

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 July 2003 (24.07.2003)

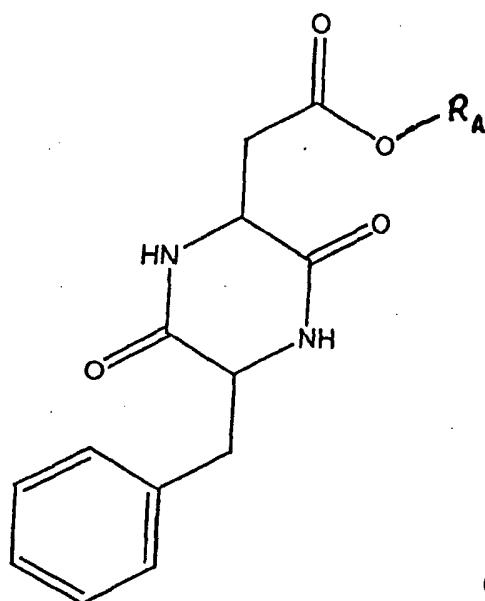
PCT

(10) International Publication Number
WO 03/059307 A1

- (51) International Patent Classification⁷: **A61K 7/32**
- (21) International Application Number: PCT/EP02/14525
- (22) International Filing Date:
19 December 2002 (19.12.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0201164.1 18 January 2002 (18.01.2002) GB
0217840.8 1 August 2002 (01.08.2002) GB
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- (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

[Continued on next page]

(54) Title: COSMETIC COMPOSITIONS COMPRISING A CYCLODIPEPTIDE COMPOUND



(I)

(57) Abstract: Cosmetic formulations containing a cosmetic active and a continuous phase comprising a water-immiscible liquid carrier, such as, amongst other materials, silicone oils, branched aliphatic alcohols or liquid aromatic/aliphatic esters that is structured by a cyclo-dipeptide derivative having the general formula (I) in which RA represents a carbocyclic or heterocyclic group containing not more than 2 rings, other than unsubstituted cyclohexyl.



WO 03/059307 A1



(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, 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, IE, IT, LU, MC, NL, PT, 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.

COSMETIC COMPOSITIONS COMPRISING A CYCLODIPEPTIDE COMPOUND

FIELD OF THE INVENTION

5 The present invention relates to cosmetic compositions for application to human skin, to the preparation and use of such compositions and to structurants for incorporation in such compositions and their preparation.

10 BACKGROUND OF THE INVENTION AND SUMMARY OF PRIOR ART

A wide variety of cosmetic compositions for application to human skin make use of a structured liquid carrier to deliver colour or some other active material to the surface
15 of the skin. Significant examples of such cosmetic compositions include antiperspirant or deodorant compositions which are widely used in order to enable their users to avoid or minimise wet patches on their skin, especially in axillary regions or to control or prevent the
20 emission of malodours, which could otherwise arise when the user perspires. Other examples of cosmetic compositions include lip sticks.

Although structuring is a term that has often been employed
25 in respect of materials which structure a carrier liquid, various other terms have been employed alternatively, including solidifying and gelling.

Antiperspirant or deodorant formulations have been provided
30 with a range of different product forms. One of these is a so-called "stick" which is usually a bar of an apparently

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firm solid material held within a dispensing container and which retains its structural integrity and shape whilst being applied. In that respect they are representative of cosmetic compositions in stick form containing other active constituents. When a portion of the stick is drawn across the skin surface, a film of the stick composition is transferred to the skin surface. Although the stick has the appearance of a solid article capable of retaining its own shape for a period of time, the material often has a structured liquid phase so that a film of the composition is readily transferred from the stick to another surface upon contact.

Antiperspirant sticks can be divided into three categories. Suspension sticks contain a particulate antiperspirant active material suspended in a structured carrier liquid phase which often is anhydrous and/or in many instances may be water-immiscible. Emulsion sticks normally have a hydrophilic phase, commonly containing the antiperspirant active in solution, this phase forming an emulsion with a second, more hydrophobic, liquid phase. The continuous phase of the emulsion is structured. Solution sticks typically have the antiperspirant active dissolved in a structured liquid phase which is polar and may comprise a polar organic solvent, which is often water-miscible, and the polar phase can contain water.

There is substantial literature on structuring of cosmetic compositions, for example as represented by antiperspirant or deodorant compositions.

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Conventionally, many sticks have been structured using naturally-occurring or synthetic waxy materials, in which term we include materials which resemble beeswax, in that they soften progressively with increase in temperature until they are fluid, generally by about 95°C. Examples of wax-structured sticks are described in an article in *Cosmetics and Toiletries*, 1990, Vol 105, P75-78, in US patents 5169626 and 4725432 and in many other publications, in some of which such materials are called solidifying agents.

10

More specifically, it has been common practice for sticks to be structured or solidified by incorporating fatty alcohol into the composition, often accompanied by a smaller amount of castor wax. Sticks which are structured with fatty alcohol tend to leave visible white deposits on application to human skin; moreover the deposits can also transfer onto clothing when it comes into contact with the skin and the wearer can, for example, find white marks at the armhole of the sleeveless garment. Fatty alcohols are often regarded as coming within the general category of waxy materials, but we have observed that they are a more significant source of white deposits than various other waxy materials.

15

20

25

Some alternative structurants or solidifying agents to waxy materials have been proposed. For example, the use of dibenzylidene sorbitol (DBS) or derivatives thereof as gellant for a polar or hydrophylic carrier liquid has been proposed in a number of publications such as EP-A-512770, WO-92/19222, US 4954333, US 4822602 and US 4725430.

30

Formulations containing such gellants can suffer from a number of disadvantages, including instability in the

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presence of acidic antiperspirants, and comparatively high processing temperatures needed in the production of sticks.

Other alternative proposed structurants include various
5 classes of esters or amides that are solid at ambient temperature and are capable of solidifying a hydrophobic or water-immiscible liquid carrier. One such class comprises ester or amide derivatives of 12-hydroxystearic acid, as described in inter alia US-A-5750096. Another class of such
10 esters or amides comprises N-acyl amino acid amides and esters, of which N-Lauroyl-L-glutamic acid di-n-butylamide is commercially available from Ajinomoto under their designation GP-1. They are described in US patent 3969087. A further class which has been disclosed as gelling agents
15 comprises the amide derivatives of di and tribasic carboxylic acids set forth in WO 98/27954 notably alkyl N,N'-dialkyl succinamides. Yet other amide structurants for water-immiscible liquid carriers are described in EP-A-1305604.

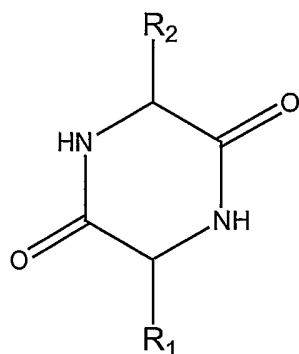
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Although many amido-structurants have been identified already, it remains an objective to locate others which may meet the exacting standards of the cosmetic industry and ameliorate or eliminate one or more of the difficulties or
25 disadvantages associated with the various amido structurants that have already been proposed or used.

One further class of compounds which contain a -CO-NH- group comprises cyclodipeptides, which are cyclic derivatives of
30 aminoacids. Various cyclodipeptides has been described in an article by K Hanabusa et al entitled Cyclo(dipeptide)s as

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low molecular-mass Gelling Agents to harden Organic Fluids, J. Chem Soc. Commun., 1994 pp1401/2. The cyclodipeptides satisfied the general formula



5 in which R_1 and R_2 are designated organic residues. The selection exemplified included two materials (8 and 9) in which R_1 represented alkyl esters, being either $-\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Me}$ or $-\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CHMeCH}_2\text{CH}_2\text{CH}_2\text{CHMe}_2$ and R_2 represented $-\text{CH}_2\text{Ph}$. This paper is herein referred to as
10 Hanabusa I.

In an introductory section, Hanabusa states that the most difficult problem for the development of low molecular mass gelling agents is how to stabilise the formed gel, in other
15 words how to prevent the transformation from the metastable gel to a crystalline state. Having conducted an extensive research programme into gels formed using low molecular mass gellants, the Applicants are able to confirm that the stabilisation of such gels often does indeed represent a
20 serious and difficult problem, and indeed a problem that can be exacerbated in cosmetic compositions by the presence of other cosmetic ingredients. Hanabusa I subsequently makes a general assertion that the formed gels (sic. employing the exemplified cyclodipeptides in the list of organic fluids
25 given in Table 1) were stable even after several months.

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Various other cyclo(dipeptides) satisfying formula 1 above were described in a second article by Hanabusa et al entitled Low Molecular Weight Gelators for Organic Fluids: Gelation using a Family of Cyclo(dipeptide)s, in the
5 Journal of Colloid and Interface Science **224**, 231-244 (2000), herein called Hanabusa II. The text disclosed materials no 22 to 28, which were further esters like those of materials 8 and 9 in Hanabusa I, except that they were derived from different alkanols. Applicants have found that
10 such esters, and in particular 27 and 28 in Hanabusa II, produced gels that were only poorly stable.

Applicants tested a number of materials as gellants in oils that are common in cosmetic formulations in accordance with
15 Formula 1 in Hanabusa I, II-27 and II-28, which seemed to be Hanabusa's best gellants. Unfortunately, the resultant products demonstrated inferior storage characteristics, at laboratory ambient temperatures. Applicants deduced that at best, the capability of cyclodipeptides to gel organic fluid
20 stably could vary significantly, depending on the chemical nature of the substituent residues R_1 and R_2 .

