

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 December 2003 (24.12.2003)

PCT

(10) International Publication Number
WO 03/105795 A1

(51) International Patent Classification⁷: **A61K 7/32**

(21) International Application Number: PCT/EP03/05471

(22) International Filing Date: 22 May 2003 (22.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0213999.6 18 June 2002 (18.06.2002) GB

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only):
UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors: **BROWN, Nathan, Charles**; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **RIELEY, Hugh**; Unilever R

& D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **SMITH, Ian, Karl**; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **STOCKTON, Joanne, Elizabeth**; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agents: **ELLIOTT, Peter, William** et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/105795 A1

(54) Title: ANTIPERSPIRANT EMULSION COMPOSITIONS

(57) Abstract: A w/o emulsion antiperspirant composition comprising a dissolved antiperspirant salt, an emulsifier and, in a disperse phase separate from the dissolved antiperspirant salt, a polymer comprising Brønsted acid groups.

- 1 -

ANTIPERSPIRANT EMULSION COMPOSITIONS

This invention relates to the field of antiperspirant and deodorant formulation science. More specifically, it
5 relates to high performance antiperspirant compositions having a water-in-oil (w/o) emulsion structure.

In co-pending application PCT/EP01/13253, the applicants disclose high performance antiperspirant compositions
10 comprising an antiperspirant salt and a polymer comprising Brønsted acid groups that acts as a co-gellant for the antiperspirant salt when mixed therewith in the presence of water, the antiperspirant salt and the polymer being physically separate from one another prior to application.

15

Other systems comprising an antiperspirant salt and a polymer comprising Brønsted acid groups are cited in the above co-pending application. However, none of these other systems offer the combination of physical stability and high
20 performance delivered by the w/o emulsion compositions of the present invention.

W/o emulsion compositions have previously been employed as antiperspirant products. For example, EP 812,182 (Unilever
25 PLC) discloses a base for an antiperspirant aerosol composition in the form of a w/o emulsion and comprising a dissolved aluminium salt, a volatile silicone, and a silicone surfactant.

30 We have now discovered that the performance of a w/o emulsion composition comprising a dissolved antiperspirant

- 2 -

salt may be enhanced by the presence, in a phase separate from the dissolved antiperspirant salt, of a polymer comprising Brønsted acid groups. In addition, such systems have acceptable physical stability; a fact which is highly surprising, considering the inherent thermodynamic instability of emulsion systems.

Thus, according to a first aspect of the present invention, there is provided a w/o emulsion antiperspirant composition comprising a dissolved antiperspirant salt, an emulsifier and, in a disperse phase separate from the dissolved antiperspirant salt, a polymer comprising Brønsted acid groups.

According to a second aspect of the invention, there is provided a method of reducing perspiration comprising the application to the human body of a w/o emulsion composition comprising a dissolved antiperspirant salt and an emulsifier, and the co-application, from a disperse phase separate from the dissolved antiperspirant salt, of a polymer comprising Brønsted acid groups.

According to a third aspect of the invention, there is provided a method of manufacture of an antiperspirant composition, said method comprising emulsification of an aqueous solution of an antiperspirant salt in an oil continuous phase, followed by mixing of the emulsion so formed with a separate phase comprising a polymer comprising Brønsted acid groups.

30

- 3 -

The w/o emulsion antiperspirant compositions of the present invention comprise an antiperspirant salt dissolved in the aqueous dispersed phase. The polymer comprising Brønsted acid groups serves to enhance the performance of the antiperspirant salt when the two components come into intimate contact on application. However, it is important that intimate contact between the two components is prevented prior to their application and it is for this reason that the polymer comprising Brønsted acid groups is applied as a separate phase. Premature interaction between the two components leads to the production of a water-insoluble complex that is not an effective antiperspirant.

Premature interaction between the two components may be prevented by applying them from different compositions and this is one method of reducing perspiration according to the invention. Alternatively, a composition according to the first aspect of the invention may be applied.

In compositions according to the first aspect of the invention, it is essential that the polymer comprising Brønsted acid groups exists in a separate phase from the dissolved antiperspirant salt. This may be accomplished by suspending the polymer comprising Brønsted acid groups as a solid in an oil continuous phase. Thus, in one embodiment, there is provided a w/o emulsion antiperspirant composition comprising a dissolved antiperspirant salt and, suspended as a solid in an oil continuous phase, a polymer comprising Brønsted acid groups.

30

- 4 -

In an alternative embodiment of the first aspect of the invention, there is provided a w/o emulsion antiperspirant composition comprising a dissolved antiperspirant salt, an emulsifier, and, emulsified as a separate dispersed phase, an aqueous solution of a polymer comprising Brønsted acid groups. Compositions of this type are described as "dual" emulsions in this specification. To achieve such compositions, it is essential that the polymer is soluble in water, preferably having a solubility of 5 g/l or greater, more preferably 10 g/l or greater and most preferably 50 g/l or greater. It is also essential that the polymer solution is emulsified in an oil phase; this may be achieved using the same emulsifier as used for the emulsification of the antiperspirant solution or a different one.

