

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 December 2004 (16.12.2004)

PCT

(10) International Publication Number
WO 2004/108105 A1

(51) International Patent Classification⁷: **A61K 7/34**, 7/38

(21) International Application Number:
PCT/US2004/016230

(22) International Filing Date: 21 May 2004 (21.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/448,996 30 May 2003 (30.05.2003) US

(71) Applicant (for all designated States except US): **COLGATE-PALMOLIVE COMPANY** [US/US]; 300 Park Avenue, New York, New York 10022 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **POPOFF, Christine** [US/US]; 7 Marseille Terrace, Morganville, New Jersey 07751 (US).

(74) Agent: **MIANO, Rosemary, M.**; Colgate-Palmolive Company, 909 River Road, P.O. Box 1343, Piscataway, New Jersey 08855 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,

CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, 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, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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.

(54) Title: A CLEAR, LOW VISCOSITY, WATER-IN-OIL EMULSION ANTIPERSPIRANT GEL COMPOSITION

(57) Abstract: The invention is a clear (50 - 250 NTU at 21.0 degrees C), high efficacy liquid gel composition which is a low viscosity (about 5,000- 75,000 centipoise) water-in-oil, elastomer-free emulsion. These liquid gels comprise a glycine containing antiperspirant active with a low metal to chloride ratio in a high water content (> 30 weight % of the formula) internal (aqueous) phase, a copolyol, and a fragrance solubilizer in the external phase. The external (oil) phase of the composition is free of silicone emollients that have a high refractive index (R.I. > 1.4200). The liquid gel antiperspirant/deodorant compositions of this invention comprise a minimum of at least 14 weight % of the active salt.



WO 2004/108105 A1

PATENT COOPERATION TREATY

PCT

h/12

RECEIVED

04 OCT 2004

WIPO

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 7338-00	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/US2004/016230	International filing date (day/month/year) 21/05/2004	(Earliest) Priority Date (day/month/year) 30/05/2003
Applicant COLGATE-PALMOLIVE COMPANY		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box II).

3. ☐ **Unity of**

4. With regard to the **title**

A CLEAR, LOW VISCOSITY, WATER-IN-OIL EMULSION ANTIPERSPIRANT GEL COMPOSITION

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regards to the **drawings**,

- a. the figure of the **drawings** to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b. ☐ none of the figures is to be published with the abstract.

A CLEAR, LOW VISCOSITY, WATER-IN-OIL EMULSION ANTIPERSPIRANT GEL COMPOSITION

FIELD OF THE INVENTION

The present invention is directed to a high efficacy liquid gel composition which is a low viscosity water in oil emulsion (5-75,000 cps at 21 degrees C), is elastomer-free, and which comprises a glycine-complexed antiperspirant active (preferably with a lower metal to chloride ratio) along with a monovalent or divalent ionizable salt and a reduced amounts of glycols and a reduced amount of emulsifiers in the active phase as well as low levels of nonvolatile ingredients in the oil phase. The gel is formulated as clear products having reduced whitening and tack as well as reduced skin irritation.

BACKGROUND OF THE INVENTION

Antiperspirant products are well known in the art. Antiperspirants have appeared in the marketplace in varied dosage forms, such as sticks, soft solids, soft gels, roll-on, aerosols and creams. Generally, these dosage forms include a solution of the active ingredient in a suitable solvent, a suspension of the active ingredient in a non-solvent, or a multiphasic dispersion or emulsion in which a solution of the active ingredient is dispersed in some continuous phase or in which the solubilized active ingredient constitutes a continuous phase.

Of the above-referred-to dosage forms, the stick form is an example of a solid form, and the soft solid and soft gel are thickened forms which may or may not be solid (for example, under some circumstances, gels can flow). The stick form can be distinguished from a soft solid or soft gel in that, in a stick, the formulated product can retain its shape for extended time periods outside the package, the product not losing its shape significantly (allowing for some shrinkage due to solvent evaporation). Adjustment of amounts of gelling or thickening agents can be used in order to form a soft gel or stick.

Soft gels or soft solids can be suitably packaged in containers which have the appearance of a stick, but which dispense through apertures (for example, slots or pores) on the top surface of the package. The soft solid products have also been called soft sticks or "smooth-ons", and hereinafter are generically called "soft solids". Reference is made to U.S. Patent Number 5,102,656 to Kasat, U.S. Patent Number 5,069,897 to Orr, and U.S. Patent Number 4,937,069 to Shin, each of which discloses such soft solids, including physical characteristics thereof such as viscosity and hardness. The contents of

each of these three U.S. patents are incorporated herein by reference in their entirety for description of characteristics of soft solids and suitable packaging for such products.

Recently, there has been significant activity in developing clear antiperspirant sticks and soft gels, particularly to provide sticks and soft gels having increased efficacy
5 (for example, by providing increased amounts of the antiperspirant active in the sticks and soft gels), improved cosmetic characteristics (including reduced whitening, reduced residue and reduced tack), and reduced skin irritation potential (e.g., providing a product that is "mild").

U.S. Patent Number 4,944,938 to Potini discloses clear, non-alcoholic, quick
10 drying, antiperspirant and deodorant gels, which are stable both at room temperatures and at higher temperatures, are non-stinging and leave no white residue on the skin. The gel is free of gelling agents, waxes, clays, or monohydric alcohols having 2-8 carbon atoms. The gels use 3-5 carbon atom trihydric alcohols as coupling agents which act as solubilizers in the system and keep the system stable and clear. The gels can include an
15 aluminum active salt; a volatile water-insoluble emollient, such as isostearyl benzoate; a soluble emollient such as cetyl ether; solubilizers such as propylene glycol and glycerin; volatile siloxanes; and water.

Some cellulosic materials, such as hydroxypropylcellulose, among others, are compatible with polyvalent metal salts and have been used in the manufacture of clear
20 lotions. These cellulosic materials, however, must be prepared with a high percentage of water or alcohol in order to insure solubilization of the active ingredient. The resulting formulations, in addition to a high irritation potential, are tacky and low in efficacy, when alcohol-based; and exhibit tackiness and long drying time when water-based.

Clear antiperspirant soft gels (which have been dispensed from containers having
25 the appearance of stick) have recently been marketed, consisting of viscous, high-internal-phase emulsions. These soft gels exhibit some advantages over the aforementioned sticks, particularly acetal-based clear sticks, in that the selection of formulation ingredients is less restricted (for example, water can be used), and often tack can be reduced significantly. Concerning these emulsions, note U.S. Patent Number
30 4,673,570 to Soldati and U.S. Patent Number 4,900,542 to Parrotta, et al. These two U.S. patents disclose clear gelled antiperspirant compositions free of waxes and conventional gelling agents, containing a volatile silicone fluid, a silicone emulsifier, a destabilizing

auxiliary emulsifier, water, non-volatile emollient, a coupling agent, an active antiperspirant component and ancillary agents such as perfume, coloring agents, etc. The silicone emulsifiers a cyclomethicone-dimethicone copolyol silicone fluid marketed by Dow Corning Corporation under the trademark DOW CORNING 3225C formulation. In particular, U.S. Patent Number 4,673,570 claim 1 is "from about 10-25% by weight of a cyclomethicone-dimethicone copolysilicone fluid (same as 1.0-2.5% on an actives basis). The contents of these two U.S. patents are incorporated herein by reference in their entirety with respect to the features of the inventions described therein.

Also to be noted is PCT (International application) Publication No. WO 92/05767.

- 10 This patent document discloses a clear gel-type cosmetic product having a viscosity of at least about 50,000 cps at 21 degrees C. and a refractive index of 1.3975-1.4025 at 21 degrees C., and having an optical clarity better than 50 NTU (Nephelometric Turbidity Units) at 21 degrees C., the product being an emulsion with a water phase having an active ingredient incorporated therein and with an oil phase. The refractive indices (measured at 5893 Angstroms) of the water and oil phases match to within 0.0004. The oil phase includes an emulsifier which when properly mixed with the water phase component yields a water-in-oil emulsion, and the water phase includes one or a combination of various polar species such as water, propylene glycol, sorbitol and ethanol. The water phase includes the deodorant and/or antiperspirant active ingredient.
- 15
- 20 The contents of this PCT (International application) Publication No. 92/05767 are incorporated herein by reference in their entirety.