A number of cyclic dipeptide derivatives have been described as gellants in Japanese Kokai No 2001-247451, in the name of
25 Pola Chemical Industries Inc and Nisshin Oil Mills Ltd. These were either alkyl derivatives, which had already been described by Hanabusa or the unsubstituted cyclohexyl derivative which likewise showed inferior stability when tested in the same manner as those proposed by Hanabusa.

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SUMMARY OF THE INVENTION

Applicants have now found that selected cyclodipeptide derivatives can be used as structurants for cosmetic compositions. When used as a modest percentage of the composition, typically not more than 15% by weight and often less than 10% by weight, they are able to structure the composition in a manner that is superior to that achieved by material II-27 and II-28 of Hanabusa. Indeed, at the same time, and where appropriate, the composition can yield a deposit with no worse than a low visible residue. It will be recognised that cyclodipeptide derivatives herein may alternatively be called diketopiperazine derivatives.

It is an object of the present invention to provide structured cosmetic compositions, in which a liquid carrier material is structured using a structuring agent which is different from those mentioned above. A further object of the invention is to provide a structurant which can exhibit a superior property to at least structurants II-27 and II-28 of Hanabusa identified above.

A yet further object of some embodiments of the invention is to provide compositions which exhibit low visible deposits.

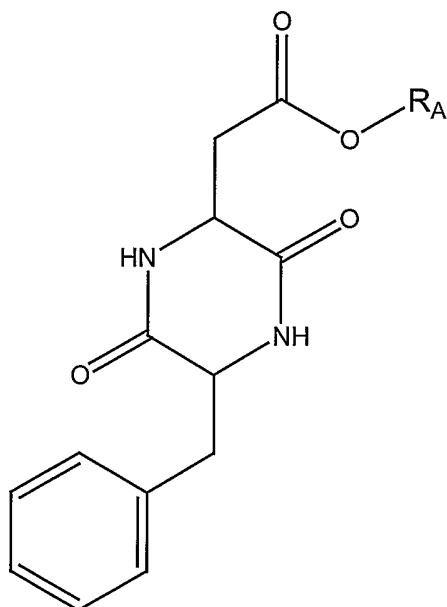
It has been found that the properties of gels in hydrophobic carrier liquids can be improved by esterifying a cyclo(dipeptide) acid with an alcohol producing a cyclic residue.

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Broadly, in a first aspect of the present invention, there is provided a cosmetic composition comprising:

- (i) an antiperspirant active material
- 5 (ii) a continuous phase which comprises water-immiscible liquid carrier, and
- (ii) a structurant therein which comprises a cyclodipeptide derivative having the general formula



- 10 in which R_A represents a carbocyclic or heterocyclic group containing not more than 2 rings, other than unsubstituted cyclohexyl.

Such cyclodipeptide compounds are sometimes referred to
15 herein as DOPA derivatives or DOPAD and the residue containing the cyclodipeptide and the carboxyl group is sometimes called herein a DOPA residue.

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For the avoidance of doubt, in the DOPA derivatives employed herein, the cyclic group within R_A is directly bonded to the DOPA residue.

5 A DOPA derivative as above serves as a structuring agent for the water-immiscible liquid carrier and when used in a sufficient amount, which is likely to be less than 15% of the total composition, is able to structure this liquid into a gel with sufficient rigidity to sustain its own shape.

10

We have observed that the structuring compounds used in this invention form fibres or strands within the liquid phase.

Without being bound to any specific theory or explanation,
15 we believe that upon gel formation a network of such fibres is formed which extends throughout the liquid phase. Upon heating the gel to the gel melting temperature, the strands of structurant dissolve and the liquid phase becomes more mobile.

20

In order to promote good sensory properties at the time of use it is preferred to include a silicone oil as at least a fraction of the water-immiscible carrier liquid. The amount of silicone oil may be at least 10% by weight of the
25 composition and/or at least 25% by weight of the water-immiscible carrier liquid.

Fatty alcohols which are solid at room temperature of 20°C, such as stearyl alcohol, lead to deposits with an opaque
30 white appearance and are preferably substantially absent, by which we mean present in an amount of no more than 3% by

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weight of the composition, more preferably less than 1% and most preferably 0%. As already mentioned, fatty alcohols are often regarded as coming within the general category of waxy materials. More generally the term "wax" is
5 conventionally applied to a variety of materials and mixtures (including some fatty alcohols) which have some diversity in chemical structure but similarity in physical properties. The term generally denotes materials which are solid at 30°C, often also solid up to 40°C, having a waxy
10 appearance or feel, but which gradually soften and eventually melt to a mobile liquid at a temperature below 95°C usually below 90°C.

Possibly the composition does not include more than 3% of
15 any material which is a wax, ie a solid at 30°C but softens at an elevated temperature and at 95°C is molten and soluble in the water-immiscible liquid, yet which is unable to form a network of fibres therein on cooling to 20°C.

20 As will be explained in more detail below, in cosmetic compositions herein, the structured water-immiscible carrier liquid may be the continuous phase in the presence of a dispersed second phase, which may comprise a suspension of particulate solid forming a suspension stick or a dispersion
25 of droplets of a lyophobic liquid. Such a solid may be a particulate antiperspirant or deodorant active or pigment. Such a dispersed liquid phase may comprise a solution of the aforementioned active or actives in water or other hydrophilic ie lyophobic solvent.

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Further advantages of preferred structurant materials of this invention are that the gels they produce are physically more stable, both during processing and in the resultant compositions, by comparison with gellants II-27 and II-28 of Hanabusa.

5 A composition of this invention will generally be marketed in a container by means of which it can be applied at time of use. This container may be of conventional type.

10 A second aspect of the invention therefore provides a cosmetic product comprising a dispensing container having an aperture for delivery of the contents of the container, means for urging the contents of the container through the said aperture, and a composition of the first aspect of the invention in the container.

20 Means for urging the contents of the container to the said aperture or apertures, for flow through them, may be moving parts operable by the user or an orifice in the container opposite the aperture providing digital access.

The compositions of this invention can be produced by conventional processes for making cosmetic solids.

25 Thus, according to a third aspect of the present invention there is provided a process for the production of a cosmetic composition comprising the steps of:

- ai) incorporating into a water-immiscible liquid carrier a structurant which is one or more structurant compounds as defined in the first aspect,

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- a2) mixing the liquid carrier with a solid or a disperse liquid phase comprising cosmetic active in particulate or dissolved form to be suspended in the water-immiscible liquid,
 - 5 • a3) heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is dissolved or dispersed in the water-immiscible liquid carrier,
 - steps a1) a2) and a3) being conducted in any order
- 10 followed by:
- b1) introducing the mixture into a mould which preferably is a dispensing container, and then
 - c1) cooling or permitting the mixture to cool to a temperature at which the liquid carrier is solidified.

15

A suspended solid may be any cosmetic active that is at least partly insoluble in the lyophobic water-immiscible liquid carrier in the amount incorporated therein and a disperse liquid phase may be a solution of such an active in

20 a hydrophilic or polar solvent.

In a fourth aspect of the present invention, the cosmetic active comprises an antiperspirant or deodorant active. According to the fourth aspect, there is provided a cosmetic

25 method for preventing or reducing perspiration or odour formation on human skin comprising topically applying to the skin a composition comprising an antiperspirant or deodorant active, a water-immiscible liquid carrier and a structurant compound as defined above in the first aspect.

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In a fifth aspect of the present invention there are provided novel ester derivatives of DOPA according to the general formula given in the first aspect.

5 In a sixth aspect of the present invention there is provided a process for making the novel esters of the fifth aspect in which DOPA acid is reacted with at least an equimolar amount of an alcohol of formula R_AOH in the presence of at least 0.5 moles of promoter per mole of DOPA acid in a reaction medium
10 comprising dimethyl sulphoxide.

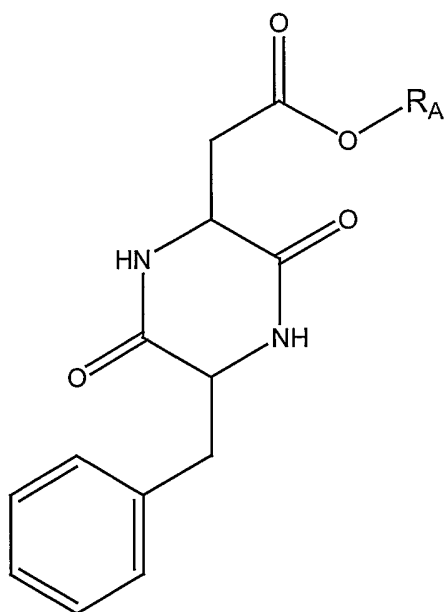
DETAILED DESCRIPTION AND EMBODIMENTS

As mentioned hereinabove, in accordance with the first
15 aspect, the invention requires a structurant compound within a water-immiscible liquid phase. Other materials may also be present depending on the nature of the composition. The various materials will now be discussed by turn and preferred features and possibilities will be indicated.

20

The structurant compounds of the present invention satisfy the general formula:

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in which R_A represents a carbocyclic or heterocyclic group containing not more than 2 rings, other than unsubstituted cyclohexyl.

5

Desirably, the carbocyclic or heterocyclic group in R_A is substituted by at least one alkyl, ether or ester substituent and/or contains at least one degree of ring unsaturation. The ring unsaturation may result in a non-
10 aromatic group, for example comprising 1 or 2 degrees of unsaturation or an aromatic group. Although gels made using the derivative in which R_A represents an unsubstituted cyclohexyl group are relatively unstable during storage under normal storage conditions, stability can be improved
15 by distributing one or more substituents around the cyclohexyl group or by introducing unsaturation or a hetero atom.