15

The compositions of the invention comprise an oil continuous phase. The compositions may comprise silicone oil, hydrocarbon oil, and/or ester oils. When more than one oil is present, it may be preferred that the oils are miscible; although immiscibility may sometimes be desirable. In order to avoid the need for shaking of liquid compositions prior to use, it is preferred that only one oil continuous phase is present in such compositions. It is preferred that compositions of the invention comprise silicone oil and it is further preferred that the silicone oil is comprised in the oil continuous phase. Silicone oils may be cyclic or linear, examples include Dow Corning silicone fluids 344, 345, 244, 245, 246, 556, and the 200 series; Union Carbide Corporation Silicones 7207 and 7158; and General Electric silicone SF1202. Alternatively or additionally, non-silicone oils may be used; such materials include mineral

30

- 5 -

oils, hydrogenated polyisobutene, polydecene, paraffins, isoparaffins of at least 10 carbon atoms, and aliphatic or aromatic ester oils (e.g. isopropyl myristate, lauryl myristate, isopropyl palmitate, diisopropyl sebecate, diisopropyl adipate, or C₈ to C₁₈ alkyl benzoates).

The compositions of the invention also comprise at least one aqueous dispersed phase. The proportion of aqueous dispersed phase(s) within the total composition (excluding any volatile propellant that may be present) is typically from 50% to 90%, particularly from 50% to 70% when used in stick compositions and particularly from 70% to 90%, especially from 75% to 85%, when used in liquid or cream/soft solid compositions, all percentages being by weight. The mean droplet size of the aqueous dispersed phase comprising the antiperspirant salt is preferably from 1 to 25 μm , in particular from 1 to 10 μm , and especially from 1 to 7 μm . When the composition also comprises an aqueous dispersed phase comprising the polymer, the mean droplet size of this dispersed phase is preferably from 1 to 25 μm , in particular from 1 to 10 μm , and especially from 5 to 7 μm . The mean droplet sizes referred to are Sauter D(4,3) means, as determined by light scattering techniques.

The Antiperspirant Salt

Antiperspirant (AP) salts for use herein are often selected from astringent salts including, in particular, aluminium, zirconium, and mixed aluminium-zirconium salts, including both inorganic salts, salts with organic anions, and

- 6 -

complexes. Preferred antiperspirant salts are aluminium, zirconium, and aluminium-zirconium chlorides, oxychlorides, and chlorohydrates salts. Particularly preferred antiperspirant salts are polynuclear in nature, meaning that the cations of the salt are associated into groups comprising more than one metal ion.

Aluminium halohydrates are usually defined by the general formula $Al_2(OH)_xQ_y \cdot wH_2O$ in which Q represents chlorine, bromine or iodine, x is variable from 2 to 5 and $x + y = 6$ while wH_2O represents a variable amount of hydration. Aluminium chlorohydrate (ACH) is an especially preferred active.

Zirconium salts are usually defined by the general formula $ZrO(OH)_{2-x}Q_x \cdot wH_2O$ in which Q represents chlorine, bromine or iodine; x is from about 1 to 2; w is from about 1 to 7; and x and w may both have non-integer values. Preferred are zirconyl oxyhalides, zirconium hydroxyhalides, and combinations thereof. Non-limiting examples of zirconium salts and processes for making them are described in Belgian Patent 825,146, Schmitz, issued August 4, 1975 and U.S. Patent 4,223,010 (Rubino).

AP salts as used in the invention may be present as mixtures or complexes. Suitable aluminium-zirconium complexes often comprise a compound with a carboxylate group, for example an amino acid. Examples of suitable amino acids include tryptophan, β -phenylalanine, valine, methionine, β -alanine and, most preferably, glycine.

- 7 -

In some embodiments, it is desirable to employ complexes of a combination of aluminium halohydrates and zirconium chlorohydrates with amino acids such as glycine, which are disclosed in US 3,792,068 (Procter and Gamble Co.). Certain
5 of these Al/Zr complexes are commonly called ZAG in the literature. ZAG actives generally contain aluminium, zirconium and chloride with an Al/Zr ratio in a range from 2 to 10, especially 2 to 6, an Al/Cl ratio from 2.1 to 0.9 and a variable amount of glycine. Actives of this preferred
10 type are available from Westwood, from Summit and from Reheis.

Other actives that may be utilised include astringent titanium salts, for example those described in GB 2,299,506.

15

AP salts are preferably incorporated into compositions of the invention in an amount of from 0.5 to 60%, particularly from 5 to 30% or 40% and especially from 5 or 10% to 30 or 35% by weight.

