate (referred to in the industry

10 by CTFA as Polyquaternium-11) such as those commercially from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymer including, for example, dimethyldiallylammonium chloride homopolymer and copolymers  
15 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  
20 described in U.S. Patent 4,009,256; and cationic polyacrylamides as described in our copending UK Application No. 9403156.4 (WO95/22311).

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

Cationic polysaccharide polymer materials suitable for use in compositions of the invention include those of the  
30 formula:

- 16 -



5

wherein: A is an anhydroglucose residual group, such as starch or cellulose anhydroglucose residual,

R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof,  
 10  $R^1$ ,  $R^2$  and  $R^3$  independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of  
 15 carbon atoms in  $R^1$ ,  $R^2$  and  $R^3$ ) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric  
 25 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 Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

- 17 -

Other cationic deposition polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (Commercially available from Celanese Corp. in their Jaguar trademark series). Other materials 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.

10 Preferably the cationic deposition polymer is selected from the group comprising cationic polyacrylamides, hydroxyalkyl cellulose ethers and cationic guar derivatives. Particularly preferred are Jaguar C13S with a cationic charge density of 0.8meq/g. Jaguar C13S is guar  
15 hydroxypropyltriemonium chloride. Other particularly suitable materials include Jaguar C15, Jaguar C17 and Jaguar C16 and Jaguar C162, A preferred cellulose ether is Polymer JR400.

20 The particular level appropriate in shampoo compositions of the present invention is dependent on the particular surfactant system employed. Generally, the level can vary from 0.01 to 10%, preferably 0.02 to 5%, typically 0.05 to 1% by weight of the total shampoo composition.

25

Shampoo compositions of this invention may optionally further comprise from 0.1 to 5 % of a silicone suspending agent. Examples are polyacrylic acids, cross linked polymers of acrylic acid, copolymers of acrylic acid with a  
30 hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked

- 18 -

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  
5 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.  
Polyacrylic acid is available commercially as Carbopol 420,  
Carbopol 488 or Carbopol 493. Polymers of acrylic acid  
10 cross-linked with a polyfunctional agent may also be used,  
they are available commercially as Carbopol 910, Carbopol  
934, Carbopol 940, Carbopol 941 and Carbopol 980. An  
example of a suitable copolymer of a carboxylic acid  
containing a monomer and acrylic acid esters is Carbopol  
15 1342. All Carbopol materials are available from Goodrich  
and Carbopol is a trade mark.

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

#### Conditioning Agent

25 Shampoo compositions of the invention may optionally further  
comprise one or more conditioning agents, in addition to the  
silicone droplets already present, which, advantageously,  
impart a conditioning benefit.

30 Suitable further conditioning agents include cationic  
surfactants, (such as quaternary ammonium halides),

- 19 -

Quaternium-5, Quaternium-31, Quaternium-18, protein hydrolysates, quaternised protein hydrolysates, perfluoropolyether materials, fatty acids, fatty alcohols and mixtures thereof.

5

Such further conditioning agents, if present, are generally present in washing compositions of the invention in a total amount of from 0.1 to 10% by weight, preferably in an amount of from 0.2 to 5% by weight of the total washing

10 composition.

#### Preparation and final form of the washing compositions

The washing compositions in accordance with the invention  
15 may be prepared by first dispersing the solid active agent into silicone fluid, and then emulsifying the dispersion so obtained, thereby forming an emulsion of silicone droplets comprising a continuous silicone phase, and a dispersed phase of the solid particulate active agent.

20

Optional ingredients as described above may be added at the emulsification stage, the emulsification being effected by high speed stirring/mixing in accordance with conventional techniques.

25

If the emulsion is to be formulated with other ingredients into the final washing composition, this is achieved by simple mixing, as is well known in the art.

30 In cases where the solid active agent is an antimicrobial such as a heavy metal (typically zinc) pyridinethione, it is

- 20 -

generally advisable that the viscosity of the silicone phase is at least 10,000, preferably at least 50,000 centistokes, e.g 60,000 centistokes, for reasons described above (see heading "Silicone Phase").

5

We have also found in such cases that it is advantageous if, in a first stage, the solid active agent is pre-wetted with a low viscosity silicone. By "low viscosity silicone" is meant a silicone fluid (typically a polyalkyl siloxane or a polyalkylaryl siloxane), with a viscosity ranging from about 10 5 to 500 centistokes, preferably from about 5 to 200 centistokes. Good results have been obtained for the solid active agent zinc pyridinethione when pre-wetted with dimethicone fluid of viscosity 100 centistokes (available 15 from Dow Corning as the "DC200" series).