Herein, R_A can comprise two fused rings, but preferably
20 comprises a single six membered ring, either carbocyclic or

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heterocyclic, or a bridged ring. When A is carbocyclic, it can be either saturated or unsaturated, preferably unsaturated or aromatic. When R_A is heterocyclic, it is preferably saturated.

5

Although the cyclic group within R_A can be unsubstituted, with the exception of cyclohexyl, it is preferably substituted by at least one alkyl substituent, which preferably contains no more than 16 carbon atoms. In some highly desirable embodiments the alkyl substituent has a longest chain length of up to 4 carbon atoms, and in certain or those a total carbon content of up to 5 carbon atoms. The alkyl substituent may be linear or branched. Preferred examples include methyl, ethyl, propyl, isopropyl, butyl isobutyl or t-butyl or isopentyl. In a number of very suitable DOPA derivatives, R_A contains two or more alkyl substituents and especially those selected from the above list of preferred examples. The alkyl substituents may be the same, such as two or more methyl substituents, or may be a combination of different substituents such as a methyl and isopropyl substituents. When R_A is saturated, the substituents may depend from the same carbon atom in the ring, such as two methyl groups, or from different carbon atoms. In several highly desirable derivatives, two alkyl substituents are meta or para to each other, for example meta methyl groups or a para methyl and isopropyl group. In yet other derivatives, the ring may include a methylene bridge, which preferably likewise completes a six membered ring.

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In some suitable DOPA derivatives, the or one alkyl substituent may be ortho or para to the bond with the DOPA residue, as in 4-methyl-phenyl-. In some or other DOPA derivatives, the bond with the DOPA residue is meta to one
5 or preferably two methyl substituents.

When R_A is heterocyclic, the heterocyclic atom is suitably nitrogen. Conveniently, the heterocyclic atom can be para to the bond with the DOPA residue. Moreover, in a number of
10 desirable derivatives, the heteroatom is ortho to at least one alkyl group, better in a saturated ring and especially to up to 4 ortho methyl groups.

The group R_A is often most easily referred to as the residue
15 from the corresponding alcohol which may be reacted with DOPA to form the ester linkage. Thus, desirable examples of R_A include the residues from 4-alkyl phenol, such as 4-nonyl-phenol, and 2,6-dialkyl- or 2,2,6,6-tetraalkyl-4-piperidinol, such as 2,2,6,6-tetramethyl-4-piperidinol.

20

In some especially preferred DOPA derivatives, the ring in R_A is carbocyclic, and is substituted by at least two alkyl groups of which at least one is methyl and the other or one of the others is isopropyl. Examples of such R_A residues
25 include menthol, thymol, isopinocampheol and 3,5-dialkyl cyclohexanol such as 3,5-dimethyl cyclohexanol. Especially desirably, the methyl group is para to the isopropyl group as in the derivatives from carvacrol. The DOPAD from thymol is particularly suitable, because of its capability to form
30 hard, clear and stable sticks.

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Although many suitable DOPAD compounds described herein are substituted by an alkyl substituent or substituents, at least one of the substituents can itself be ethylinically unsaturated ie comprise an alkenyl group which in many instances contains from 2 to 6 carbons. Suitable examples include isopropenyl and isobutenyl. Such an unsaturated group may be employed instead of the corresponding saturated alkyl group containing the same number of carbon atoms as described hereinabove. One suitable DOPAD compound comprises the derivative from carveol.

In further compositions, the DOPAD compound may be substituted by an ether or ester, particular in respect of aromatic derivatives, such as benzoate esters. Such esters typically contain up to 10 carbons in the ester substituent. Suitable DOPAD groups containing an ester substituent include ethyl benzoate, butyl benzoate, and hexyl benzoate.

The DOPA derivatives used in this invention may be a mixture of compounds within the general formulae given, or may be a single compound.

These DOPA derivatives can be prepared by reacting the respective alcohol with DOPA in acid form (DOPAA), or possibly with an acid chloride, or possibly an anhydride or an ester containing a DOPA residue. DOPAA can be obtained by cyclising aspartame.

The amount of the said DOPA derivatives in a composition of this invention is likely to be from 0.1 to 15% by weight of the whole composition and preferably from 0.1 up to 10%, and

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more commonly at least 0.3% and in many instances not more than 5%. In some especially desirable embodiments, the amount of DOPA structurant is from 0.5% to 3.5%. Herein, unless other wise stated, a % is by weight based on the entire composition. If the composition is an emulsion with a separate disperse phase, the amount of structurant compound(s) is likely to be from 0.15 to 20% by weight of the continuous phase, more likely from 0.4% to 8% of this phase. In some highly desirable embodiments the hydrophobic carrier phase contains from 1.5 to 4.5% by weight based on that phase of the DOPAD. It will be recognised that the invention DOPA structurants are particularly advantageous because they are able to produce hard gels at even low concentrations of structurant. This is beneficial, not only because reduces the cost of the structurant, often a relatively expensive ingredient, but also releases formulation space for incorporating other desirable ingredients in the composition and reduces the amount of ingredient which might contribute to visible deposits. Use of a smaller amount of structurant can also assist during the preparation of gelled compositions, offering more flexibility to the step forming a carrier liquid with well dispersed or dissolved gellant.

25 Carrier liquid

The water-immiscible carrier liquid comprises one or a mixture of materials which are relatively hydrophobic so as to be immiscible in water. Some hydrophilic liquid may be included in the carrier, provided the overall carrier liquid mixture is immiscible with water. It will generally be

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desired that this carrier is liquid (in the absence of
structurant) at temperatures of 15°C and above. It may have
some volatility but its vapour pressure will generally be
less than 4kPa (30 mmHg) at 25°C so that the material can be
5 referred to as an oil or mixture of oils. More
specifically, it is desirable that at least 80% by weight of
the hydrophobic carrier liquid should consist of materials
with a vapour pressure not over this value of 4kPa at 25°C.

10 It is preferred that the hydrophobic carrier material
includes a volatile liquid silicone, i.e. liquid
polyorganosiloxane. To class as "volatile" such material
should have a measurable vapour pressure at 20 or 25°C.
Typically the vapour pressure of a volatile silicone lies in
15 a range from 1 or 10 Pa to 2 kPa at 25°C.

It is desirable to include volatile silicone because it
gives a "drier" feel to the applied film after the
composition is applied to skin.

20

Volatile polyorganosiloxanes can be linear or cyclic or
mixtures thereof. Preferred cyclic siloxanes include
polydimethylsiloxanes and particularly those containing from
3 to 9 silicon atoms and preferably not more than 7 silicon
25 atoms and most preferably from 4 to 6 silicon atoms,
otherwise often referred to as cyclomethicones. Preferred
linear siloxanes include polydimethylsiloxanes containing
from 3 to 9 silicon atoms. The volatile siloxanes normally
by themselves exhibit viscosities of below 10^{-5} m²/sec (10
30 centistokes), and particularly above 10^{-7} m²/sec (0.1

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centistokes), the linear siloxanes normally exhibiting a viscosity of below 5×10^{-6} m²/sec (5 centistokes). The volatile silicones can also comprise branched linear or cyclic siloxanes such as the aforementioned linear or cyclic siloxanes substituted by one or more pendant -O-Si(CH₃)₃ groups. Examples of commercially available silicone oils include oils having grade designations 344, 345, 244, 245 and 246 from Dow Corning Corporation; Silicone 7207 and Silicone 7158 from Union Carbide Corporation; and SF1202 from General Electric.

The hydrophobic carrier employed in compositions herein can alternatively or additionally comprise non-volatile silicone oils, which include polyalkyl siloxanes, polyalkylaryl siloxanes and polyethersiloxane copolymers. These can suitably be selected from dimethicone and dimethicone copolyols. Commercially available non-volatile silicone oils include products available under the trademarks Dow Corning 556 and Dow Corning 200 series. Other non volatile silicone oils include that bearing the trademark DC704. Incorporation of at least some non-volatile silicone oil having a high refractive index such as of above 1.5, eg at least 10% by weight (preferably at least 25% to 100% and particularly from 40 to 80%) of the silicone oils is often beneficial in some compositions, because this renders it easier to match the refractive index of the constituents of the composition and thereby easier to produce transparent or translucent formulations.

The water-immiscible liquid carrier may contain from 0% to 100% by weight of one or more liquid silicones. Preferably,

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there is sufficient liquid silicone to provide at least 10%, better at least 15%, by weight of the whole composition.

Silicon-free hydrophobic liquids can be used instead of, or more preferably in addition to liquid silicones. Silicon-free hydrophobic organic liquids which can be incorporated include liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected to exhibit a low viscosity. Further examples of liquid hydrocarbons are polydecene and paraffins and isoparaffins of at least 10 carbon atoms.

Other suitable hydrophobic carriers comprise liquid aliphatic or aromatic esters. Suitable aliphatic esters contain at least one long chain alkyl group, such as esters derived from C₁ to C₂₀ alkanols esterified with a C₈ to C₂₂ alkanolic acid or C₆ to C₁₀ alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they each have a melting point of below 20°C. These esters include isopropyl myristate, lauryl myristate, isopropyl palmitate, diisopropyl sebacate and diisopropyl adipate.

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl benzoates. Examples of such esters include suitable C₈ to C₁₈ alkyl benzoates or mixtures thereof, including in particular C₁₂ to C₁₅ alkyl benzoates eg those available under the trademark Finsolv. Incorporation of such alkyl benzoate esters as at least a fraction of the hydrophobic carrier liquid can be advantageous, because they can raise the average of

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volatile-silicone-containing carriers, and thereby render it easier to obtain translucent or transparent formulations.