20

The AP salt is generally dissolved in water prior to emulsification. The aqueous AP salt solution is typically of concentration from 10% to 70%, in particular from 25% to 60%, and especially from 40% to 60% by weight. The w/o
25 emulsion formed from the AP salt solution, prior to the addition of the separate polymer phase and any volatile propellant, has a typical proportion of dispersed phase of from 50% to 90%, in particular from 50% to 70% when used in stick compositions and from 70% to 90%, especially from 75%
30 to 85%, when used in liquid or cream/soft solid compositions, all percentages being by weight.

The Polymer

The polymers of the present invention comprise Brønsted acid groups and act as co-gellants for the AP salt when mixed therewith in the presence of water, for example water in human sweat, at a temperature of 37°C or less. The co-gelation results in a thickened state of matter - that is to say, the three component system (polymer, AP salt, water) has a higher viscosity than that of an aqueous solution of either the polymer or AP salt alone. Without wishing to be bound by theory, it is believed that the co-gelation involves chemical interaction between the Brønsted acid groups on the polymer and hydrated metal cations of the AP salt.

15

A simple test may be used to determine whether or not a polymer is able to act as a co-gellant: if mixing of an aqueous solution of the polymer with an aqueous solution of the AP salt results in an increase in viscosity, then the polymer is a co-gellant for the AP salt.

20

In many embodiments of the invention, it is preferred that the water solubility of the polymers used, when measured at 37°C, is preferably 5g/l or greater, more preferably 10g/l or greater, and most preferably 50g/l or greater. It is preferred that the polymers form true solutions in water, rather than dispersions; such true solutions typically having an absorbance of less than 0.2, preferably less than 0.1 (for a 1 cm pathlength at 600 nm) measured using a Pharmacia Biotech Ultrospec 200 Spectrophotometer or similar instrument. It is also desirable that the polymer is water

30

- 9 -

soluble at pH 7; the attainment of said pH generally requiring a certain amount of neutralisation of the Brønsted acid groups present.

5 When the polymer is present as a suspended solid, it is preferred (particularly in liquid compositions) that the polymer is slow to dissolve in water, taking more than 8 weeks, preferably more than 16 weeks, at ambient temperature, to dissolve in the aqueous phase comprising the
10 dissolved antiperspirant salt to an extent that causes thickening or precipitation of solid.

The Brønsted acid groups in the polymer may be present in their protonated form or may be present in their neutralised
15 form as salt groups. Both partially-neutralised and fully-neutralised acidic polymers may be employed in the present invention. Suitable Brønsted acid groups include carboxylic acid groups, sulphonic acid groups, and phosphonic acid groups. Carboxylic acid groups are particularly preferred.
20 Brønsted acid groups are preferably present at a concentration of greater than 0.1 mmole per gram of polymer, more preferably at a concentration of greater than 1.0 mmole/g of polymer, and most preferably at a concentration of greater than 3.0 mmole/g of polymer. Concentrations
25 expressed of Brønsted acid groups relate to monobasic Brønsted acid groups and should be reduced *pro rata* for polybasic Brønsted acid groups. Latent Brønsted acid groups, such as anhydrides or other groups that generate Brønsted acid groups on addition to water, may also be
30 present.

- 10 -

When the polymer is present as a suspended solid, it is preferred (particularly in liquid compositions) that the level of Brønsted acid groups in the polymer is limited to a level of less than 6 mmole/g, more preferably less than 5 mmole/g, and most preferably less than 4 mmole/g. In this way, more stable compositions result.

Preferred polymers are organic polymers, in particular, organic polymers possessing only limited positive charge, that is to say having less than 50 mole%, preferably less than 25 mole%, of positively-charged monomer units. Especially preferred organic polymers are nonionic and anionic polymers. Typical polymers possess carbon backbones, optionally interrupted by ester or amide links.

15

The acid value of a polymer is a widely used means of characterisation. Acid values generally express the acidity of a polymer in terms of the number of milligrams of potassium hydroxide base required to fully neutralise one gram of the polymer. Thus, the unit of measurement can be abbreviated to mg KOH/g.

20

Typical polymers used in the present invention have acid values of greater than 160. The polymers preferably have acid values of greater than 320, more preferably greater than 450. Especially preferred polymers have acid values greater than 580. These acid values are based on the polymer in its fully protonated state; that is to say, the actual in-use extent of neutralisation of the polymer is ignored in respect of the 'acid value'. Acid values may be measured experimentally or may be estimated theoretically.

30

- 11 -

When using the latter method, acid anhydride groups present in a polymer should be counted as two acid groups, such latent acid groups generally being hydrolysed to di-acids by potassium hydroxide.

5

The preferred carboxylic acid groups may be introduced into the polymer by inclusion of monomers such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, maleic anhydride, or itaconyl anhydride in the polymer.