However this pre-wetting step may not always be necessary if an appropriate mixing regime is employed to facilitate incorporation of the solid active agent.

20

#### Use of the washing composition

The compositions of the invention may take any suitable form appropriate to the solid active agent which they contain and are intended to deposit. By suitable selection of essential 25 and non-essential ingredients and relative amounts thereof, the washing compositions of the invention may be in the form of, for example, hair shampoos and other rinse-off hair treatment compositions, body shampoos, shower gels, facial washing compositions, bar soaps, bath foams and the like. 30 Preferred compositions in the form of body or hair shampoos

- 21 -

may be applied to the skin or hair, as appropriate, and worked to create a lather. The lather may be retained at the applied site for a short time, e.g. one or several minutes, before rinsing, or may be immediately rinsed. The  
5 procedure may be repeated if desired.

Retention of the lather at the site of application and repetition of the application regime may be of additional benefit in enhancing even further the amount or rate of  
10 deposition of the solid active agent on the skin or hair surface, and/or its delivery to the hair follicle.

#### Other Applications

15 In general, however, a washing composition according to this invention may also be one suitable for the washing of fabrics, where the solid active agent comprises particles of a fabric conditioning or treating agent, for example an acrylic latex; or for the washing of hard surfaces where the  
20 solid active agent may comprise a germicide, as in, for example, compositions for the cleaning of toilets.

Alternatively, the solid active agent may comprise a polymer latex designed to leave a polymer film on a cleaned surface, for example to provide a glossy appearance to the surface.

25 The washing composition of the invention may also find application in the field of oral hygiene where the deposition during use of an oral treatment composition of particles comprising an active compound for the care of the oral cavity, may be beneficial.

30

- 22 -

The invention is further illustrated by the following non-limiting Examples.

#### EXAMPLES

5

##### EXAMPLE 1

Preparation of an emulsion of silicone droplets containing the solid antimicrobial active Zinc Pyrithione in the  
10 silicone phase

5 g of Zinc Pyrithione (Aldrich, dry powder) was mixed with 15 g of silicone oil (100 Cs, Dow Corning) to form a creamy viscous liquid. To this mixture, a further 30 g of high  
15 viscosity silicone oil (60,000 Cs, Dow Corning) was added and the mixture stirred thoroughly.

150 g of SLES-2EO (26 %) was stirred, and 11g of the Zinc Pyrithione/silicone oil mixture prepared as described above  
20 was added. The mixture was stirred until a homogeneous dispersion was formed. To this was added 11g of a 10% Carbopol gel and the mixture again stirred until homogeneous.

25 Observation under optical microscopy showed that the product comprised an emulsion of silicone oil droplets, with Zinc Pyrithione predominantly encased within the silicone oil droplets.



- 23 -

EXAMPLE 2Preparation of a shampoo composition

5 The emulsion of Example 1 was formulated into a shampoo composition by mixing with a solution of SLES-2EO, JAGUAR C13S and formalin to give a shampoo having the composition shown in the Table below, in which all amounts are expressed in % by weight of the total shampoo composition.

10

Table

	<u>Ingredient</u>	<u>% by weight</u>
15	Zinc Pyrithione	0.55
	silicone oil (100 Cs)	1.65
	silicone oil (60,000 Cs)	3.30
	SLES-2EO	16.00
	JAGUAR C13S	0.30
20	Carbopol	0.55
	Formalin	0.10
	Water	to 100

- 24 -

### CLAIMS

1. A washing composition for washing a surface to deposit thereon a solid active agent, the washing composition comprising an emulsion of silicone droplets, the silicone droplets comprising:
  - (a) a continuous silicone phase, and;
  - (b) a dispersed phase of solid particulate active agent.
2. A washing composition according to claim 1, in which the solid active agent is a solid antimicrobial, preferably zinc pyridinethione.
3. A washing composition according to claim 1 or claim 2, in which the silicone droplets have an average particle size of from 1 to 100 microns, preferably from 2 to 30 microns, more preferably 3 to 10 microns.
4. A washing composition according to any one of claims 1 to 3, which is in the form of a rinse-off cleansing shampoo composition for the hair or the body, the shampoo composition comprising:
  - (a) from 0.1 to 50% by weight based on total weight of one or more surfactants;
  - (b) from 0.001% to 5% by weight based on total weight of solid active agent which is preferably a solid

- 25 -

antimicrobial agent, most preferably zinc  
pyridinethione;

(c) from 0.01 to 10% by weight based on total weight  
of silicone;

(d) from 0.01% to 10% by weight based on total weight  
of a deposition polymer, which is preferably  
selected from the group comprising cationic  
polyacrylamides, cationic hydroxyalkyl cellulose  
ethers and cationic guar derivatives.