- U.S. Patent Number 6,007,799, assigned to the same owner as this case, describes clear cosmetic gels that are water-in-oil emulsions and which comprise at least one coupling agent, silicone fluids and an alkoxylated, alkyl substituted silicone surface active agent.
- 25

U.S. Patent Numbers 5,587,153 and 5,863,525 issued to Gillette also describe gel products that (1) contain silicone in the oil phase and (2) does not control the propylene glycol content.

- U.S. Patent Number 5,925,338 issued to Gillette describes a clear gel comprising selected amounts of various types of silicones.
- 30

U.S. Patent Number 6,419,910 assigned to Unilever describes a clear emulsion and gel-type antiperspirant and deodorant composition which comprises a water in oil

emulsion which is essentially free of glycols and low and middle chain alcohols. The composition comprises 25-35% of an oil phase comprising at least one non-volatile ester or at least one nonvolatile silicone wherein at least one oil phase soluble ingredients has a refractive index of about 1.40 to about 1.45. The active phase contains a water soluble,
5 non-simple glycol component which raises the refractive index of the aqueous solution.

U.S. Patent Number 6,410,002 and U.S. Patent Application 2002/10051138 A1 also assigned to Unilever, describes an essentially glycol free clear emulsion and gel-type antiperspirant and deodorant composition in which the water phase further differentiated by containing at least one polymeric ethylene oxide glycol and is essentially free of
10 glycols and low and middle chain alcohols

U.S. Patent Number 6,042,816 describes enhanced efficacy antiperspirant salt compositions containing calcium and an amino acid or a hydroxy acid, methods of making such enhanced efficacy antiperspirant salt compositions, stabilized aqueous solutions of such enhanced efficacy antiperspirant salt compositions, and topical
15 compositions containing such enhanced efficacy antiperspirant salt compositions.

U.S. Patent 6,468,512 assigned to Avon describes a clear antiperspirant/deodorant gel composition. The composition is a water-in-oil emulsion having a viscosity about 7,000 cps to about 25,000 cps and a clarity from about 30 NTU or less. The composition further has an antiperspirant active, water, silicone gelling agent,
20 and one or more silicone oils.

U.S. Patent Number 4,673,570 relates to clear gel compositions having a silicone emulsifier with a viscosity of 600 - 2,000 cps.

U.S. Patent Number 5,393,518 provides an antiperspirant composition having cyclomethicone, Al/Zr tetrahydrochloride, and dimethicone copolyol with a viscosity less
25 than 1000 cps.

U.S. Patent 6,485,716 assigned to the same owner as the present case describes a clear, elastomer-free, gel composition comprising: (a) 0.1-25 weight % of an antiperspirant active having a low metal to chloride ratio in the range of 0.9-1.3: 1; (b) 9-23.95 weight % of one or more volatile silicones having a flash point of 100 degrees C or less; (c) 0.05-0.5 weight % of a silicone surfactant having an HLB value less than or
30 equal to 8; (d) 30-70 weight % water; (e) 0-50 weight % selected water soluble organic solvents; and (f) 0-10 weight % of an emollient; wherein the composition is a liquid gel

having a viscosity in the range of 5-50,000 centipoise and a ratio of oil phase to water phase in the range of 10:90 to 24:76.

U.S. Patent Number 6,500,412 assigned to the same owner as this case describes a non-sticky, clear water-in-oil emulsion comprising: (a) 65-90 weight % of an internal phase comprising 5-35 weight % of an antiperspirant salt (anhydrous basis) having a metal:chloride ratio in the range of 0.9-1.4:1; 5-15 weight % of tripropylene glycol; and 35-70 weight % water; and (b) 10-35 weight % of an external phase comprising 1-40 weight % of a volatile silicone which is not an elastomer; 0.1-5 weight % of a silicone copolyol surfactant; and 0-20 weight % of a nonvolatile silicone which is not an elastomer; wherein the composition is free of (1) C1-5 saturated alcohols, (2) added propylene glycol, (3) elastomer gelling agents, (4) soap gelling agents (5) borate gelling agents, and (6) coupling agents, and wherein all amounts are in % by weight based on the total weight of the composition.

While various cosmetic gel compositions, including antiperspirant and deodorant compositions that are clear are known, it is still desired to provide a cosmetic liquid gel composition (e.g., clear antiperspirant and/or deodorant composition) which has improved efficacy in comparison to other products, especially other commercially available gel products which is due, in part, to its low viscosity (from about 5,000 to about 75,000 cps). It is a further object of the invention to provide products which have (a) reduced whitening, (b) low tack, (c) a quick dry down profile and (d) reduced skin irritation potential relative to commercially available products. It is yet another object of the invention to provide liquid gel antiperspirant/deodorant products which are free of oil soluble high refractive index (> 1.420) emollients (which tend to slow down drying time of the gel composition due to their low volatility). This invention has an oil phase which has a relatively low refractive index, thereby reducing the level of water soluble organic or silicone based refractive index matching agents (such as glycols and other monohydric or polyhydric alcohols, ionizable monovalent or divalent inorganic salts, sugars, esters and amino acids) used to match the refractive index of the water (internal) phase to the oil (external) phase to obtain a clear liquid gel.

SUMMARY OF THE INVENTION

The invention is a clear (50 – 250 NTU at 21.0 degrees C), high efficacy liquid gel composition which is a low viscosity (about 5,000-75,000 centipoise) water-in-oil, elastomer-free emulsion. These liquid gels comprise a glycine containing antiperspirant active with a low metal to chloride ratio in a high water content (> 30 weight % of the formula) internal (aqueous) phase, a copolyol, and a fragrance solubilizer in the external phase. The external (oil) phase of the composition is free of silicone emollients that have a high refractive index ($R.I. > 1.4200$). The liquid gel compositions of this invention can include increased amounts of the cosmetically active ingredient (which must be added in an amount of at least 14 weight %). These cosmetic liquid gels are quick drying due to the combination of low levels of nonvolatile materials in the oil phase and low levels (3.85-10 weight %) of glycols but provided that the amount of propylene glycol should not exceed 7.5 weight %. The overall level of silicone emollients is also controlled and is limited to ≤ 1 weight %. Monovalent or divalent salt is used as refractive index modifying agents in the aqueous phase so as to match the refractive index of the oil phase, thus rendering a clear liquid gel.

The invention is a clear water-in-oil emulsion having an external oil phase and internal water phase wherein:

(I) the oil phase comprises:

- (a) 7.0-23.8 weight % (more particularly 9-20 weight %) of one or more cyclomethicones having a flash point of 100 degrees C or less;
- (b) 0.1-0.5 weight % on an active basis (particularly 0.15-0.3 %) of a silicone surfactant having an HLB value (hydrophilic lipophilic balance) ≤ 8 ;
- (c) 0.1-3.0 weight % of a non-siliconized organic fragrance solubilizer (particularly 0.5-2%) selected from the group consisting of silicone compatible straight or branched hydrocarbons with a molecular weight less than 1000, alkyl substituted phenyl esters with an alkyl carbon chain length between C-1 to C-20, and ethoxylated and or propoxylated ethers with a carbon chain length from C-1 to C-25 and ethoxylation and or propoxylation from 1-10 (for example, a member of the group consisting of hydrogenated polyisobutene (Polyiso 250), C12-15 alkyl benzoate (FINSOLV TN), and PPG-3 myristyl ether (particularly PPG-3 myristyl ether) which can help to solubilize the fragrance oils in

the otherwise all silicone based oil phase and which does not negatively affect the skin feel and dry down characteristics of the composition. Aesthetic skin feel attributes such as wetness, stickiness, and residue have been evaluated by a 10 member trained panel both on the forearm and underarm by rating some of the antiperspirant liquid gels described in this invention along with a commercial gel. Significant differences in performance between some of the formulas described herein and a commercial gel were noted at the 95% confidence level.

(d) 0-1 weight % (particularly 0-.25 weight % or 0.1-1%) of a low refractive index (R.I.< 1.4200 at 21 degrees C) silicone emollients (by definition excluding (a) and (b) of this section) selected from the group consisting of (i) volatile linear polydialkylsiloxanes with a flash point is $\leq$ 100 degrees C (particularly low viscosity dimethicones); (ii) nonvolatile linear polydialkylsiloxanes with a flash point is >100 degrees C; and (iii) silanols (for example dimethiconols such as DC 9023 and DC 1501 from Dow Corning) in which one or two of the alkyl groups of the foregoing materials (i) or (ii) are replaced with a hydroxyl group; (note that combinations of these low refractive index silicone emollients may also be used, however, the maximum level of silicone emollients must still be $\leq$ 1 weight %) (note also that one particular embodiment of the invention is free of volatile linear silicones (e.g. volatile dimethicones) and/or free of non-volatile silicones).