10 When the only source of Brønsted acid groups are anhydride monomers, it is required that the anhydride groups are at least partially hydrolysed prior to use of the polymer. Polymers comprising a mixture of any of the above acid and/or anhydride monomers may also be advantageously
15 employed. Particularly preferred polymers are those derived, at least in part, from maleic acid and/or maleic anhydride monomers.

It is sometimes desirable to include other monomers in the
20 polymer. Suitable monomers include methyl vinyl ether, C₁-C₈ alkyl acrylates and methacrylates, vinyl acetate, ethylene, and propylene. The inclusion of such monomers may aid polymer synthesis, ease handling and/or formulation of the polymer, and may improve the performance of the polymer as a
25 co-gellant.

The molecular weight of the polymer is preferably in the range of 500 to 5,000,000, in particular 10,000 to 3,000,000 and especially 100,000 to 2,500,000. Selection of an appropriate molecular weight for the polymer may lead to
30 benefits in terms of ease of formulation, product aesthetics (particularly product feel), and product performance.

- 12 -

Particularly preferred polymers are co-polymers of methyl vinyl ether and maleic acid/anydride.

The polymer is preferably incorporated into a composition in an amount of from 0.1% to 10% by weight, more preferably from 0.5% to 5% by weight, and most preferably from 1% to 4% by weight of said composition.

When the polymer is present as a suspended solid, the particle size of the polymer is generally between 0.1 and 200 μm , preferably with a mean particle size of from 3 to 50 μm , the mean particle size being the Sauter D(4,3) mean, as determined by light scattering techniques.

When the polymer is present as an aqueous solution emulsified as a separate dispersed phase, it is preferably used as a solution of concentration from 5% to 50%, more preferably from 10% to 30%, and most preferably from 15% to 20% by weight. When a w/o emulsion is formed from the polymer salt solution, prior to mixing with the w/o AP emulsion, it typically has a proportion of dispersed phase of from 50% to 90%, in particular from 50% to 70% when used in stick compositions and from 70% to 90%, especially from 75% to 85%, when used in liquid or cream/soft solid compositions, all percentages being by weight.

The weight ratio of the AP salt to the polymer is preferably 25:1 or less, 1:10 or greater, particularly between 25:1 and 1:10, and especially between 10:1 and 1:5.

30

The Emulsifier

An emulsifier is an essential component of the w/o emulsion comprising the dissolved antiperspirant salt and may also be associated with the independent polymer phase. The emulsifier may be an anionic, cationic, zwitterionic, or nonionic surfactant; nonionic surfactants being preferred. The proportion of emulsifier in the total composition may be from 0.1% to 5%, preferably from 0.2% to 3.5%, more preferably from 0.25% to 2.5%, and most preferably from 0.4% to 0.6%, particularly for liquid compositions.

It is desirable to use an emulsifier or a mixture of emulsifiers with an overall HLB value in a range from 2 to 10, preferably from 3 to 8. A mixture of emulsifiers may comprise a surfactant of high HLB and a surfactant of low HLB, blended to give a suitable overall HLB.

High HLB emulsifiers include nonionic esters or ethers comprising a polyoxyalkylene moiety, especially a polyoxyethylene (POE) moiety containing from 2 to 80, and especially from 5 to 60, ethylene oxide (EO) units. Polyoxypropylene (POP) emulsifiers may also be employed, as may emulsifiers comprising one or more polyhydroxylated units such as glycerol, sorbitol, or some other alditol. The emulsifier must also comprise a hydrophobic moiety, for example an alkyl, alkenyl, or aralkyl group, normally containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched and is often saturated, though it can be unsaturated, and it is optionally fluorinated. The

- 14 -

hydrophobic moiety can comprise a mixture of chain lengths, for example those deriving from tallow, lard, palm oil, sunflower seed oil or soya bean oil. Examples of suitable high HLB emulsifiers include C₁₆ to C₁₈ alcohols ethoxylated with 10 to 25 ethylene oxide residues and PEG-15-25 stearate or distearate. Other suitable examples include C₁₀-C₂₀ fatty acid mono, di or tri-glycerides. Further examples include C₁₈-C₂₂ fatty alcohol ethers of polyethylene oxides with 8 to 12 EO units.

10

Low HLB emulsifiers, typically of HLB from 2 to 6, include fatty acid mono- or possibly di-esters of polyhydric alcohols such as glycerol, sorbitol, erythritol or trimethylolpropane. The fatty acyl moiety is often from C₁₄ to C₂₂ and is saturated in many instances, including cetyl, stearyl, arachidyl and behenyl. Examples include monoglycerides of palmitic or stearic acid, sorbitol mono or diesters of myristic, palmitic or stearic acid, and trimethylolpropane monoesters of stearic acid.