Further instances of suitable hydrophobic carriers comprise
5 liquid aliphatic ethers derived from at least one fatty alcohol, such as myristyl ether derivatives e.g. PPG-3 myristyl ether or lower alkyl ethers of polyglycols such as an ether having named as PPG-14 butyl ether by the CTFA.

10 Aliphatic alcohols which are liquid at 20°C may be employed, and it is especially desirable to employ those which are water-immiscible. These include branched chain alcohols of at least 10 carbon atoms such as isostearyl alcohol and octyl dodecanol. Such alcohols can assist in the process of
15 forming a solution of the DOPA derivatives in a water-immiscible carrier liquid during the manufacture of structured gels. Such alcohols can often constitute from at least 10% or 15% by weight of the water-immiscible liquid carrier mixture, in many desirable mixtures comprising up to
20 70% or 80% of the mixture. In a number of convenient formulations, the proportion of such aliphatic alcohols in said mixture is from 10 or 15% to 30% by weight and in some others, the proportion is greater than 30% by weight.

25 However, aliphatic alcohols which are solid at 20°C, normally linear alcohols, such as stearyl alcohol are preferably absent or present in no more than 3% by weight of the whole composition, as indicated hereinbefore, since they lead to visible white deposits when a composition is
30 topically applied to skin.

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Silicon-free liquids can constitute from 0-100% of the water-immiscible liquid carrier, but it is preferred that silicone oil is present and that the amount of silicon-free constituents preferably constitutes up to 50 or 60% or even up to 80% of water-immiscible carrier liquid and in many instances from 10 to 60% by weight, eg 15 to 30% or 30 to 60% by weight, of the carrier liquid.

Liquid Disperse Phase in emulsions

10

If the composition is an emulsion in which the DOPA derivative acts as a structurant in the hydrophobic continuous phase, the emulsion will contain a more polar or lyophobic disperse phase. The disperse phase may be a solution of an active ingredient.

15

The hydrophilic disperse phase in an emulsion commonly comprises water as solvent and can comprise one or more water soluble or water miscible liquids in addition to or in replacement of water. The proportion of water in an emulsion according to the present invention is often selected in the range of up to 60%, and particularly from 10% up to 40% or 50% of the whole formulation.

20

One class of water soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C₁ to C₄ and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. Ethanol gives a cooling effect on application to skin, because it is very volatile. It is preferred that the content of ethanol or any other monohydric alcohol with a vapour pressure above

30

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1.3kPa (10 mmHg) is not over 15% better not over 8% by weight of the composition.

A further class of hydrophilic liquids comprises diols or polyols preferably having a melting point of below 40°C, or which are water miscible. Examples of water-soluble or water-miscible liquids with at least one free hydroxy group include ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, 2-ethoxyethanol, diethylene glycol monomethylether, triethyleneglycol monomethylether and sorbitol. Especially preferred are propylene glycol and glycerol.

In an emulsion the disperse phase is likely to constitute from 5 to 80 or 85% of the weight of the composition preferably from 5 to 50 or 65% more preferably from 25 or 35% up to 50 or 65%, while the continuous phase with the structurant therein provides the balance from 15 or 35% up to 95% of the weight of the composition. Compositions with high proportion of disperse phase, i.e. from 65 to 85% disperse phase, may be advantageous because they can give good hardness even though the concentration of structurant may be only a small percentage of the total composition. However, compositions with a lower proportion of disperse phase can also be advantageous because they tend to offer a drier and warmer feel.

An emulsion composition will generally include one or more emulsifying surfactants which may be anionic, cationic, zwitterionic and/or nonionic surfactants. The proportion of emulsifier in the composition is often selected in the range

- 25 -

up to 10% by weight and in many instances from 0.1 or 0.25 up to 5% by weight of the composition. Most preferred is an amount from 0.1 or 0.25 up to 3% by weight. Nonionic emulsifiers are frequently classified by HLB value. It is
5 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.

It may be convenient to use a combination of two or more
10 emulsifiers which have different HLB values above and below the desired value. By employing the two emulsifiers together in appropriate ratio, it is readily feasible to attain a weighted average HLB value that promotes the formation of an emulsion.

15

Many suitable emulsifiers of high HLB are nonionic ester or ether emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often containing from about 2 to 80, and especially 5 to 60 oxyethylene units,
20 and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditol as hydrophilic moiety. The hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a hydrophobic alkyl, alkenyl or aralkyl moiety, normally containing from about 8
25 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 is optionally fluorinated. The hydrophobic moiety can comprise a mixture of chain lengths, for example those deriving from
30 tallow, lard, palm oil, sunflower seed oil or soya bean oil. Such nonionic surfactants can also be derived from a

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polyhydroxy compound such as glycerol or sorbitol or other alditols. Examples of emulsifiers include cetareth-10 to 25, ceteth-10-25, steareth-10-25 (i.e. 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 (8 to 12 EO).

10 Examples of emulsifiers, which typically have a low HLB value, often a value from 2 to 6 are fatty acid mono or possibly diesters 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 A particularly desirable class of emulsifiers comprises dimethicone copolymers, namely polyoxyalkylene modified dimethylpolysiloxanes. The polyoxyalkylene group is often a polyoxyethylene (POE) or polyoxypropylene (POP) or a copolymer of POE and POP. The copolymers often terminate in C₁ to C₁₂ alkyl groups.

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

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Cosmetic Actives

The cosmetic actives employable herein can comprise antiperspirant or deodorant actives or pigments.

5 Antiperspirant Actives

The composition preferably contains an antiperspirant active. Antiperspirant actives, are preferably incorporated in an amount of from 0.5-60%, particularly from 5 to 30% or 40% and especially from 5 or 10% to 30 or 35% of the weight
10 of the composition.

Antiperspirant actives for use herein are often selected from astringent active salts, including in particular aluminium, zirconium and mixed aluminium/zirconium salts,
15 including both inorganic salts, salts with organic anions and complexes. Preferred astringent salts include aluminium, zirconium and aluminium/zirconium halides and halohydrate salts, such as chlorohydrates and activated aluminium chlorohydrates.

20

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.
25 Especially effective aluminium halohydrate salts, known as activated aluminium chlorohydrates, are described in EP-A-6739 (Unilever NV et al), the contents of which specification is incorporated herein by reference. Some activated salts do not retain their enhanced activity in the
30 presence of water but are useful in substantially anhydrous

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formulations, i.e. formulations which do not contain a distinct aqueous phase.

Zirconium actives can usually be represented by the empirical
5 general formula: $ZrO(OH)_{2n-nz}B_z \cdot wH_2O$ in which z is a variable in
the range of from 0.9 to 2.0 so that the value $2n-nz$ is zero
or positive, n is the valency of B, and B is selected from the
group consisting of chloride, other halide, sulphamate,
sulphate and mixtures thereof. Possible hydration to a
10 variable extent is represented by wH_2O . Preferable is that B
represents chloride and the variable z lies in the range from
1.5 to 1.87. In practice, such zirconium salts are usually not
employed by themselves, but as a component of a combined
aluminium and zirconium-based antiperspirant.

15

The above aluminium and zirconium salts may have co-
ordinated and/or bound water in various quantities and/or
may be present as polymeric species, mixtures or complexes.
In particular, zirconium hydroxy salts often represent a
20 range of salts having various amounts of the hydroxy group.
Zirconium aluminium chlorohydrate may be particularly
preferred.

Antiperspirant complexes based on the above-mentioned
25 astringent aluminium and/or zirconium salts can be
employed. The complex often employs a compound with a
carboxylate group, and advantageously this is an amino
acid. Examples of suitable amino acids include dl-
tryptophan, dl- β -phenylalanine, dl-valine, dl-methionine
30 and β -alanine, and preferably glycine which has the formula
 $CH_2(NH_2)COOH$.

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It is highly desirable to employ complexes of a combination of aluminium halohydrates and zirconium chlorohydrates together with amino acids such as glycine, which are disclosed in US-A-3792068 (Luedders et al). Certain of those 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 type are available from Westwood, from Summit and from Reheis.

Other actives which may be utilised include astringent titanium salts, for example those described in GB 2299506A.

15

The proportion of solid antiperspirant salt in a suspension composition normally includes the weight of any water of hydration and any complexing agent that may also be present in the solid active. However, when the active salt is incorporated in solution in a hydrophilic solvent such as a glycol, its weight commonly excludes any water present.

20

If the composition is in the form of an emulsion the antiperspirant active will be dissolved in the disperse phase. In this case, the antiperspirant active will often provide from 3 to 60% by weight of the disperse phase, particularly from 10% or 20% up to 55% or 60% of that phase. Alternatively, the composition may take the form of a suspension in which antiperspirant active in particulate form is suspended in the water-immiscible liquid carrier. Such a composition will probably not have any separate

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- 30 -

aqueous phase present and may conveniently be referred to as "substantially anhydrous" although it should be understood that some water may be present bound to the antiperspirant active or as a small amount of solute within the water-immiscible liquid phase. In such compositions, the particle size of the antiperspirant salts often falls within the range of 0.1 to 200 μm with a mean particle size often from 3 to 20 μm . Both larger and smaller mean particle sizes can also be contemplated such as from 20 to 50 μm or 0.1 to 3 μm .

10

Deodorant Actives

Suitable deodorant actives can comprise deodorant effective concentrations of antiperspirant metal salts, deoperfumes, and/or microbicides, including particularly bactericides, such as chlorinated aromatics, including biguanide derivatives, of which materials known as Igasan DP300TM (triclosan), TriclobanTM, and Chlorhexidine warrant specific mention. A yet another class comprises biguanide salts such as are available under the trade mark CosmosilTM. Deodorant actives are commonly employed at a concentration of from 0.1 to 25% by weight.