(e) 0-5 weight % fragrance or odor masking component; and

(II) the aqueous phase comprises:

(a) 14-30 weight % on an anhydrous basis (particularly 17-30 weight % and, more particularly, 17-25 weight %) of a glycine containing antiperspirant active salt comprising either aluminum or aluminum and zirconium metals such that (i) if aluminum and zirconium salt is used then the metal/Cl ratio of the salt should be low, such as 0.9 - 1.3:1 (more particularly in the range of 0.9-1.05 : 1); the glycine/Zr ratio should be > 1.2, and Peak-5/Peak-3 should be > 1.0; (ii) if aluminum salt is used then the aluminum to chloride molar ratio should be in the range of 0.5 – 2.5:1; the glycine/Al molar ratio should be in the range of 0.05 – 0.26 :1 (preferably in the range of 0.05 – 0.16 :1); wherein the glycine containing antiperspirant active salt has a pH in the range of 2-4 (when measured in water at a concentration of 15%), is free of any other halide

scavenging material, and has a value of at least .50 for the ratio calculated as:

$$\frac{\text{area of Peak 5}}{\text{total area under Peak 2 + Peak 3 + Peak 4 + Peak 5}}$$

5 (b) 30-70 weight % water (particularly 45-65% and, more particularly, 50-60%);

(c) 3.85-10 weight % (particularly 4-8%) of a water soluble glycol system which comprises at least 0.2% propylene glycol and an additional glycol component selected from the group consisting of ethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; propylene glycol; dipropylene glycol; tripropylene glycol; 1,3
10 propanediol; 2-methyl propanediol; methyl propanediol; 1,6-hexanediol; 1,3 butanediol; 1,4 butanediol; PEG-4 through PEG-600; PPG-9 through PPG-34; neopentyl glycol; trimethylpropanediol; 2,2 dimethyl-1,3propanediol; 2,2,4,4-tetramethyl-1,3-cyclobutanediol; and mixtures thereof in which the amount of propylene glycol does not exceed 7.5 % (particularly not exceeding 5%). (More particular examples of the glycol component
15 include one or more members of the group consisting of propylene glycol, dipropylene glycol, 2-methyl-1, 3 propanediol, methyl propylene glycol, low molecular weight (less than 600) polyethylene glycol and mixtures of any of the foregoing.)

(d) 0.2-4 weight % (particularly 0.8-3 weight %) of a monovalent or divalent ionizable, water-soluble inorganic or organic salts to help increase the refractive index of
20 the active phase and optimize the glycol level. These salts are of the form M_aX_b where $a=1$, or 2 and $b=1$ or 2; M is a member selected from the group consisting of Na^{+1} , Li^{+1} , K^{+1} , Mg^{+2} , Ca^{+2} , Sr^{+2} and Zn^{+2} and X is a member selected from the group consisting of chloride, bromide, iodide, citrate, gluconate, lactate, glycinate, glutamate, ascorbate, aspartate, nitrate, phosphate, hydrogenphosphate, dihydrogenphosphate, formate,
25 malonate, maleate, succinate, carbonate, bicarbonate, sulfate, and hydrogensulfate. Salts of particular utility are NaCl and $ZnCl_2$.

(e) 0-5% of a water soluble carbon based high refractive index (R.I. > 1.4200) agent selected from the group consisting of additional glycine (which is not part of the original salt), glycerin, trimethylglycine ("Betaine,"), alanine, diglycereth-7, triglycereth-
30 7 citrate, glycereth-7 glycolate, glycereth-5 lactate, lauramidopropyl glycerin, glycereth-5 lactate, glycereth-7 glycolate, and glycereth-20 benzoate (Ethox GB-2) (for example, 0.5-3 weight % of a high refractive index agent selected from the group consisting of

diglycereth-7 citrate, glycereth-7 glycolate, glycereth-5 lactate, lauramidopropyl glycerin, glycereth-5 lactate, glycereth-7 glycolate and glycereth-20 benzoate; or, as a second example, 0.5-3 weight % of a high refractive index agent selected from the group consisting of additional glycine (which is not part of the original salt), glycerin,
5 trimethylglycine, and alanine;

(f) 0-10 weight % (particularly 0-4% or 1-5%) of an alcohol having 2-4 carbons (for example, ethanol);

wherein (i) all amounts are based on the weight of the entire composition, (ii) the composition is an emulsion having a viscosity in the range of 5,000-75,000 centipoise
10 (for example, in the range of 10,000-50,000 centipoise), (iii) the composition has a ratio of oil phase to water phase in the range of 10:90 to 24:76, and (iv) the composition is free of elastomers, waxes, borate crosslinkers, soap gelling agents, cellulose, alginates, and secondary water-soluble surfactants having an HLB value ≥ 9 .

Compositions of the invention according to a first aspect of the present invention,
15 various of the foregoing objects are achieved through a low viscosity emulsion having (1) an aqueous phase containing water (or water and a water soluble organic solvent as defined above); the antiperspirant active containing aluminum and zirconium metals having a low M:Cl ratio (0.9 to 1.3 : 1; and at least one monovalent or divalent salt, a combination of propylene glycol and another glycol containing two hydroxy groups or
20 polymeric glycol in which the total level of glycol species does not exceed 10 weight percent; and (2) an oil phase containing a volatile organic or silicone material, and the composition further including (3) a suitable silicone based surfactant such as an alkoxyated, alkyl substituted siloxane surface active agent in an amount of 0.1-0.5 weight % (on an actives basis) which suitable to form a low viscosity liquid gel as
25 described above and (4) a suitable fragrance solubilizer such as myristyl ether which helps to solubilize the fragrance oils in the predominantly silicone based oil phase.

The refractive index of the active phase is matched to the oil phase (comprised of fragrance, surfactants, fragrance solubilizers silicones) by adding glycols, monovalent and/or divalent salts and optionally monohydric alcohols such that the refractive index of
30 the active phase differs from the refractive index of the oil phase by an amount of about 0.000 to 0.0040 units. This renders a clear product have an NTU (Nephelometric Turbidity Units) value in the range of between 50 and 250 and an R.I. in the range of

1.4025 to 1.4150. Most preferably the refractive index of the active phase is lower than that of the fragranced oil phase thereby minimizing the level of glycols. If added to the composition, the fragrance oils typically have refractive indices ranging from 1.4450 – 1.4850 and are used typically at levels ranging from 0.50 – 2.0 weight percent. Ionizable
5 monovalent and divalent inorganic salts, antiperspirant salts, water and optional ingredients such as alcohol are optimized to provide a quick drying liquid gel composition.

Refractive index measurements are made at a temperature of about 20-25 degrees C using a Bausch and Lomb Abbe 3L Refractometer. Turbidity measurements as
10 described herein are made with an Orbeco-Hellige #965 Direct-Reading Turbidimeter.

One embodiment of the invention is comprised of an oil phase composition such that the addition of the fragrance component (if fragrance is added to the composition) provides a refractive index in the range from about 1.4015 to about 1.4150; especially from about 1.4025 to about 1.4090.

15 One of the benefits of adding a non-siliconized organic fragrance solubilizer is to improve the solubility of the fragrance within the silicone (primarily cyclomethicones) based oil phase of the liquid gel emulsion. The limited solubility of some fragrances in the cyclomethicone and linear polydialkylorganosiloxanes (if present) is easily determined by the turbidity of the aforementioned silicone(s) when approximately 10-30
20 weight % of fragrance is added to the silicone. To those skilled in the art, it is known that the addition of as little as 5-10 weight % (the amount depending on the fragrance) of the fragrance solubilizers previously described (e.g PPG-3 myristyl ether) to the silicone/fragrance mixture results in a clear solution.

The low viscosity liquid gel compositions of the present invention include an
25 antiperspirant active agent in an amount sufficient to have a deodorizing effect and/or in an amount sufficient to reduce the flow of perspiration when the composition is applied to a human. For the antiperspirant active used in the internal (also called “active”) phase various antiperspirant active materials that can be utilized according to the present invention provided that they are soluble at a suitable concentration in the active phase.