20

Emulsifiers that are silicone derivatives, by which it is meant emulsifiers that have a lipophilic silicone chain, are particularly preferred, especially when the continuous phase of the composition comprises silicone oil. Examples of such emulsifiers include polyoxyalkylene derivatives of dimethylpolysiloxanes, in particular POE, POP, or POE-co-POP derivatives. Such derivatives may terminate in C₁ to C₁₂ alkyl groups. Such emulsifiers may also be named dimethicone copolyol silicone surfactants, for example cetyl dimethicone copolyol.

30

- 15 -

Suitable emulsifiers and co-emulsifiers are widely available under many trade names including Abil™, Arlacel™, Brij™, Cremophor™, Dehydrol™, Dehymuls™, Emerest™, Lameform™, Pluronic™, Prisorine™, Quest PGPH™, Span™, Tween™, SF1228, DC3225C and Q2-5200.

Other Components

10 Other components may optionally be included in the compositions of the invention.

Structurants and emulsifiers are highly desirable in certain product forms. Structurants, when employed, are preferably present at from 1% to 30% by weight of a composition, whilst emulsifiers are preferably present at from 0.1% to 10% by weight of a composition. In roll-on compositions, such materials help control the rate at which product is dispensed by the roll ball. In stick compositions, such materials can form gels or solids from solutions or suspensions. Suitable structurants for use in such compositions include cellulosic thickeners such as hydroxypropyl cellulose and hydroxyethyl cellulose, fibre-forming structurants such as 12-hydroxystearic acid, esters of 12-hydroxystearic acid, amides of 12-hydroxystearic acid, stearic acid, behenic acid and di- and tri-glycerides thereof, N-lauroyl-glutamic acid dibutyl amide, 2-dodecyl-N,N'-dibutyl-succinamide, and dibenzylidene sorbitol. Partially or fully esterified disaccharides, for example cellobiose octanoates, may also be used, as may structurants like dextrin palmitate or an aliphatic ester having a C₁₂-C₃₀

- 16 -

fatty acyl group and a C₁₂-C₂₄ fatty alcohol residue, like cetearyl behenate. Sterols (e.g. β -sitosterol) and sterol esters (e.g. oryzanol) are also suitable for use, when used in combination. Emulsion pump sprays, roll-ons, creams, and gel compositions can be formed using a range of oils, waxes, and emulsifiers. Suitable emulsifiers include steareth-2, steareth-20, steareth-21, cetareth-20, glyceryl stearate, cetyl alcohol, cetearyl alcohol, PEG-20 stearate, and dimethicone copolyol. Suspension aerosols, roll-ons, sticks, and creams require structurants to slow sedimentation (in fluid compositions) and to give the desired product consistency to non-fluid compositions. Suitable structurants include sodium stearate, stearyl alcohol, cetyl alcohol, hydrogenated castor oil, beeswax, synthetic waxes, microcrystalline wax, paraffin waxes, candelilla wax, dibutyl lauroyl glutamide, alkyl silicone waxes, quaternium-18 bentonite, quaternium-18 hectorite, silica, and propylene carbonate. Some of the above materials also function as suspending agents in certain compositions.

A volatile propellant is an additional component used in most aerosol compositions. Volatile propellants may be used at a level of from 95% to 30%, preferably from 90% to 40% by weight. The invention is also suitable for use in low-VOC aerosol compositions comprising propellant at a level from 30% to 50% or 55% by weight. Suitable propellants include liquefied hydrocarbons or halogenated hydrocarbon gases (particularly fluorinated hydrocarbons such as 1,1-difluoroethane and/or 1-trifluoro-2-fluoroethane) that have a boiling point of below 10°C and especially those with a

- 17 -

boiling point below 0°C. It is especially preferred to employ liquefied hydrocarbon gases, and especially C₃ to C₆ hydrocarbons, including propane, isopropane, butane, isobutane, pentane and isopentane and mixtures of two or
5 more thereof.

Other propellants that may be used include alkyl ethers, such as dimethyl ether or compressed non-reactive gases such air, nitrogen or carbon dioxide.

10

Certain sensory modifiers are further desirable components in the compositions of the invention. Such materials are preferably used at a level of up to 20% by weight of the composition. Emollients, humectants, volatile oils, non-
15 volatile oils, and particulate solids that impart lubricity are all suitable classes of sensory modifiers. Examples of such materials include cyclomethicone, dimethicone, dimethiconol, isopropyl myristate, isopropyl palmitate, talc, finely-divided silica (e.g. Aerosil 200), particulate
20 polyethylene (e.g. Acumist B18), polysaccharides, corn starch, C12-C15 alcohol benzoate, PPG-3 myristyl ether, octyl dodecanol, C7-C14 isoparaffins, di-isopropyl adipate, isosorbide laurate, PPG-14 butyl ether, glycerol, hydrogenated polyisobutene, polydecene, titanium dioxide,
25 phenyl trimethicone, dioctyl adipate, and hexamethyl disiloxane.