20

Optional ingredients

Other optional ingredients include wash-off agents, often present in an amount of up to 10% w/w to assist in the removal of the formulation from skin or clothing. Such wash-off agents are typically nonionic surfactants such as esters or ethers containing a C₈ to C₂₂ alkyl moiety and a hydrophilic moiety which can comprise a polyoxyalkylene group (POE or POP) and/or a polyol.

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A further optional constituent of the formulation comprises one or more further structurants which can be employed in addition to the DOPA derivative. Herein, the DOPAD may be the primary structurant, by which is meant that is employed
5 at a concentration that is higher than that of the further structurant. However, in some advantageous embodiments, the further structurant may be present in an amount that is at least that of the DOPAD. In such advantageous embodiments, the DOPAD is acting to moderate the properties of the
10 further structurant such that the properties using the combined structurant system are superior in at least one desirable respect to using the further structurant alone. The amount of such further structurants in the formulation is often from zero to not more than 15% of the formulation.
15 In some instances, the further structurant is present in a weight ratio to the DOPAD of from 10:1 to 1:10.

The further structurants employable herein can be non-polymeric or polymeric. Solid linear fatty alcohol and/or a
20 wax may be included but are not preferred. In anhydrous compositions notably antiperspirants which are suspension sticks, non-polymeric further structurants, sometimes referred to as gellants, can be selected from fatty acids or salts thereof, such as stearic acid or sodium stearate or
25 12-hydroxy stearic acid. Linear fatty acids are preferably not used in aqueous sticks, e.g. aqueous emulsion sticks because they can form insoluble precipitates with aluminium ions. Other suitable gellants can comprise dibenzylidene alditols, e.g. dibenzylidene sorbitol. Further suitable
30 gellants can comprise selected N-acyl amino acid derivatives, including ester and amide derivatives, such as

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N-lauroyl glutamic acid dibutylamide, which gellants can be contemplated in conjunction with 12-hydroxy stearic acid or an ester or amide derivative thereof. Still further gellants include amide derivatives of di or tribasic
5 carboxylic acids, such as alkyl N,N' dialkylsuccinamides, e.g. dodecyl N,N'-dibutylsuccinamide. When employing further structurants comprising N-acyl amino acid derivatives, in some highly desirably formulations their weight ratio to DOPAD is selected in the range of 1:1 to 6:1.

10

Polymeric structurants which can be employed can comprise organo polysiloxane elastomers such as reaction products of a vinyl terminated polysiloxane and a cross linking agent or alkyl or alkyl polyoxyalkylene-terminated poly (methyl
15 substituted) or poly (phenyl substituted) siloxanes. A number of polyamides have also been disclosed as structurants for hydrophobic liquids. Polymers containing both siloxane and hydrogen bonding groups, which might be used as secondary structurants, have been disclosed in
20 WO 97/36572 and WO 99/06473. If an aqueous disperse phase is present, polyacrylamides, polyacrylates or polyalkylene oxides may be used to structure or thicken this aqueous phase.

25 It has also been found that invention formulations can include a dibenzylidene alditol, such as dibenzylidene sorbitol, as additional structurant, possibly in conjunction with an N-acyl amino acid derivative. Desirably, the proportion of the alditol in the formulation is selected in
30 the range of from 0.1 to 0.5% by weight. In such formulations, the weight ratio of DOPAD to the alditol, eg

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dibenzylidene sorbitol, is often selected within the range of 3:1 to 10:1. When an N-acyl amino acid derivative such as GP-1 is also employed, then the weight ratio of DOPAD to alditol is often selected in the range of from about 4:1 to 5 10:1 and the weight ratio of GP-1 or other amino acid derivative to DOPAD is commonly selected in the range of from about 5:2 to 2:3.

10 It is highly desirable that any further structurant employed herein is itself fibre-forming, that is to say forms a fibrous structure within the hydrophobic phase. Most preferably the fibre-forming structurant is one in which the fibrous structure is not visible to the human eye.

15 The compositions herein can incorporate one or more cosmetic adjuncts conventionally contemplatable for cosmetic solids or soft solids. Such cosmetic adjuncts can include skin feel improvers, such as talc or finely divided polyethylene, for example in an amount of up to about 10%; skin benefit 20 agents such as allantoin or lipids, for example in an amount of up to 5%; colours; skin cooling agents other than the already mentioned alcohols, such a menthol and menthol derivatives, often in an amount of up to 2%, all of these percentages being by weight of the composition. A commonly 25 employed adjunct is a perfume, which is normally present at a concentration of from 0 to 4% and in many formulations from 0.25 to 2% by weight of the composition.

Product Form

30 The sticks produced employing the DOPAD structurants can be either opaque or translucent or even transparent, depending

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at least partly on the extent to which the refractive indices (RI) of the appropriate ingredients are matched. Translucent or transparent formulations are possible in respect of the invention formulations because the DOPAD
5 structurant forms a fibrous structure within the liquid hydrophobic carrier that is not seen by the human eye. By matched herein is meant that the difference between the refractive indices is less than 0.005 and preferably less than 0.002. In suspension sticks, to achieve at least
10 translucency, it is necessary to match the RI of the suspended cosmetic active, eg the particulate antiperspirant salt, with the RI of the suspending carrier oil mixture. This can be assisted by a suitable choice of oils, and in particular mixtures containing those having an RI of above
15 1.46, such as from 1.46 to 1.56. In regard to suspended particulates, RI matching can be assisted by two factors. One comprises crushing or grinding the particulates so as to reduce substantially or ideally eliminate hollow spheres which have a different RI, and the second comprises
20 controlling the particle size during the manufacture process or in a subsequent classification process to produce a particle size distribution having no more than a minor fraction in the region of 1 to 10 μM . Matching can be further assisted by modifying the RI of the suspended
25 cosmetic active, such as an aluminium-containing antiperspirant active by post treating it with water (re-hydration) or by retaining a comparatively high water content during the manufacture process. In emulsion formulations, the relevant ingredients to RI match comprise
30 the disperse and continuous liquid phases.

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It is highly desirable to employ RI matching as indicated above in conjunction with the exclusion, to the extent necessary, of additional suspended materials having a different refractive index from the suspending medium, such as for example a suspended filler or additional cosmetic active, to enable the resultant composition to transmit at least 1% light (in the test described hereinafter).

Mechanical Properties and Product Packages

10 The compositions of this invention are structured liquids and are firm in appearance. A composition of this invention will usually be marketed as a product comprising a container with a quantity of the composition therein, where the container has an aperture for the delivery of composition, and means for urging the composition in the container towards the delivery aperture. Conventional containers take the form of a barrel of oval cross section with the delivery aperture at one end of the barrel.

20 A composition of this invention may be sufficiently rigid that it is not apparently deformable by hand pressure and is suitable for use as a stick product in which a quantity of the composition in the form of a stick is accommodated within a container barrel having an open end at which an end portion of the stick of composition is exposed for use. The opposite end of the barrel is often closed.

Generally the container will include a cap for its open end and a component part which is sometimes referred to as an elevator or piston fitting within the barrel and capable of relative axial movement along it. The stick of composition

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is accommodated in the barrel between the piston and the open end of the barrel. The piston is used to urge the stick of composition along the barrel. The piston and stick of composition may be moved axially along the barrel by manual pressure on the underside of the piston using a finger or rod inserted within the barrel. Another possibility is that a rod attached to the piston projects through a slot or slots in the barrel and is used to move the piston and stick. Preferably the container also includes a transport mechanism for moving the piston comprising a threaded rod which extends axially into the stick through a correspondingly threaded aperture in the piston, and means mounted on the barrel for rotating the rod. Conveniently the rod is rotated by means of a hand-wheel mounted on the barrel at its closed end, i.e. the opposite end to the delivery opening.

The component parts of such containers are often made from thermoplastic materials, for example polypropylene or polyethylene. Descriptions of suitable containers, some of which include further features, are found in US patents 4865231, 5000356 and 5573341.

Composition Preparation

Compositions of this invention can be produced by conventional processes for making cosmetic solids. Such processes involve forming a heated mixture of the composition at a temperature which is sufficiently elevated that all the structurant dissolves, pouring that mixture into a mould, which may take the form of a dispensing

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container, and then cooling the mixture whereupon the structurant solidifies into a network of fibres extending through the water-immiscible liquid phase.

5 A convenient process sequence for a composition which is a suspension comprises first forming a solution of the structurant in the water-immiscible liquid or one of the water-immiscible liquids. This is normally carried out by agitating the mixture at a temperature sufficiently high
10 that all the structurant dissolves (the dissolution temperature) such as a temperature in a range from 50 to 140°C. Thereafter, the particulate constituent, for example particulate antiperspirant active, is blended with the hot mixture. This must be done slowly, or the particulate solid
15 must be preheated, in order to avoid premature gelation. The resulting blend is then introduced into a dispensing container such as a stick barrel. This is usually carried out at a temperature 5 to 30°C above the setting temperature of the composition. The container and contents are then
20 cooled to ambient temperature. Cooling may be brought about by nothing more than allowing the container and contents to cool. Cooling may be assisted by blowing ambient or even refrigerated air over the containers and their contents.