30 Antiperspirant actives can be incorporated into compositions according to the present invention in amounts in the range of 14-30 weight % (on an anhydrous solids basis), particularly 17-25 weight % of the total weight of the composition. Mixtures of

actives can also be used. The amount used will depend on the formulation of the composition. At amounts at the higher end of the range a good antiperspirant effect can be expected. As noted above, the active is preferably included in the compositions of the invention by premixing the active with water and possibly small amount of propylene glycol.

Antiperspirant actives can be incorporated into compositions according to the present invention in amounts as described above. At lower levels the antiperspirant active material may not completely reduce the flow of perspiration, but will reduce malodor, for example, by acting as an antimicrobial material. At amounts of 15 - 25% by weight of the total weight of the composition (on an actives basis), an antiperspirant effect may be observed.

Particularly preferred are antiperspirant actives having the specific low metal to chloride ratio specified above and those described in U.S. Patent Number 6,375,937 and patent application assigned to the same owners as this case (Attorney Docket number IR 6997, U.S. Serial Number 10/314,712 filed 12/9/02).

In one particular type of salt of interest, an aluminum zirconium tetrasalt with glycine is used wherein aluminum zirconium tetrachlorohydrate glycine salt having a metal to chloride ratio in the range of 0.9 to 1.2:1 (especially in the range of 0.9 to 1.1:1 and, more particularly in the range of 0.9 to 1.0:1); and a glycine:zirconium mole ratio greater than 1.2:1, particularly greater than 1.4:1. This type of salt may be made in a variety of ways as described in U.S. Patent 6,375,937 as referenced above.

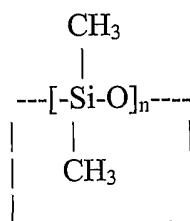
Another particular type of salt of interest is an aluminum chloride salt buffered by glycine, wherein the salt has a metal to chloride ratio in the range of 0.9 to 1.2:1 (especially in the range of 0.9 to 1.1:1 and, more particularly in the range of 0.9 to 1.0:1). Also of interest are salts which include Betaine, additional glycine, or another amino acid such as alanine to further increase the refractive index of the glycine-containing active complex.

Examples of salts include those made as follows:

Method A: An aluminum chlorohydrate (ACH) solution of ACH salt in water of suitable concentration is mixed with an aqueous solution of zirconyl chloride ($ZrOCl_2$) of suitable concentration and powdered glycine. The mixture is stirred at room temperature to obtain the salt.

Method B: A suitable commercially available aluminum zirconium tetrachlorohydrate glycine salt is obtained and mixed with a sufficient amount of an aqueous aluminum chloride (AlCl_3) solution and powdered glycine. The mixture is stirred at room temperature to obtain the salt. When Method B is used, a suitable salt to use as a starting material includes various types of tetra salts such as aluminum zirconium tetrachlorohydrate gly, aluminum zirconium tetrachlorohydrate gly propylene glycol complex, aluminum zirconium tetrachlorohydrate gly dipropylene glycol complex, and mixtures of any of the foregoing. These salts may be referred to hereinafter as experimental salts or carry an "exp" suffix in their designation. It is preferred that the experimental salt be used in the form of a 28-50% water solution when added to form the compositions of the invention.

The cyclomethicones used in this invention are one or more members selected from the group consisting of cyclic polydimethylsiloxanes such as those represented by Formula III:



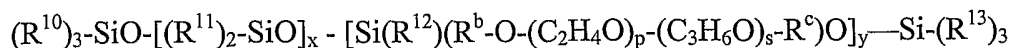
Formula III

where n is an integer with a value of 4-6, particularly 5-6. These include a tetramer (D4), a pentamer (D5), and a hexamer (D6), and mixtures of any two or three of the foregoing. For example, DC-245 fluid and DC-345 from Dow Corning Corporation (Midland, Michigan) are types of cyclomethicones which can be used. It is to be noted that for purposes of the present invention cyclomethicones are not considered as silicone emollients.

Suitable silicone surfactants include silicone polyglucosides (for example, octyl dimethicone ethoxy glucoside) and silicone copolyols having an HLB value (hydrophilic lipophilic balance) ≤ 8 . The HLB value may be measured in a variety of ways such as described in conventional references or found listed in tables of data recording such values. It is intended that any type of HLB measurement technique may be used.

A silicone copolyol (especially dimethicone copolyol) may be used in an amount of 0.1-0.5 weight % (actives basis), particularly 0.15-0.3.

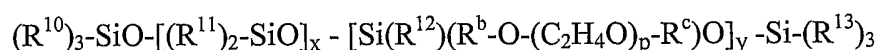
In general, silicone copolyols useful in the present invention include copolyols of the following Formulae I and II. Formula I materials may be represented by:



Formula I

wherein each of R^{10} , R^{11} , R^{12} and R^{13} may be the same or different and each is selected from the group consisting of C1-C6 alkyl; R^b is the radical $-C_mH_{2m}-$; R^c is a terminating radical which can be hydrogen, an alkyl group of one to six carbon atoms, an acyl group such as an ester group with a terminal alkyl group of 1-4 carbons, or an aryl group such as phenyl; m has a value of two to eight; p and s have values such that the oxyalkylene segment $-(C_2H_4O)_p-(C_3H_6O)_s-$ has a molecular weight in the range of 200 to 5,000; the segment preferably having fifty to one hundred mole percent of oxyethylene units $-(C_2H_4O)_p-$ and one to fifty mole percent of oxypropylene units $-(C_3H_6O)_s-$; x has a value of 8 to 400; and y has a value of 2 to 40. Preferably each of R^{10} , R^{11} , R^{12} and R^{13} is a methyl group; R^c is H; m is preferably three or four whereby the group R^b is most preferably the radical $-(CH_2)_3-$; and the values of p and s are such as to provide a molecular weight of the oxyalkylene segment $-(C_2H_4O)_p-(C_3H_6O)_s-$ of between about 1,000 to 3,000. Most preferably p and s should each have a value of about 18 to 28.

A second siloxane polyether (copolyol) has the Formula II:



Formula II

wherein p has a value of 6 to 16; x has a value of 6 to 100; and y has a value of 1 to 20 and the other moieties have the same definition as defined in Formula I.

It should be understood that in both Formulas I and II shown above, that the siloxane-oxyalkylene copolymers of the present invention may, in alternate embodiments, take the form of endblocked polyethers in which the linking group R^b , the oxyalkylene segments, and the terminating radical R^c occupy positions bonded to the ends of the siloxane chain, rather than being bonded to a silicon atom in the siloxane chain. Thus, one or more of the R^{10} , R^{11} , R^{12} and R^{13} substituents which are attached to the two terminal silicon atoms at the end of the siloxane chain can be substituted with the

segment $-R^b-O-(C_2H_4O)_p-(C_3H_6O)_s-R^c$ or with the segment $-R^b-O-(C_2H_4O)_p-R^c$. In some instances, it may be desirable to provide the segment $-R^b-O-(C_2H_4O)_p-(C_3H_6O)_s-R^c$ or the segment $-R^b-O-(C_2H_4O)_p-R^c$ at locations which are in the siloxane chain as well as at locations at one or both of the siloxane chain ends.

5 Particular examples of suitable dimethicone copolyols are available either commercially or experimentally from a variety of suppliers including Dow Corning Corporation, Midland, MI; General Electric Company, Waterford, NY; Witco Corp., Greenwich, CT; and Goldschmidt Chemical Corporation, Hopewell, VA. Examples of specific products include DOW CORNING® 5225C from Dow Corning which is a 10%
10 dimethicone copolyol in cyclomethicone; DOW CORNING® 2-5185C which is a 45-49% dimethicone copolyol in cyclomethicone; SILWET L-7622 from Witco; ABIL EM97 from Goldschmidt which is a 85% dimethicone copolyol in D5 cyclomethicone; and various dimethicone copolyols available either commercially or in the literature.

It should also be noted that various concentrations of the dimethicone copolyols in
15 cyclomethicone can be used. While a concentration of 10% in cyclomethicone is frequently seen commercially, other concentrations can be made by stripping off the cyclomethicone or adding additional cyclomethicone. The higher concentration materials such as DOW CORNING® 2-5185 material is of particular interest.

In one particular embodiment 1-5 weight % (particularly 1.5-3% of a 10 %
20 silicone copolyol such as dimethicone copolyol in cyclomethicone mixture may be used), wherein the amount of mixture added is selected so that the level of silicone copolyol in the cosmetic composition is in the range of 0.1-0.5 % (particularly 0.15-.3%) (for example, 2.5 % of a 10 % dimethicone copolyol in cyclomethicone mixture).