Fragrance is also a desirable additional component in the compositions of the invention. Suitable materials include
30 conventional perfumes, such as perfume oils and also include so-called deo-perfumes, as described in EP 545,556 and other

- 18 -

publications. Levels of incorporation are preferably up to 4% by weight, particularly from 0.1% to 2% by weight, and especially from 0.7% to 1.7% by weight.

- 5 It should be noted that certain components of compositions perform more than one function. Such components are particularly preferred additional ingredients, their use often saving both money and formulation space.
- 10 Further additional components that may also be included are colourants, conventional anti-microbials, and preservatives, for example C₁-C₃ alkyl parabens.

Product Form

15

- The antiperspirant composition of the invention may take any of the forms known in the art. The composition may take the form of a stick, gel, cream, roll-on, squeeze spray, pump spray, or aerosol. Gel and cream compositions are given the
- 20 collective name "soft solid" compositions, whilst roll-on, squeeze spray, pump spray, and aerosol compositions are collectively termed "liquid" compositions. Each product form contains its own selection of additional components, some essential and some optional. The types of components
- 25 typical for each of the above product forms may be incorporated in the corresponding compositions of the invention.

30

Method of Manufacture

The method of manufacture of antiperspirant compositions according to the invention comprises emulsification of an aqueous solution of an antiperspirant salt in an oil continuous phase, followed by mixing of the emulsion so formed with a separate phase comprising a polymer comprising Brønsted acid groups. In general, the separate phase comprising the polymer comprising Brønsted acid groups is added as dispersion of the polymer in an oil continuous phase. The dispersed polymer may be in the form of solid particulates or as emulsified aqueous solution droplets. Preferably the oil continuous phase of the polymer dispersion comprises one or more oils common to the continuous phase of the antiperspirant salt emulsion to which it is added.

Dual emulsions according to the invention are manufactured by preparing independent emulsions of the polymer solution and the antiperspirant salt solution and then mixing the two. The emulsion of the antiperspirant salt solution is preferably subjected to high shear mixing, typically involving shearing at over 4000 rpm, prior to mixing with the polymer phase. This can lead to a stability benefit. Once formed, a dual emulsion composition may be used as a liquid or soft solid composition, or, with a suitable structurant present, it may be cooled to give a stick composition. For aerosol compositions, the preferred manufacturing procedure involves addition of a volatile propellant after the formation of the dual emulsion.

Examples

The invention will now be further described by means of the following non-limiting examples.

5

Table 1: Emulsion Aerosol Compositions with Solid Polymer

| Product Ingredients | | Level (wt%) | |
|-----------------------------|--|-------------|-----------|
| Trade Name | Chemical Name | Example 1 | Example 2 |
| Abil EM 90 emulsifier | Cetyl dimethicone copolyol | 0.12 | 0.12 |
| DC245 | Cyclomethicone | 2.78 | 2.78 |
| Eutanol G | Octyldodecanol | 0.50 | 0.50 |
| Aloxicoll L | ACH (50% solution) | 10.00 | 20.00 |
| DC1501 | D5 cyclopentasiloxane and dimethiconol | 1.00 | 1.00 |
| Gantrez AN-119 ¹ | Poly(methyl vinyl ether-co-maleic anhydride) | 1.00 | 1.50 |
| Water | Distilled water | 10.00 | - |
| CAP 40 propellant | Butane, isobutane, propane | 74.60 | 74.10 |

- 10 1. The Gantrez AN-119 used was partially hydrolysed, having a weight ratio of di-acid to anhydride of approximately 1:2 and a level of Brønsted acid groups of 3.7 mmole/g.

Examples 1 and 2 were prepared in the following manner.

- 15 First, the oil phase components were stirred together at room temperature. Next, the Aloxicoll L (50% aqueous solution of ACH) and water were slowly added with an increasing amount of shear. To the w/o emulsion so formed, the Gantrez AN-119 polymer was added as a powder with

minimal shear. Finally, the resulting base composition was transferred to an aluminium can and the liquefied propellant gas was added using standard techniques.

5 Table 2: Dual Emulsion Aerosol Compositions

| Trade Name | Level (wt%) | | | |
|---------------------------|------------------|--------------|-----------|-----------|
| | Polymer emulsion | ACH emulsion | Example 3 | Example 4 |
| Abil EM 90 | 0.5 | 0.5 | 0.1 | 0.2 |
| DC245 | 10.0 | 10.0 | 2.08 | 4.16 |
| Fluid AP ¹ | 5.0 | 5.0 | 1.04 | 2.08 |
| Perfume | 2.4 | 2.4 | 0.6 | 1.2 |
| Eutanol G | 2.0 | 2.0 | 0.42 | 0.84 |
| Aloxicoll L(50% ACH) | - | 80.0 | 10.0 | 20.0 |
| Gantrez S-95 ² | 12 | - | 1.0 | 2.0 |
| Water | 68.1 | 0.1 | 5.67 | 11.34 |
| CAP 40 propellant | - | - | 79.09 | 58.18 |

1. PPG-14 butyl ether
2. Poly(methyl vinyl ether co-maleic acid)

10

Dual emulsion aerosol composition Examples 3 and 4 were prepared in the following manner. First, the AP emulsion of Table 2 was formed in a manner analogous to that used in the preparation of the AP emulsion of Examples 1 and 2.