25 In a suitable procedure for making emulsion formulations, a solution of the structurant in the water-immiscible liquid phase is prepared at an elevated temperature just as for suspension sticks. If any emulsifier is being used, this is conveniently mixed into this liquid phase. Separately an
30 aqueous or hydrophilic disperse phase is prepared by introduction of antiperspirant active into the liquid part

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of that phase (if this is necessary: antiperspirant actives can sometime be supplied in aqueous solution which can be utilised as is). If possible, this solution of antiperspirant active which will become the disperse phase is preferably heated to a temperature similar to that of the continuous phase with structurant therein, but without exceeding the boiling point of the solution, and then mixed with the continuous phase. Alternatively, the solution is introduced at a rate which maintains the temperature of the mixture. If it is necessary to work at a temperature above the boiling temperature of the disperse phase, or at a temperature where evaporation from this phase is significant, a pressurised apparatus could be used to allow a higher temperature to be reached. With the structurant materials of this invention this is usually unnecessary. After the two phases are mixed, the resulting mixture is filled into dispensing containers, typically at a temperature 5 to 30°C above the setting temperature of the composition, and allowed to cool as described above for suspension sticks.

Many of the cosmetic composition according to the present invention employ a mixture of hydrophobic carrier fluids. In some convenient preparative routes, it is desirable to dissolve the DOPAD structurant in a liquid component of the composition, such as an alcohol, eg an alcoholic carrier fluid, ie, a branched aliphatic alcohol, eg isostearyl alcohol or octyldodecanol, optionally in conjunction with an alcohol having some water-miscibility and boiling point above the dissolution temperature of DOPAD in the alcoholic fluid. This enables the remainder of the carrier fluids to

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avoid being taken to the temperature at which the DOPA dissolves or melts. The proportion of the carrier fluids for dissolving the DOPA is often from 15 to 65% by weight of the carrier fluids, and particularly from 20 to 40%.

5

Structurant Preparation

The DOPA derivatives employed as structurants herein can be made by esterifying DOPA in acid form with the alcohol corresponding to the residue desired in the DOPA derivative.

10

In one convenient precursor step, the DOPA acid (DOPAA) can be made by cyclising aspartame, preferably in the presence of a substantial excess of a low molecular weight aliphatic alcohol, such as isopropanol, under reflux for a long period. Desirably, the alcohol is employed in a weight ratio to aspartame of greater than 50:1 such as up to 100:1, and the reaction is continued for at least 10 hours at reflux temperature, such as from 15 to 24 hours. During the reaction, the aspartame gradually dissolves. On cooling, the resultant solution yields a white powder. Removal of the solvent from the filtrate yields a solid which, after washing with acetone, provides a further amount of the white product, confirmed by a combined yield of the DOPA acid of 79 %.

25

DOPAA can be reacted with the relevant alcohol of formula R_AOH , preferably in a mole ratio to the DOPAA of at least 1:1 to 10:1, particularly from 1.5:1 to 7:1 and especially at least 2:1 in dimethyl sulphoxide, conveniently in a ratio of at least 4:1 (vol:wt), preferably from 6:1 to 12:1, and preferably in the presence of a promoter, such as a

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carbonyldiimidazole, in an amount preferably from 0.5 to 2 moles of promoter per mole of DOPA acid. The reaction is conveniently carried out at a mildly elevated temperature, such as up to 60°C and particularly from 40 to 60°C for a
5 period of at least 6 hours and preferably from 9 to 24 hours. The resultant solution is quenched in excess ambient or cooler water, desirably after the solution has cooled to ambient, a solid precipitates and is filtered off, water washed until no residual diimidazole remained and then can
10 be purified by washing with diethyl ether or toluene, and dried.

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EXAMPLES**Example 1 and Comparisons CA to CI****Preparation of Structurants**

5 These Examples and Comparisons were carried out by the following general method employing (2S-cis)-(-)-5-benzyl-3,6-dioxo-2-piperazine acetic acid (DOPAA) which was reacted with the alcohols and the amounts of reagents and promoter specified in Table 1 below.

10

A 250 ml 3 necked round bottomed flask equipped with a stirrer was charged with (2S-cis)-(-)-5-benzyl-3,6-dioxo-2-piperazine acetic acid (DOPAA), and methyl sulfoxide (8mls per 1g of DOPAA) was then introduced at laboratory ambient
15 temperature (about 22°C) with stirring. The DOPAA dissolved only partially. 1,1'-carbonyldiimidazole was then introduced with stirring in the amount specified in the Table. Vigorous effervescence occurred and the reaction mixture was left stirring at room temperature for 45 minutes
20 after which time the reaction mixture went clear. The specified alcohol was stirred into the clear reaction mixture and maintained at 50°C overnight (between 16 and 20 hours), whereupon it was allowed to cool to ambient temperature (about 22°C), and poured into water, producing a
25 precipitate which was filtered off and washed with further quantities of water until any residual diimidazole had been removed (as shown by ¹Hnmr). The washed precipitate was then washed with diethyl ether, except for CB which was washed with toluene. The washed product was dried in a vacuum oven
30 to constant weight and its melting point determined, the results quoted herein being obtained by DSC with a heating

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rate of 10°C/min, except for those marked ^{ET}, which were obtained using a an Electrothermal 9109 digital melting point measuring apparatus. The purity of certain of the products could be determined by the selected HPLC method,
5 because such derivatives were not elutable.

The DOPAD materials in Examples 1.16 to 1.18 were produced on a smaller scale using a modified reaction method in which the DOPAA was activated with CDI in a single reaction vessel
10 in 125ml DMSO solution. Once activated, this was transferred by volume to a reaction tube in a Radleys'™ 12 place reaction carousel containing the appropriate amount of the chosen alcohol.

15 The purity of DOPAD materials Ex1.1 to Ex 1.19 and CA to CK was measured by reverse phase HPLC with ultraviolet (UV) detection.

A mobile phase was made comprising 300ml aliquot of
20 deionised water, to which was added a 700ml aliquot of HPLC grade acetonitrile and 1.0ml of trifluoroacetic acid (Aldrich spectrophotometric grade, TFA) and mixed thoroughly.

0.001g of CDP sample was weighed into a 2 ml HPLC vial and made up to volume with the mobile phase.

25 The sample was then analysed in a Hewlett Packard HPLC analyser equipped with a Hypersil ODS™ 5µm C₁₈, 250 x 4.6mm @ Room Temp column, a Hewlett-Packard 1050 Series Autosampler and Hewlett-Packard 1050 UV Diode Array @ 210nm Detector. The analysis was carried under the following
30 conditions:-

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Isocratic/gradient : Isocratic
 Flow rate : 1.2ml/minute
 Run time : 5 minutes
 Temperature : Ambient
 5 Injection volume : 20 μ l

Table 1

Ex or Comp	Alcohol	CDI			DOPA		Yield		Purity	MP
		mmol	mmol	mmol	g	%	%	$^{\circ}$ C		
1.1	(1S,2R,5S) - (+) Menthol	18	4.0	3.68	0.75	49	98.7	238		
1.2	Thymol	73.6	16.2	14.7	3.3	56	99.3	212		
1.3	Menthol (racemic)	73.6	16.2	14.7	1.0	17	48.4	216		
1.4	3,5-dimethyl- cyclohexanol	92	22	18.4	1.5	21	94	212		
1.5	2,2,6,6- tetramethyl-4- piperidinol	92	22	18.4	1.2	16	97.8	225		
1.6	1R,2R,3R,5S- (-) -iso- pinocamphenol	92	22	18.4	4.16	55	68	>200		
1.7	Nonylphenol	92	22	18.4	4.07	46	83.6	191		
1.8	(1R,2S,5S) - (-) -Menthol	92	22	18.4	7.72	51	85.9	233		
1.9	4-t-butyl phenol	95.3	22.9	19.1	7.13	94.6	99.1	237		
1.10	4-t-amyl phenol	95.3	22.9	19.1	6.86	87.9	100	211		
1.11	4-isopropyl- phenol	66.3	26.5	22.9	7.31	83.8	99.4	>230		

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1.12	3,5-dimethyl phenol	66.3	26.5	22.9	6.95	83.7	99.6	>200
1.13	butyl-4-hydroxy benzoate	95.4	22.9	19.1	6.96	83.1	98.5	217
1.14	Carveol	95.3	22.9	19.1	4.22	55.7	95.0	215 ^{ET}
1.15	Carvacrol	95.3	22.9	19.1	6.62	87.9	99.1	229 ^{ET}
1.16	5,6,7,8-tetra- hydro naphth-2-ol	18.4	4.6	3.8	1.14	76.5	99.3	220 ^{ET}
1.17	decahydro naphth- 2-ol	19.0	4.6	3.8	0.27	17.8	69.7	189 ^{ET}
1.18	2-isopropoxy- phenol	19.0	4.6	3.8	0.57	37.8	98.8	178 ^{ET}
1.19	Phenol	147.4	35.4	30.5	8.95	87.9	99.7	246
CA	2-ethyl-butanol	165.5	36.4	33.0	7.82	70	94.5	174
CB	3,5,5-tri- methylhexanol	114.5	25.0	22.9	6.51	71	100	121
CC	Oleyl alcohol	92	20	18.4	5.15	67	cnd	143
CD	Cyclohexyl- methanol	92	22	18.4	2.04	30	98.4	187
CE	Cholesterol	121.2	36.3	24.2	3.23	35	100	>210
CF	Norbonane- menthol	92	22	18.4	4.95	68	100	201
CG	(1R) - (-) - Myrentol	92	22	18.4	7.11	65	99.4	160
CH	Cyclohexanol	147.4	35.4	30.5	2.12	20.4	91.4	224
CI	n-dodecanol	95.0	22.8	19.1	6.8	80	99.3	182 ^{ET}
CJ	n-octadecanol	95.3	22.8	19.1	5.11	52	cnd	175 ^{ET}
CK	benzyl alcohol	95.2	22.8	19.1	5.8	87	99.7	222 ^{ET}