Emollient selection is limited to those which have a relatively low refractive index
25 (R.I. < 1.4200) in order to reduce the refractive index of the oil phase thereby making it easier to match the refractive index of the internal active phase. Emollients are a known class of materials in this art, imparting a soothing effect to the skin. They are ingredients which help to maintain the soft, smooth and pliable appearance of the skin. Emollients are also known to reduce whitening on the skin and/or improve aesthetics. Examples of
30 suitable emollients which meet the low refractive index requirement are limited to silicone-based structures which are absent of phenyl groups.

Preferably linear silicones, are selected from the group consisting of polydialkylsiloxanes represented by the formulae:

(1) $(R^{10})_3SiO(Si(R^{11})_2O)_xSi(R^{12})_3$ where R^{10} , R^{11} and R^{12} can be the same or different and are each independently selected from the group consisting of C1-C10 alkyl (with particular examples being polydimethylsiloxanes (dimethicones), especially low viscosity dimethicones (viscosity <100 cps) (with the R groups and x values being selected to maintain the RI limits);

(2) silanols and/or dimethiconols in which one or two of the alkyl (such as methyl) groups of the foregoing formula may be replaced with a hydroxyl group and is represented by formulae:

$HO(R^{14})_2SiO(Si(R^{15})_2O)_xSi(R^{16})_2OH$ and $R^{17}(R^{14})_2SiO(Si(R^{15})_2O)_xSi(R^{16})_2OH$ where R^{14} , R^{15} and R^{16} and R^{17} can be the same or different and are each independently selected from the group consisting of C1-C10 alkyl (with a particular example being methyl) (with the R groups and x values being selected to maintain the RI limits);

Particular examples of suitable silicone emollients include, but are not limited to, members of the group consisting of dimethicones having a viscosity in the range of 0.5-5.0 centistokes (e.g. Dow Corning® DC 200), dimethiconol (Dow Corning® DC1501), Dow Corning 2501 cosmetic wax (dimethicone copolyol) dimethiconol behenate, C₃₀₋₄₅ alkyl methicone, stearoxytrimethylsilane, and stearyl dimethicone) as well as silanol DC 9023 also from Dow Corning).

The low refractive index emollient or emollient mixture or blend thereof incorporated in compositions according to the present invention can, illustratively, be included in amounts of 0-1 weight % inclusive, preferably 0.5-1 %.

The oil phase according to the present invention is, desirably, a silicone oil phase, so as to provide a water-in-silicone oil emulsion. The total of oil phase and siloxane surface-active agent preferably makes up from about 10% to about 24 % by weight, of the total weight of the composition. This surface-active agent is an emulsifier which, when properly mixed with the aqueous phase components, and oil phase components, yields a water-in-oil emulsion. The oil phase is desirably a blend of liquids, but does not contain any significant amount of non-volatiles (that is, less than 1.0 weight % of any material having a flash point greater than 100 degrees C.). Moreover, the nonvolatile silicone

based emollients described in this composition all have a refractive index lower than 1.420.

The refractive index of the oil phase (including fragrance) is determined, and, if necessary, adjusted to be in the range of 1.4015 to about 1.4150; especially from about 1.4025 to about 1.4090 and the refractive index of the aqueous phase is determined and adjusted (if necessary) to differ from the refractive index of the oil phase by less than 0.0050, preferable less than 0.0030 units. The aqueous phase is then mixed with the oil phase (for example, the aqueous phase is slowly added to the oil phase with turbulent agitation), and then additional additives, or other active ingredients, are added with mixing. Alternatively the fragrance can be added after the active phase is added to the oil phase. In this instance the refractive index of the oil phase (absent of fragrance) and aqueous phase should differ less than 0.0020. The resulting emulsion is then passed through, for example, a colloid mill or other high shear emulsifier so as to provide a liquid gel. The gel then being transferred to a suitable applicator or container for use by the consumer. Desirably, according to the present invention the aqueous phase further includes a glycol mixture consisting of propylene glycol and 2-methyl propanediol and/or dipropylene glycol providing advantages in the final product as discussed previously.

A particular example of an alkoxyated, alkyl substituted siloxane surface active agent is preferably, but not limited to, a dimethicone copolyol. An illustrative alkoxyated silicone-containing surfactant utilizable according to the present invention is cetyl dimethicone copolyol, referred to in U.S. Patent No. 5,162,378 to Guthauser. Illustratively, the alkoxyated, alkyl substituted siloxane surface active agent is included in the composition in an amount of 6.0% to 9.0% by weight, of the total weight of the composition. Another example of a suitable surfactant is octyl dimethicone ethoxy glucoside (from Wacker-Belsil, Adrian, MI).

A specific cyclomethicone-dimethicone copolyol fluid which can be utilized to provide the alkoxyated silicone-containing surface-active agent is a mixture of cyclomethicone and dimethicone copolyol designated as DC 5225C from Dow Corning Corporation. This is a polyether substituted silicone of cyclomethicone and dimethicone copolyol (refractive index (RI)=1.3994) at about 20-25 degrees C. This DC 5225C, which is an emulsifying agent, is useful for preparing stable water-in-oil emulsions where a silicone makes up a large portion of the oil phase, and is a dispersion of a silicone

surfactant (dimethicone copolyol) (10% by wt.) in cyclomethicone (Dow Corning 245) (90% by weight).

The mixture of cyclomethicone and dimethicone copolyol fluid is present in the composition, illustratively, in an amount of from about 7.0% to about 23.8 % by weight, of the total weight of the composition.

According to another aspect of the present invention, the aqueous phase of the clear cosmetic liquid gel composition further includes a glycol system in a low amount (3.85-10 weight % preferably 4-8%) comprising propylene glycol and, preferably, at least one other glycol or polyglycol to help increase the refractive index of the active phase so as to match it within 0.0000 – 0.0040 units (preferably 0.0010-0.0030 units) of the fragranced oil phase. Illustratively, tripropylene glycol can be utilized as the additional polypropylene glycol. According to this aspect of the present invention, propylene glycol can be used in combination with the glycols up to a limited amount. Incorporation of glycols, particularly MP-diol (2-methyl 1,3 propanediol) and dipropylene glycol in the liquid gel composition also improves cosmetic properties, including a reduction of tack and a decrease in the whitening and in the residue after application of the composition. Moreover, compositions incorporating polypropylene glycol, particularly, tripropylene glycol, have improved mildness (that is, reduced skin irritation potential) relative to commercially available products. The glycol or polyglycol is selected from the group consisting of ethylene glycol, propylene glycol, 1,2 propanediol, 2-methyl propanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, methyl propanediol, 1,6-hexanediol, 1,3 butanediol, 1,4 butanediol, PEG-4 through PEG-600, PPG-9 through PPG-34, neopentyl glycol, trimethylpropanediol, 2,2 dimethyl-1,3 propanediol, 2,2,4,4-tetramethyl-1,3-cyclobutane-diol and mixtures thereof. More particular examples of the glycols which can be used with the propylene glycol are one or more members of the group consisting of dipropylene glycol, 2-methyl-1, 3 propanediol, methyl propylene glycol, low molecular weight (less than 600) polyethylene glycol and mixtures of any of the foregoing in which the amount of propylene glycol does not exceed 7.5%.

Clear liquid gel compositions of the invention further include at least one ionizable inorganic salt which helps to increase the refractive index of the active phase and optimize the glycol level. Higher levels of glycols, although good for reducing

tackiness tend to increase dry-down time. These ionizable salts are of the form M_aX_b , where $a=1$, or 2 and $b=1$ or 2; M is a member selected from the group consisting of Na^{+1} , Li^{+1} , K^{+1} , Mg^{+2} , Ca^{+2} , Sr^{+2} and Zn^{+2} and X is a member selected from the group consisting of chloride, bromide, iodide, citrate, gluconate, lactate, glycinate, glutamate, ascorbate, aspartate, nitrate, phosphate, hydrogenphosphate, dihydrogenphosphate, formate, malonate, maleate, succinate, carbonate, bicarbonate, sulfate, hydrogensulfate. Salts of particular utility are NaCl and $ZnCl_2$. As will be appreciated by those skilled in the art, while it may be possible under certain circumstances to add a salt directly to a portion of the mixture during manufacturing, it is preferred to add the salt as a mixture or solution of the salt in a carrier or solvent, particularly water. Of course various concentrations of the salt premix can be made such as in the range of 1-40%.