- 15 Independently, the polymer emulsion of Table 2 was also formed in a conventional manner without the use of high shear. The required amounts of the two emulsions were then mixed to give the dual emulsion and the required amount of

- 22 -

this base was transferred to aluminium cans and the liquefied propellant gas added using standard techniques.

Clinical evaluation of the antiperspirancy performance of Examples 1 and 3 showed 39% and 41% reduction in sweat production respectively, compared with 29% reduction in sweat production for a similar emulsion aerosol composition also comprising 10% Aloxicoll L (i.e. 5% ACH), but without the added polymer phase. Examples 2 and 4 showed 45% and 51% reduction in sweat production respectively, compared with 43% reduction in sweat production for a similar emulsion aerosol composition also comprising 20% Aloxicoll L (i.e. 10% ACH), but without the added polymer phase.

Table 3: Dual Emulsion Aerosol Composition

| Ingredient | Amount | | |
|--------------------------|------------------|--------------|-----------|
| | Polymer emulsion | ACH emulsion | Example 5 |
| Abil EM 90 | 0.5 | 0.5 | 0.1 |
| Finsolv TN ¹ | - | 10.0 | 1.25 |
| DC245 | 10.0 | - | 0.83 |
| Fluid AP | 5.0 | 5.0 | 1.04 |
| Eutanol G | 2.0 | 2.0 | 0.42 |
| Aloxicoll L (50% ACH) | - | 80.0 | 10.0 |
| Gantrez S-95 | 12.0 | - | 1.0 |
| Water | 70.5 | 2.5 | 6.2 |
| CAP 40 | - | - | To 100 |

1. C₁₂-C₁₅ alkyl benzoate

Example 5 was prepared in analogous manner to Examples 3 and 4; the main difference being the use of Finsolv TN as the continuous phase of the ACH emulsion and the resulting

production of a dual emulsion having a continuous phase comprising both silicone oil and ester oil.

Table 4: Dual Emulsion Cream Composition

5

| Ingredient | Level (wt%) | | |
|----------------------------|------------------|--------------|-----------|
| | Polymer emulsion | ACH emulsion | Example 6 |
| Silkflo 364NF ¹ | 10.3 | 10.3 | 10.3 |
| Abil EM 90 | 1.0 | 1.0 | 1.0 |
| Aloxicoll L (50% ACH) | - | 64.4 | 41.0 |
| Gantrez S-95 | 11.6 | - | 4.1 |
| Glycerol | 2.1 | 2.1 | 2.1 |
| Water | To 100 | To 100 | To 100 |

1. Polydecene

Example 6 was manufactured via independent preparation of
 10 the polymer emulsion and the AP emulsion, in an analogous
 manner to that used for Examples 3 and 4, followed by mixing
 of the appropriate quantities and pouring into a soft solid
 dispenser pack.

Table 5: Dual Emulsion Stick Composition

| Ingredient | Level (wt%) | | |
|-----------------------------|------------------|--------------|-----------|
| | Polymer emulsion | ACH emulsion | Example 7 |
| Kester Wax K62 ¹ | 12.7 | 12.7 | 12.7 |
| DC245 | 12.8 | 12.8 | 12.8 |
| Finsolv TN | 8.5 | 8.5 | 8.5 |
| Abil EM 90 | 0.5 | 0.5 | 0.5 |
| Aloxicoll L (50% ACH) | - | 62.5 | 40.0 |
| Gantrez S-95 | 11.25 | - | 4.05 |
| Acumist B18 ² | 2.0 | 2.0 | 2.0 |
| Perfume | 1.0 | 1.0 | 1.0 |
| Water | 51.25 | - | 18.45 |

1. Cetearyl behenate
- 5 2. Micronised polyethylene

Example 7 was manufactured via independent preparation of the polymer emulsion and the AP emulsion, both at 85°C with addition of the aqueous phase accompanying increasing shear to the emulsion being formed. After cooling to 75°C, the required quantities were mixed and poured into a stick barrel. Cooling and solidification gave the final product.