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Materials

The materials used in gel studies or the preparation of cosmetic formulations, and their proprietary names, other than the products of Example 1, were as follows:

- 5 1) Isostearyl alcohol (ISA) (Pricerine 3515™ - Unigema)
- 2) C₁₂₋₁₅ alkyl benzoate (Finsolv TN™ from Finetex Inc)
- 3) Octyl dodecanol (Eutanol G™ - Cognis)
- 4) Volatile cyclomethicone (DC 245™ - Dow Corning Inc)
- 5) Hydrogenated Polydecene (Silkflo 364 NF™ - Albemarle)
- 10 6) 1,1,5,5-tetraphenyl trisiloxane (DC704™: Dow Corning Inc)
- 7) N-lauroyl-L-glutamic acid Di-n-butylamide (GP-1™ - Ajinomoto Co Inc)
- 8) Dimethicone Copolyol (Abil EM90™ - Th. Goldschmidt AG)
- 15 9) Al/Zr Tetrachlorohydrate glycine complex (Reach 908™ - Reheis Inc)
- 10) Milled Macrospherical AACH (A418™ - Summit)
- 11) 50% aqueous solution of Al/Zr pentachlorohydrate (Zirconal 50™ - BK Giulini)
- 20 12) Water-modified AZAG, made in house by freeze drying a solution of AZAG (Rezal 67™) and sieving to obtain particulate solid free from hollow particles (~37% of particles <10µm) and water treated to RI =1.526.
- 13) PG5 - Al/Zr pentachlorohydrate glycine complex (BK Giulini) free from hollow particles (~25% particles <10µm) (RI = 1.530)
- 25 14) BMA - Benzyl alcohol - Acros
- 15) DBS - Dibenzylidene sorbitol (Roquette Corp)
- 16) 12-HSA - 12-hydroxystearic acid (CasChem Inc)

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- 17) Rezal 36 GP (solid Al/Zr tetrahydrochlorex glycine salt
from Reheis Inc)
- 18) Reach 908 (solid Al/Zr tetrahydrochlorex glycine salt
from Reheis Inc)
- 5 19) Versamid 930 - polyamide from Cognis
- 20) DDK H18, Silica from Wacker-Chemie GmbH
- 21) HDD H30, silica from Wacker-Chemie GmbH
- 22) HDD H30RX, silica from Wacker-Chemie GmbH
- 23) tri(1,2-propanediol) n-butyl ether (Dowanol TPnB™ from
10 Dow Corning Inc
- 24) propane-1,2-diol from Fisher
- 25) di (propane-1,2-diol) from Acros
- 26) PEG-30 dipolyhydroxystearate (Arlacel P135™ from Uniqema

15 **Example 2 - Structured Gels**

In this Example, gels were made or attempted to be made in a
number of representative organic solvents, having the
refractive index shown in Table 2 below, using the
structurants produced in Example 1 or the comparisons.

20

The gels were prepared in 30ml clear glass bottles. The
solvent and gelling agent were weighed directly into the
bottle to give a total mixture weight of 10g. A small
Teflon stirrer bar was placed in the bottle and the mixture
25 stirred and heated until the cyclo dipeptide had dissolved.
The bottle was then removed from the heat and the solution
allowed to cool and gel under quiescent conditions.

The gel hardness was determined by a skilled assessor of
30 gels using a qualitative assessment by comparison with
standard gels after the gels had been stored at ambient

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temperature for 1 day or 3 days if over a week-end. The clarity was determined by visual assessment by comparison with standards and for some samples, light transmission measurements were made by the general method described in WO 00/61082, incorporated herein by reference. The results are summarised herein in Table 4.

Gel stability was assessed of a number of samples employing the structurant at a concentration of 1.5% by weight by storing them for a long period at ambient temperature (20 to 25°C) and observing the change, if any in their appearance or properties after the stated length of time, which time month. The results are summarised in Table 5.

15

Table 2

Solvent	RI
ISA	1.4559
Finsolv TN	1.4841
Eutanol G	1.4538
50:50 ISA: DC245	1.4278
50:50 ISA: Finsolv TN	1.4700
50:50 ISA : Silkflo 364NF	1.4552
50:50 ISA:DC704	1.5059

Table 3

Transparency		Hardness of gel		Descriptor	
O	Opaque	0	Very soft	G	Gel
t	Translucent	1	Soft	U	Undissolved Solids
T	Transparent	2	Soft/Medium	P	Paste
*	% light	3	Medium	L	Liquids present
	transmitted	4	Medium/Hard	D	Did not dissolve
		5	Hard	nd	not determined
		r	Rubbery		

Table 4

Product of	Ex 1.1		CA		Ex 1.2	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	t,3,G	1.5	T,3,G	1.5	T,5,G
	2.5	t,5,G	2.5	t,5,G		
	5.0	t,5,G				
Finsolv TN	2.5	T,3,G	2.5	t,5,G		
Eutanol G	2.5	t,3,G	2.5	t,3,G		
50:50	1.0	t,2,G	1.0	t,2,G	1.5	T,5,G
ISA: DC245	1.5	t,3,G	1.5	t,3,G		
50:50 ISA:	1.5	T*93,3,G	1.5	t,3,G	1.5	T*83,5,G
Finsolv TN	2.5	t,5,G	2.5	t,5,G		
50:50 ISA :	1.5	t,4,G	1.5	t,3,G	1.5	T*81,5,G
Silkflo 364NF						
50:50	1.5	T*91,5,G			1.5	T,5,G
ISA:DC704						

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Product of	Ex 1.3		Ex 1.4		Ex 1.5	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	t,1,G	1.5	T,3,G	1.5	T,r,G+U
50:50 ISA: DC245	1.5	t,1,G+U	1.5	T,3,G+U	1.5	T,r,G+U
50:50 ISA: Finsolv TN	1.5	t,1,G+U	1.5	T*84,3,G	1.5	T,r,G+U
50:50 ISA : Silkflo 364NF	1.5	t,1,G+U	1.5	T,3,G	1.5	T,r,G+U

Product of	Ex 1.6		Ex 1.7		Ex 1.8	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	T,3,G	1.5	T,3,G	1.5	T,3,G
50:50 ISA: DC245	1.5	t,2,G+U	1.5	O,3,G	1.5	U+L
50:50 ISA: Finsolv TN	1.5	T*68,3,G	1.5	t/O,3,G	1.5	T,3,G
50:50 ISA : Silkflo 364NF	1.5	t,1,G	1.5	O,3,G	1.5	t,3,G

Product of	Ex 1.9		Ex 1.10		Ex 1.11	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	T,3,G	1.5	t,3,G	1.5	T,3,G
50:50 ISA: DC704	1.5	t,3,G	1.5	T,3,G		
25:75 ISA: DC704	1.5	T,3,G	1.5	T,3,G		

Product of	Ex 1.12		Ex 1.13		Ex 1.14	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	T,3,G	1.5	t,3,G	1.5	T,5,G
25:75 ISA: DC704			1.5	t,3,G	1.5	T,4,G
50:50 ISA: Finsolv TN					1.5	t,3,G

Product of	Ex 1.15		Ex 1.16		Ex 1.17	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	t,3,G	1.5	t,3,G	1.5	T,3,G
25:75 ISA: DC704		T,4,G			1.5	T,3,G
50:50 ISA: Finsolv TN		t,3,G				

Product of	Ex 1.18					
	wt%	Result				
ISA	1.5	t,3,G				
25:75 ISA: DC704	1.5	T,2,G				
50:50 ISA: Finsolv TN	1.5	T,3,G				

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Product of	CB		CC		CD	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	t,2,G	1.5	O,0r,G	1.5	O,P
50:50 ISA: DC245	1.5	t,3,G	1.5	T,1,G (leaky)	1.5	U+L
50:50 ISA: Finsolv TN	1.5	t,1,G	1.5	T,1r,G	1.5	O,P
50:50 ISA : Silkflo 364NF	1.5	t,2,G	1.5	T,1r,G	1.5	O,P

Product of	CE		CF		CG	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	U+L	1.5	O,P	1.5	O,P
50:50 ISA: DC245	1.5	U+L	1.5	U+S	1.5	O,P
50:50 ISA: Finsolv TN	1.5	U+L	1.5	O,P	1.5	O,P
50:50 ISA : Silkflo 364NF	1.5	U+L	1.5	U+S	1.5	O,P

Product of	CI		CJ		CK	
	wt%	Result	wt%	Result	wt%	Result
ISA	1.5	L+O,P	1.5	O,P	1.5	O,P
50:50 ISA: DC704	1.5	O,0,g	1.5	O,P	1.5	O,P

5 It will be recognised from the foregoing that the comparison gelators, a number of which have been praised in the prior art, are manifestly inferior to the gelators employed in the instant invention.