The present invention also includes methods of forming low viscosity cosmetic liquid gel compositions described herein. In such methods an aqueous phase comprising water and the antiperspirant active is formed separately from the oil phase containing an alkoxyated, alkyl substituted siloxane surface active agent, an organic fragrance solubilizer and cyclomethicone and optional fragrance. The two phases are then combined and homogenized to achieve the desired viscosity.

For one embodiment the active phase is a water phase containing 17-30 weight % (anhydrous) of the low metal:chloride glycine-containing antiperspirant active, 4.05-14 weight % of the water-soluble glycol system with the monovalent or divalent ionizable water-soluble salt. Illustratively, free water is included in the composition in the range of 30-70 weight % based on the total weight of the composition. The water phase can also include, for example, (along with the antiperspirant active, water-soluble glycol system and ionizable divalent or monovalent salt) 1-5 weight % of a water-soluble carbon-based, high refractive index agent (particularly additional glycine (an additional amount that is not part of the original salt), glycerin, alanine and/or Betaine (as defined above, trimethylglycine).

A particular embodiment of the invention comprises:

(a) 17-23 weight % of an oil phase comprising:

- (i) 9--20 weight % of the cyclomethicones;
- (ii) 0.15-0.3 weight % on an active basis of the silicone surfactant;

(iii) 0.5-2 weight % of the fragrance solubilizer;

(iv) 0-0.25 weight % of the low refractive index silicone emollient; and

(b) 77-83 weight % of an aqueous phase comprising:

(i) 17-25 weight % on an anhydrous basis of the antiperspirant active salt;

5 (ii) 4-8% weight % of the water soluble glycol system which comprises at least 0.2% propylene glycol and an additional glycol component selected from the group consisting of dipropylene glycol, tripropylene glycol, 2-methyl 1,3 propanediol, 1,3 propanediol, methyl propylene glycol, low molecular weight polyethylene glycol;

10 (iii) 1-5% ethanol or propanol;

(iv) 0.8-3 weight % of the monovalent or divalent ionizable, water soluble inorganic or organic salt;

wherein the amounts are based on the weight of the entire composition.

15 The compositions of the present invention may be prepared by a batch process, or a continuous or semi-continuous process, and the processes yield compositions which are stable, highly efficacious and possess excellent aesthetic qualities.

The compositions according to the present invention are applied in the same manner as conventional cosmetic liquid gel compositions.

20 As a further aspect of the present invention, the dispensing container can be clear and can be tinted so as to for example, fit to the fragrance hedonics. The composition has reduced tack, quick dry down, a cool sensation, and a silky feel and imparts much less or no white residue on dry down compared to commercially available products. Moreover, compositions of the present invention incorporating a polypropylene glycol component have improved mildness (have reduced skin irritation potential) as compared to
25 commercially available products, and have improved cosmetic properties (including reduced tackiness) and reduced white residue upon application. The liquid gel emulsions according to the present invention are stable and optically clear are cosmetically elegant, and are capable of being delivered from a suitable applicator package.

30 Throughout the present specification, the antiperspirant active materials, when utilized in an antiperspirant effective amount in the composition, act to reduce body malodor by reducing production of perspiration; however, these antiperspirant active materials can also have a deodorant function, e.g., as an antimicrobial agent. The

deodorant active materials do not substantially reduce the production of perspiration, but reduce malodor in other ways, e.g., as fragrances masking the malodor or reducing the malodor intensity, as odor absorbents, as antimicrobial agents, as agents chemically reacted with malodorous materials, etc.

5 The amount of active component that can be used will vary with the particular active ingredient incorporate. The product comprises antiperspirant active materials in amounts sufficient to combat body malodor either as a deodorant or as an antiperspirant when applied to the axillary regions of the body. As a general rule, an antiperspirant product should contain an active antiperspirant material in an amount anywhere from
10 about 9% to about 25% by weight, of the total weight of the composition. However, for the present invention it has been found that a minimum of at least 14 weight % of antiperspirant salt must be used to obtain the clarity desired. The active antiperspirant material utilized in the compositions of the present invention can be pre-dissolved in water or in another solvent (for example, in propylene glycol), and may be buffered or
15 unbuffered. Preferably, the antiperspirant materials are present in solution in a solvent.

Where a deodorant active material is utilized other than lower amounts of an antiperspirant active, any deodorant active material, which can be dissolved in the oil phase, can be utilized in an amount sufficient to have a deodorant effect. Illustratively, the deodorant active material can be 2, 4, 4'-trichloro-2'-hydroxy diphenyl ether
20 (triclosan), and/or benzethonium chloride and/or octoxyglycerin (Sensiva® SC 50). Where the deodorant ingredient is used in place of the antiperspirant active ingredient, a deodorant liquid gel composition (rather than an antiperspirant liquid gel composition) would be provided.

Throughout the present specification, where compositions are described as
25 including or comprising specific components or materials, it is contemplated by the inventors that the compositions of the present invention also consist essentially of, or consist of, the recited components or materials. Accordingly, throughout the present disclosure any described composition of the present invention can consist essentially of, or consist of, the recited components or materials.

30 A desired feature of the present invention is that a clear cosmetic liquid gel composition (e.g., clear deodorant or antiperspirant liquid gel composition) can be provided. The term clear (that is clarity), according to the present invention, is intended to

connote its usual dictionary definition; thus, a clear, e.g., cosmetic liquid gel composition of the present invention allows ready viewing of objects behind it. By contrast, a translucent composition allows light to pass through, but causes the light to be so scattered that it will be impossible to see objects behind the translucent composition.

- 5 Optical clarity of compositions of the present invention can be measured using a turbidimeter as described above, and desirably lies between 50 and 250 NTU measured at room temperature (20°-25° C.).

Moreover, the clear cosmetic liquid gel composition of the present invention, which is in the form of a macro-emulsion as contrasted to a micro-emulsion, does not
10 need to contain wax or gelling agents such as soaps, cellulosic materials or alginates. Furthermore, the composition according to the present invention does not require polydimethylcyclsiloxane, although the present compositions may contain this material.

Various materials incorporated in the water-based phase and in the oil-based phase, and their refractive indices (as measured using the Bausch and Lomb Abbe 3 L
15 Refractometer) are set forth in the following particular formulations:

1.0-5.0 weight % dimethicone copolyol/cyclomethicone (10%) (for example, Dow Corning 5225C);

7-23.8 weight % preferably 8-15 weight percent cyclomethicone (D4, D5, D6 or mixtures thereof);

20 0.1- 3.0 weight % PPG-3 myristyl ether;

17-25 weight % antiperspirant active (for example, Al-Zr tetrachlorohydrate gly (such as Z-522, 27.5% from Summit Research Labs, Huguenot, NY) and aluminum dichlorohydrate (such as Westchlor 100, 36.1% to which glycine has been added so that the molar ratio of gly/Al is in the range of 0.05-0.26:1) such as, for example, described in

25 U.S. Patent Number 6,375,937 and patent application assigned to the same owners as this case (Attorney Docket number IR 6997, U.S. Serial Number 10/314,712 filed 12/9/02);

30 - 70 weight % water;

0.2 to 4.0 weight % of an ionizable salt or combinations of ionizable salts of the form M_aX_b where $a = 1$ or 2 ; $b = 1$ or 2 ; M is a member selected from the group consisting of

30 Na^{+1} , Li^{+1} , K^{+1} , Mg^{+2} , Sr^{+2} and Zn^{+2} , Ca^{+2} and X is a member selected from the group

consisting of chloride, bromide, iodide, citrate, gluconate, lactate, glycinate, glutamate, ascorbate, aspartate, nitrate, phosphate, hydrogenphosphate, dihydrogenphosphate, formate, malonate, maleate, succinate, carbonate, bicarbonate, sulfate and hydrogensulfate (preferred salts are ZnCl_2 and NaCl or combinations thereof);

5 4-8 weight % of the glycol system as described above in the definition of the invention;

0-1 weight % of a low refractive index emollients ($\text{RI} < 1.4200$) such as dimethiconol, dimethicones, silanol and combinations thereof;

0-1.0 weight % sage oil (any type such as Clary or Dalmation);

0-5 weight % fragrance or odor masking component;

10 0-10 % of a water soluble non-glycol organic solvent selected from the group consisting of 2-4 carbon chain alcohols (for example ethanol),

0-5 weight % of a water-soluble carbon based high refractive index agent such as additional glycine which is not part of the original salt, trimethylglycine, alanine, glycerin, Diglycereth-7, Triglycereth-7 citrate, glycereth-7 glycolate, glycereth-5 lactate,

15 lauramidopropyl glycerin, glycereth-5 lactate, Glycereth-7 glycolate, and glycereth-20 benzoate;

wherein the composition has a phase ratio in the range of 10:90 - 25:75 of oil to water and a viscosity is in the range of 5,000-75,000 centipoise.