Table 6: Dual Emulsion Roll-On Composition

| Ingredient | Level (%) | | |
|--------------------------|------------------|--------------|-----------|
| | Polymer emulsion | ACH emulsion | Example 8 |
| Abil EM 90 | 0.7 | 0.7 | 0.5 |
| DC245 | 10.0 | 12.3 | 34.4 |
| Fluid AP | 5.0 | 5.0 | 3.7 |
| Eutanol G | 2.0 | 2.0 | 1.5 |
| Aloxicoll L (50% ACH) | - | 80.0 | 44.0 |
| Gantrez S-95 | 12.0 | - | 2.2 |
| Perfume | - | 2.3 | 1.3 |
| Water | 68.0 | - | 12.5 |

Example 8 was manufactured via independent preparation of
5 the polymer emulsion and the AP emulsion, in analogous
manner to Examples 3 and 4, followed by mixing of these
emulsions with additional DC245 in the required amounts
(polymer emulsion: ACH emulsion: DC245 = 18.3: 55: 26.7).

Claims

1. A w/o emulsion antiperspirant composition comprising a dissolved antiperspirant salt, an emulsifier and, in a disperse phase separate from the dissolved antiperspirant salt, a polymer comprising Brønsted acid groups.
5
2. An antiperspirant composition according to claim 1, wherein the polymer comprising Brønsted acid groups is suspended as a solid in an oil continuous phase.
10
3. An antiperspirant composition according to claim 1, comprising an aqueous solution of the polymer comprising Brønsted acid groups emulsified as a separate dispersed phase.
15
4. An antiperspirant composition according to any of the preceding claims, comprising a silicone oil.
20
5. An antiperspirant composition according to any of the preceding claims, wherein the emulsifier is a silicone derivative.
- 25 6. An antiperspirant composition according to any of the preceding claims, wherein the emulsifier is present at from 0.4% to 0.6% by weight.
- 30 7. An antiperspirant composition according to claim 2, wherein the level of Brønsted acid groups in the polymer is less than 4 mmole/g.

- 27 -

8. An antiperspirant composition according to any of the preceding claims, wherein the proportion of aqueous dispersed phase(s) within the total composition is from 50% to 90% by weight, excluding any volatile propellant that may be present.
9. A method of reducing perspiration comprising the application to the human body of a w/o emulsion composition comprising a dissolved antiperspirant salt and an emulsifier, and the co-application, from a disperse phase separate from the dissolved antiperspirant salt, of a polymer comprising Brønsted acid groups.
10. A method of manufacture of an antiperspirant composition, said method comprising emulsification of an aqueous solution of an antiperspirant salt in an oil continuous phase, followed by mixing of the emulsion so formed with a separate phase comprising a polymer comprising Brønsted acid groups.

INTERNATIONAL SEARCH REPORT

Intern application No
PCT/EP 03/05471A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/32

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 7 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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | GB 714 551 A (ROHM & HAAS) 1 September 1954 (1954-09-01) the whole document --- | 1-10 |
| A | EP 0 260 030 A (UNILEVER PLC ;UNILEVER NV (NL)) 16 March 1988 (1988-03-16) the whole document --- | 1-10 |
| A | US 6 319 491 B1 (WHIPPLE MICHAEL B) 20 November 2001 (2001-11-20) the whole document --- | 1-10 |
| A | EP 0 812 182 A (UNILEVER PLC ;UNILEVER NV (NL)) 17 December 1997 (1997-12-17) cited in the application the whole document ----- | 1-10 |

 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

12 August 2003

Date of mailing of the international search report

20/08/2003

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

Yon, J-M

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern Application No

PCT/EP 03/05471

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|--|----|------------------|-------------------------|------------------|
| GB 714551 | A | 01-09-1954 | NONE | |
| EP 0260030 | A | 16-03-1988 | AT 81966 T | 15-11-1992 |
| | | | AU 590959 B2 | 23-11-1989 |
| | | | AU 7739487 A | 03-03-1988 |
| | | | BR 8704413 A | 19-04-1988 |
| | | | CA 1296645 C | 03-03-1992 |
| | | | DE 3782479 D1 | 10-12-1992 |
| | | | DE 3782479 T2 | 29-04-1993 |
| | | | EP 0260030 A2 | 16-03-1988 |
| | | | ES 2036576 T3 | 01-06-1993 |
| | | | JP 1797943 C | 12-11-1993 |
| | | | JP 5007364 B | 28-01-1993 |
| | | | JP 63068518 A | 28-03-1988 |
| | | | ZA 8706402 A | 26-04-1989 |
| US 6319491 | B1 | 20-11-2001 | NONE | |
| EP 0812182 | A | 17-12-1997 | AU 716526 B2 | 24-02-2000 |
| | | | AU 4432196 A | 27-08-1996 |
| | | | BR 9510451 A | 19-05-1998 |
| | | | DE 69520235 D1 | 05-04-2001 |
| | | | DE 69520235 T2 | 21-06-2001 |
| | | | EP 0812182 A1 | 17-12-1997 |
| | | | WO 9624326 A1 | 15-08-1996 |
| | | | ZA 9600047 A | 04-07-1997 |