5. A washing composition according to claim 4, which  
further comprises from 0.1 to 5 % of a silicone  
suspending agent.

6. A washing composition according to claim 4 or claim 5,  
which further comprises from 0.1 to 10% by weight based  
on total weight of a conditioning agent selected from  
cationic surfactants, Quaternium-5, Quaternium-31,  
Quaternium-18, protein hydrolysates, quaternised  
protein hydrolysates, perfluoropolyether materials,  
fatty acids, fatty alcohols, and mixtures thereof.

7. A method of making an emulsion of silicone droplets  
comprising:

(a) a continuous silicone phase, and;

(b) a dispersed phase of solid particulate active  
agent,

- 26 -

for incorporation into a washing composition, the method comprising the steps of:

- 5           (a) dispersing the solid active agent into silicone fluid, and
- (b) emulsifying the dispersion so obtained, thereby forming an emulsion of silicone droplets
- 10           comprising:
- (a) a continuous silicone phase, and;
- (b) a dispersed phase of solid particulate active
- 15           agent.
8.   A method according to claim 7, in which the solid active agent is an antimicrobial, preferably zinc pyridinethione, and in which the viscosity of the
- 20   silicone phase is at least 10,000, preferably at least 50,000 centistokes, and further in which, in a first stage, the solid active agent is pre-wetted with a low viscosity silicone, of viscosity ranging from 5 to 500 centistokes, preferably from 5 to 200 centistokes.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/07536

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/00 A61K7/06

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)

IPC 6 A61K

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)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1 066 207 A (REVLON INC) 19 April 1967 see page 2, line 39 - line 43 see page 2, line 65 - line 68 see page 3, line 64 - line 68 see page 3, line 93 - line 111 see claims	1-8
Y	EP 0 552 024 A (UNILEVER PLC ET AL.) 21 July 1993 cited in the application see page 2, line 42 - line 46 see page 2, line 52 - line 56 see page 3, line 9 - line 14 see page 3, line 44 - line 58 see claims	1-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 April 1999

Date of mailing of the international search report

22/04/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Pelli Wablat, B

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/07536

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 96 41610 A (UNILEVER PLC ET AL.)  27 December 1996  see page 3, line 13 - line 18  see page 3, last paragraph  see page 8, line 14 - line 35  see page 9, paragraph 4  see examples</p> <p>---</p>	1-8
A	<p>EP 0 074 819 A (AMWAY CORP) 23 March 1983  see the whole document</p> <p>---</p>	1,2,4-6
A	<p>FR 2 258 165 A (PETROLITE CORP)  18 August 1975  see page 1, line 31 - line 34  see examples 1,5,17,26  see claims</p> <p>-----</p>	1-3,5

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/EP 98/07536

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1066207 A		BE 671120 A	19-04-1966
		CA 793290 A	
		DE 1492112 A	06-11-1969
		FR 1452987 A	21-12-1966
<hr/>			
EP 0552024 A	21-07-1993	AU 3181393 A	22-07-1993
		AU 6562896 A	07-11-1996
		BR 9300143 A	27-07-1993
		CA 2087140 A	16-07-1993
		JP 5279232 A	26-10-1993
		ZA 9300269 A	15-07-1994
<hr/>			
WO 9641610 A	27-12-1996	AU 6001496 A	09-01-1997
		CA 2222059 A	27-12-1996
		CN 1192671 A	09-09-1998
		EP 0833600 A	08-04-1998
<hr/>			
EP 0074819 A	23-03-1983	AU 553445 B	17-07-1986
		AU 8819982 A	24-03-1983
		CA 1197785 A	10-12-1985
		JP 58065210 A	18-04-1983
		US 4557928 A	10-12-1985
<hr/>			
FR 2258165 A	18-08-1975	DE 2408663 A	07-08-1975
		JP 1370008 C	25-03-1987
		JP 50104187 A	16-08-1975
		JP 61027094 B	24-06-1986