EXAMPLES

20 The following Examples are offered as illustrative of the invention and are not to be construed as limitations thereon. In the Examples and elsewhere in the description of the invention, chemical symbols and terminology have their usual and customary meanings. In the Examples as elsewhere in this application values for n, m, etc. in formulas, molecular weights and degree of ethoxylation or propoxylation are averages.

25 Temperatures are in degrees C unless otherwise indicated. The amounts of the components are in weight percents based on the standard described; if no other standard is described then the total weight of the composition is to be inferred. Various names of chemical components include those listed in the CTFA International Cosmetic Ingredient Dictionary (Cosmetics, Toiletry and Fragrance Association, Inc., 7th ed. 1997).

30 Refractive Indices ("RI") are determined at a temperature in the range of 20-25 degrees C.

Examples 1-7

For Examples shown in Table A the following procedure may be used with the types and amounts of ingredients. The sample sizes are about 500 grams. Silicone copolyol, cyclomethicone and fragrance are weighed and combined in a beaker. The mixture is stirred at 400-600 rpm using a Lightnin Mixer Model LI003. After the mixture becomes visually homogeneous, the active phase containing the antiperspirant active and ionizable salts in water and the rest of the ingredients (propylene glycol and MP diol) are added to the oil phase while mixing. The entire mixture is mixed for 15 minutes. The mixture is then homogenized for 1-3 minutes at a reading of 40-60 on Powerstat Variable Transformer (Superior Electric Co., Bristol, CT) using a homogenizer from Greerco Corp. (Hudson, NH).

TABLE A

Ingredients (weight %)	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex 6	Ex 7
Cyclomethicone	15.20	15.20	13.90	14.70	13.70	14.0	14.2
Dimethicone copolyol/cyclomethicone (DOW Corning 5225C, (10%))	3.00	3.00	3.50	3.50	3.50	2.4	3.0
Myristyl ether	2.00	2.00	1.80	1.00	2.00	1.80	1.50
Fragrance	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Active A*	69.70	69.70	70.00	70.0	0.00	0.0	0.0
Active A**	0.00	0.00	0.00	0.00	64.6	0.0	0.0
Summit Z 498***	0.00	0.00	0.00	0.00	0.00	0.00	66.5
Westchlor 100****	0.00	0.00	0.00	0.00	0.00	55.00	0.00
glycine	0.00	0.00	0.00	0.00	0.00	1.30	0.00
MP Diol	3.50	3.50	0.30	0.00	0.00	4.00	0.00
Dipropylene glycol	0.00	0.00	0.00	3.55	4.70	3.00	7.0
Water	3.30	2.46	2.70	3.40	7.80	12.30	1.6
Zinc chloride solution (70.5 w/w%)		2.84	2.60	2.75	2.60	2.60	2.60
NaCl (granular)	2.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethanol	0.00	0.00	0.00	0.00	0.00	2.50	2.50
Propylene glycol	0.50	0.50	4.40	0.30	0.30	0.3	0.30

*Al-Zr tetrachlorohydrate glycine complex (EXP Z522, 27.5% in water from Summit Research Labs which is a salt of the type described in Methods A and B above.

** Al-Zr tetrachlorohydrate glycine complex (EXP Z522, 29.3% in water from Summit Research Labs.

*** Al-Zr tetrachlorohydrate glycine complex (29% in water; M:Cl ratio of 1.2 : 1.0 from Summit Research Labs

**** Aluminum dichlorohydrate complex (36% in water from Westwood Chemicals)

CLAIMS

1. The invention is a clear water-in-oil emulsion having an external oil phase and internal water phase wherein:

5 (I) the oil phase comprises:

(a) 7.0-23.8 weight % of one or more cyclomethicones having a flash point of 100 degrees C or less;

(b) 0.1-0.5 weight % on an active basis of a silicone surfactant having a hydrophilic lipophilic balance ≤ 8 ;

10 (c) 0.1-3.0 weight % of a non-siliconized organic fragrance solubilizer selected from the group consisting of silicone compatible straight or branched hydrocarbons with a molecular weight less than 1000, alkyl substituted phenyl esters with an alkyl carbon chain length between C-1 to C-20, and ethoxylated and/or propoxylated ethers with a carbon chain length from C-1 to C-25 and ethoxylation and/or propoxylation from 1-10.

15 (d) 0-1 weight % of a silicone emollient having a refractive index < 1.4200 at 21 degrees C and selected from the group consisting of (i) volatile linear polydialkylsiloxanes with a flash point is ≤ 100 degrees C; (ii) nonvolatile linear polydialkylsiloxanes with a flash point is > 100 degrees C; and (iii) silanols in which one or two of the alkyl groups of the foregoing materials (i) or (ii) are replaced with a
20 hydroxyl group;

(e) 0-5 weight % fragrance or odor masking component; and

(II) the aqueous phase comprises:

(a) 14-30 weight % on an anhydrous basis of a glycine containing antiperspirant active salt comprising either aluminum or aluminum and zirconium metals such that (i) if
25 an aluminum and zirconium salt is used then the metal/Cl ratio of the salt is in the range of 0.9 - 1.3:1; the glycine/Zr ratio is > 1.2 , and Peak-5/Peak-3 is > 1.0 ; (ii) if an aluminum salt is used the aluminum to chloride molar ratio is in the range of 0.5 - 2.5:1; and the glycine/Al molar ratio is in the range of 0.05 - 0.26 :1;

wherein the glycine containing antiperspirant active salt has a pH in the range of 2-4
30 when measured in water at a concentration of 15%, is free of any other halide

scavenging material, and has a value of at least .50 for a ratio calculated as:

$$\frac{\text{area of Peak 5}}{\text{total area under Peak 2 + Peak 3 + Peak 4 + Peak 5}} ;$$

5 (b) 30-70 weight % water;

(c) 3.85-10 weight % of a water soluble glycol system which comprises at least 0.2% propylene glycol and an additional glycol component selected from the group consisting of ethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; propylene glycol; dipropylene glycol; tripropylene glycol; 1,3 propanediol; 2-methyl
10 propanediol; methyl propanediol; 1,6-hexanediol; 1,3 butanediol; 1,4 butanediol; PEG-4 through PEG-600; PPG-9 through PPG-34; neopentyl glycol; trimethylpropanediol; 2,2 dimethyl-1,3propanediol; 2,2,4,4-tetramethyl-1,3-cyclobutane-diol; and mixtures thereof in which the amount of propylene glycol does not exceed 7.5 % ;

(d) 0.2-4 weight % of a monovalent or divalent ionizable, water-soluble
15 inorganic or organic salt of the form M_aX_b where $a=1$, or 2 and $b=1$ or 2; M is a member selected from the group consisting of Na^{+1} , Li^{+1} , K^{+1} , Mg^{+2} , Ca^{+2} , Sr^{+2} and Zn^{+2} and X is a member selected from the group consisting of chloride, bromide, iodide, citrate, gluconate, lactate, glycinate, glutamate, ascorbate, aspartate, nitrate, phosphate, hydrogenphosphate, dihydrogenphosphate, formate, malonate, maleate, succinate,
20 carbonate, bicarbonate, sulfate, and hydrogensulfate;

(e) 0-5% of a water soluble carbon based agent having a refractive index > 1.4200 and selected from the group consisting of additional glycine which is not part of the original salt, glycerin, trimethylglycine, alanine, diglycereth-7, triglycereth-7 citrate, glycereth-7 glycolate, glycereth-5 lactate, lauramidopropyl glycerin, glycereth-5 lactate,
25 glycereth-7 glycolate, and glycereth-20 benzoate; and

(f) 0-10 weight % of an alcohol having 2-4 carbons;

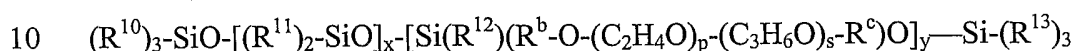
wherein (i) all amounts are based on the weight of the entire composition, (ii) the composition is an emulsion having a viscosity in the range of 5,000-75,000 centipoise, (iii) the composition has a ratio of oil phase to water phase in the range of 10:90 to 24:76,
30 and (iv) the composition is free of elastomers, waxes, borate crosslinkers, soap gelling agents, cellulose, alginates, and secondary water-soluble surfactants having an HLB value ≥ 9 .

2. A clear emulsion according to Claim 1 wherein the clarity of said product is between 50 and 250 NTU at 21 degrees C.
- 5 3. A clear emulsion according to Claim 1 wherein the refractive index of the oil phase is between 1.4025 and 1.4090.
4. A clear emulsion according to Claim 1 wherein the aluminum to chloride molar ratio is in the range of 0.05 – 0.16:1.
- 10 5. A clear emulsion according to Claim 1 comprising 17-25 weight % of the antiperspirant active.
6. A clear emulsion according to Claim 1 wherein the ionizable salt is selected from
15 the group consisting of NaCl and ZnCl₂.
7. A clear emulsion according to Claim 1 wherein the water soluble glycol system is a member selected from the group consisting of propylene glycol; dipropylene glycol; tripropylene glycol; 2-methyl-1,3 propanediol; 1,3 propanediol; methyl propylene glycol;
20 low molecular weight polyethylene glycol; and mixtures of any of the foregoing.
8. A clear emulsion according to Claim 1 wherein the amount of propylene glycol does not exceed 5% .
- 25 9. A clear emulsion according to Claim 1 wherein the water phase includes 1-5 weight % ethanol.
10. A clear emulsion according to Claim 1 additionally comprising 0.5- 3 weight % of a water soluble carbon based high refractive index agent selected from the group
30 consisting of diglycereth-7 citrate, glycereth-7 glycolate, glycereth-5 lactate, lauramidopropyl glycerin, glycereth-5 lactate, glycereth-7 glycolate and glycereth-20 benzoate.

11. A clear emulsion according to Claim 1 additionally comprising 0.5- 3 weight % of a water soluble carbon based high refractive index agent selected from the group consisting of additional glycine (which is not part of the original salt), glycerin,
 5 trimethylglycine and alanine.

12. A clear emulsion according to Claim 1 wherein the silicone surfactant is a silicone copolyol selected from the group consisting of compounds of Formulae I and II wherein:

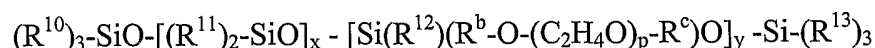
(a) Formula I is:



Formula I

wherein each of R^{10} , R^{11} , R^{12} and R^{13} may be the same or different and each is selected from the group consisting of C1-C6 alkyl; R^b is the radical $-C_mH_{2m-}$; R^c is a terminating radical which is hydrogen, an alkyl group of one to six carbon atoms, an ester group
 15 having a terminating alkyl group of 1-4 carbons, or phenyl; m has a value of two to eight; p and s have values such that oxyalkylene segment $-(C_2H_4O)_p-(C_3H_6O)_s-$ has a molecular weight in the range of 200 to 5,000; the oxyalkylene segment has fifty to one hundred mole percent of oxyethylene units $-(C_2H_4O)_p-$ and one to fifty mole percent of oxypropylene units $-(C_3H_6O)_s-$; x has a value of 8 to 400; and y has a value of 2 to 40;

20 (b) Formula II is:



Formula II

wherein p has a value of 6 to 16; x has a value of 6 to 100; and y has a value of 1 to 20 and the other moieties have the same definition as defined in Formula I; and

25 (c) alternate embodiments of both Formulae I and II wherein the linking group R^b , the oxyalkylene segments, and the terminating radical R^c occupy positions bonded to the ends of the siloxane chain and are not bonded to a silicon atom in the siloxane chain.

13. A clear emulsion according to Claim 1 wherein the non-siliconized organic
 30 fragrance solubilizer is selected from the group consisting of PPG-3 myristyl ether, hydrogenated polyisobutene, and C12-15 alkyl benzoate.

14. A clear emulsion according to Claim 1 additionally comprising 0.1 – 1.0 weight % of the silicone emollient.
15. A clear emulsion according to Claim 1 comprising 0.5 – 2 weight % of the fragrance solubilizer.
16. A clear emulsion according to Claim 1 additionally comprising a fragrance or odor masking component.
17. A clear emulsion according to any one of Claims 1-16 which is free of waxes, cellulose and alginates.
18. A clear emulsion according to Claim 1 comprising:
- (a) 17-23 weight % of an oil phase comprising:
- (i) 9--20 weight % of the cyclomethicones;
- (ii) 0.15-0.3 weight % on an active basis of the silicone surfactant;
- (iii) 0.5-2 weight % of the fragrance solubilizer; and
- (iv) 0-0.25 weight % of the low refractive index silicone emollient; and
- (b) 77-83 weight % of an aqueous phase comprising:
- (i) 17-25 weight % on an anhydrous basis of the antiperspirant active salt;
- (ii) 4-8% weight % of the water soluble glycol system which comprises at least 0.2% propylene glycol and an additional glycol component selected from the group consisting of dipropylene glycol, tripropylene glycol, 2-methyl 1,3 propanediol, 1,3 propanediol, methyl propylene glycol, low molecular weight polyethylene glycol;
- (iii) 1-5% ethanol or propanol; and
- (iv) 0.8-3 weight % of the monovalent or divalent ionizable, water soluble inorganic or organic salt;
- wherein the amounts are based on the weight of the entire composition.
19. A clear emulsion according to Claim 1 comprising 3-7 weight % of propylene glycol in combination with either 2-methyl propane diol or dipropylene glycol.

20. A clear emulsion according to Claim 1 comprising 0.15-0.3 weight % of the silicone surfactant.
21. A clear emulsion according to Claim 1 comprising 45-65 weight % water.
- 5 22. A clear emulsion according to any one of Claims 1-16, or 18-21 which is free of volatile linear silicones and/or free of non-volatile silicones.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/016230

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/34 A61K7/38

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/192172 A1 (MOGHE BHAL ET AL) 19 December 2002 (2002-12-19) examples	1-9
X	US 4 822 602 A (SABATELLI ANTHONY D) 18 April 1989 (1989-04-18) claims; examples	1-9
X	US 2003/031638 A1 (JOSHI VIJAY KUMAR ET AL) 13 February 2003 (2003-02-13) paragraphs '0042!, '0061!, '0065!, '0105!, '0114!, '0119!	1-9
X	US 6 500 412 B1 (BRAHMS JOHN ET AL) 31 December 2002 (2002-12-31) claims; examples	1-9, 12-22
	-/--	

☒ 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.
- *Z* document member of the same patent family

Date of the actual completion of the international search

29 September 2004

Date of mailing of the international search report

06/10/2004

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

Irwin, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/016230

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 403 069 B1 (FEI LIN ET AL) 11 June 2002 (2002-06-11) column 5, line 30 - column 14, line 14; examples -----	1-9, 12-22
A	EP 1 177 784 A (UNILEVER PLC ; UNILEVER NV (NL)) 6 February 2002 (2002-02-06) the whole document -----	1-22

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/016230

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2002192172	A1	19-12-2002	US 6468511 B1	22-10-2002
			AU 6325501 A	03-12-2001
			BR 0110980 A	08-04-2003
			CA 2409274 A1	29-11-2001
			EP 1289481 A2	12-03-2003
			HU 0302282 A2	28-10-2003
			WO 0189465 A2	29-11-2001
			ZA 200209449 A	20-11-2003
US 4822602	A	18-04-1989	NONE	
US 2003031638	A1	13-02-2003	CA 2390824 A1	26-01-2003
			GB 2378653 A ,B	19-02-2003
			ZA 200205749 A	25-07-2003
US 6500412	B1	31-12-2002	WO 03086339 A1	23-10-2003
US 6403069	B1	11-06-2002	BR 0114788 A	12-08-2003
			CA 2426583 A1	08-08-2002
			EP 1326582 A2	16-07-2003
			WO 02060403 A2	08-08-2002
EP 1177784	A	06-02-2002	EP 1177784 A2	06-02-2002
			US 2002037263 A1	28-03-2002