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Table 5

Product of	Initial Gel Description	Gel Description after Storage at Room Temperature
Ex 1.1	transparent, medium gels	unchanged after 12 months
Ex 1.2	transparent, hard gels	unchanged after 12 months
Ex 1.3	transparent, soft gels + undissolved solid	unchanged after 12 months
Ex 1.4	transparent, medium gels	unchanged after 12 months
Ex 1.5	transparent, soft, rubbery gels + undissolved solid	DC245 / Finsolv mixture initially started to turn opaque and leak solvent after 1 day, but did not deteriorate after 8 months.
Ex 1.6	translucent, soft/medium gels	unchanged after 12 months
Ex 1.7	transparent/opaque medium gels	slight loss of clarity after 3 months, but no further change in next 9 months.
Ex 1.8	transparent medium gels. No gel with DC245 mixture.	unchanged after 8 months)
Ex1.9	transparent medium gels	unchanged after 6 months

Ex 1.10	transparent/translucent medium gels	unchanged after 6 months
Ex 1.11	transparent medium gel	unchanged after 6 months
Ex 1.12	transparent hard gel	unchanged after 6 months
Ex 1.13	translucent medium gels	unchanged after 6 months
Ex 1.14	transparent medium/hard gels	unchanged after 3 months
Ex 1.15	translucent medium gels	unchanged after 3 months
Ex 1.16	translucent medium gel	unchanged after 2 months (will update)
Ex 1.17	transparent medium gel	unchanged after 2 months (will update)
Ex 1.18	transparent medium gel	unchanged after 1 month (will update)
Ex 1.19	transparent medium or medium hard gel	unchanged after at least 7 months

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Product of	Initial Gel Description	Gel Description after Storage at Room Temperature
CA	transparent/ translucent, soft / medium gels	gels were unsuitable to make sticks because they became very soft and opaque within 2 weeks and leaky within 4 to 6 weeks
CB	translucent, soft/medium gels	gels were unsuitable to make sticks because they became very soft and opaque within 2 weeks and leaky within 4 to 6 weeks
CC	translucent, soft, rubbery gels	gels were unsuitable to make sticks because they became opaque and collapsed within 1 day
CD	opaque pastes or white precipitates in clear solution	not a gel
CE	no gels	not a gel
CF	did not dissolve or precipitated as opaque crystalline slush	not a gel
CG	opaque pastes	not a gel
CH	translucent medium or medium/soft gel	gel became opaque, often within days and collapsed within 1 to 6 weeks

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From Table 4, it can be seen than the invention structurants were able to produce gels in a wide range of representative hydrophobic liquid carrier systems, whereas various related structurants in RA did not satisfy the criteria of the instant invention were not so able. Some comparative structurants produced opaque pastes or simply produced a mixture of undissolved solids plus supernatant liquid.

From Table 5, it can be seen that even those structurants which produced gels initially, such as CA, CB and CC, exhibited poor stability, becoming opaque and soft, followed by leaking, and/or collapsed quickly, whereas those gels produced using structurants according to the present invention were considerably more stable. Many of the invention gels were not showing any discernible change after several months. It will further more be recognised that the invention gellants employing R_A that is unsaturated in the ring or a ring that is substituted by an alkyl ether or ester group is superior to a comparison DOPAD in which R_A represents cyclohexyl. Likewise, it can be seen that the invention DOPADs in which the ring is a direct substituent of the cyclic dipeptide are superior to comparisons in which an unsaturated (phenyl) ring is separated from the cyclic dipeptide by an intervening methylene group.

25

Examples 3 to 6 - Cosmetic Stick Formulations

A number of cosmetic stick compositions were prepared, containing the ingredients specified in Tables 6 and 8 to 10 below. Their properties were measured by the methods described hereinafter and at the times indicated in the summaries.

30

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Example 3 - Opaque Suspension Sticks

In Example 3, opaque sticks were made by dissolving the specified cyclo dipeptide structurant in the liquid alcohol or alcohol mixture, eg isostearyl alcohol whilst with heated
5 and stirring using an overhead paddle stirrer until complete dissolution had occurred. In formulations additionally containing a further structurant, namely GP1 DBS and/or 12-HSA, the latter was dissolved into solution of the cyclo dipeptide structurant at a temperature of about 5 to 10°C
10 lower. The remaining carrier oils were heated to approximately 50°C and stirred using a stirrer bar and the desired solid antiperspirant active was introduced slowly and with gentle stirring into them. When all the active had been added, the mixture was sheared using a Silverson mixer
15 at 7000rpm for 5 minutes to ensure the active was fully dispersed. The active/oil mixture was then heated in an oven to 85°C and mixed into the structurant solution which had been allowed to cool to 90°C. The temperature of the stirred mixture was kept at 85°C until it was poured into
20 conventional commercial 50g stick barrels and allowed to cool except for formulations containing GP1 which were poured at approximately 75°C.

The formulations and properties of the sticks are summarised
25 in Table 6 below.

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Table 6

Example No	Ex 3.1	Ex 3.2	Ex 3.3	Ex 3.4	Ex 3.5
Ingredient	% by weight				
Ex 1.2 Product	2.5	2.5	1.5	1	
Ex 1.6 Product					1.5
GP1			2.5	3.0	2.5
Prisorine 3515	35.75	35.75	30	28.2	30
Finsolv TN	35.75			20.9	
DC704		35.75	40		40
DC245				20.9	
Reach 908	26.0	26.0	26.0	26.0	26.0
Properties					
Hardness (mm)	16.5	15.2	13.8	18.6	14.3
pay-off (g) at t ₀ on WatorDry	0.35	0.25	0.31	0.27	0.3
whiteness t=24hr on WatorDry	13	16	14	27	20
pay-off (g) at t ₀ on wool	0.99	0.63	0.82	0.63	1.08
whiteness t=24hr on wool	17	17	16	15	20

Comparative data for a commercial suspension stick
5 structured using GP1 (GS) and a commercial wax-structured
suspension stick (WS) is given in Table 7 below.

Table 7

Comparison	GS	WS
Hardness (mm)	11.3	10.3
pay-off (g) at t_0 on WatorDry	0.40	0.39
whiteness $t=24hr$ on WatorDry	28	121
pay-off (g) at t_0 on wool	0.61	1.10
whiteness $t=24hr$ on wool	23	110

From Table 7, it can be seen that sticks of acceptable firmness can be obtained using the invention structurants at comparatively low concentrations of the structurant. Moreover, even though suspension sticks that are structured using the invention structurants are a little softer (as measured by a penetrometer) than either the GS or WS sticks and therefore might be expected to suffer from a higher pay-off and higher visible deposits, the pay-off is similar to such sticks and the whiteness is, on balance, lower.

Example 4 - Transparent Suspension Sticks

The sticks in this Example were made using the process of Example 3 together with a preparatory step. In the preparatory step, the RI of the antiperspirant active was first measured using a standard procedure (Becke line test). The proportions of each of the carrier oils were then determined (through calculation and measurement) such that their weight averaged refractive index was closely matched

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to that of the active. The formulations are summarised in Table 8 below.

Table 8

Example No	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4comp
Ingredient	% by weight							
Ex 1.2	1.51	1.5	1.5				1.0	
Ex 1.4				0.70				
Ex 1.7						1.5		
Ex 1.1					1.0			
GP-1		3.0	4.0	4.05	3.5	4.0	3.0	5.0
ISA	18.34	17.61	17.36	17.55	17.61	17.36	16.71	17.49
DC704	55.03	52.89	52.14	52.7	52.89	52.14	54.29	52.51
A418	25.12	25.0	25.0	25.0	25.0	25.0		25.0
AZAG H2							25.0	
Properties								
Hardness (mm)	23	14.7	13.1	16.1	14.8	n/d	16.2	15.9
Clarity (%T)	44	12.7	15.4	12.0	9.9	1.6%	0.7	5.9
Visual Score	8	2	1	3	0	<-12	<-12	-2
pay-off (g) at t. on wool	nd	0.88	0.54	0.92	0.58	n/d	0.83	0.97
whiteness t=24hr on wool	nd	15	17	20	17	n/d	17	13

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Table 8 (cont)

Example No	4.8	4.9	4.10	4.11	4.12	4.13
Ingredients	% by weight					
Ex1.2	2.81		1.5	1.7	1.5	1.5
Ex1.9		3.0				
GP-1			2.0			4.0
DBS			0.25	0.4		
12-HSA					5.0	
ISA	8.81		17.8	18.46	15.51	15.735
DC704	42.36	29.47	53.45	52.48	52.99	53.765
Benzyl Alcohol	8.81	19.68		1.96		
Finsolv TN	12.21	22.83				
A418	25.0	25.0	25.0	25.0	25.0	
P5G						25.0
Properties						
Hardness (mm)	14.0	20.1	13.5	17.2	13.3	12.1
Clarity (% T)	23.0	6.1	19.4	15.3	12.2	2.2
Clarity (visual score)	n/d	n/d	2	3	0	-9

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Table 8 (cont)

Example No	4.14	4.15	4.16	4.17	4.18
Ingredients	% by weight				
Ex1.2	1.7	2.0			
Ex1.14			1.0		
Ex1.15				0.7	
Ex1.16					0.4
GP-1	2.0	2.0	4.0	4.0	4.0
ISA	16.14	17.98	15.848	15.916	15.32
DC704	55.16	51.1	54.152	54.384	53.30
Benzyl Alcohol		1.92			1.98
A418		25.0	25.0	25.0	25.0
P5G	25.0				
Properties					
Hardness (mm)	14.4	14.2	13.7	14.2	16.9
Clarity (% T)	13.2	26.6	27.5	15.0	8.7
Clarity (visual score)	7	6	4	1	0

nd indicates the property was not determined.

- 5 From Table 8, it can be seen that a comparatively soft stick was obtainable using an extremely low concentration of structurant according to the present invention, a stick having excellent clarity. Sticks containing GP-1 as co-structurant were harder, and still retained acceptable
- 10 clarity. Sticks with similar hardness were obtainable with the incorporation of dibenzylidene sorbitol.

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Example 5 - Opaque Emulsion Sticks

In a first step in making opaque emulsion sticks according to the present invention, a solution of the selected invention structurant, and if present GP1, in ISA was made by the same method as in the process for making suspension sticks (Example 3). The remaining water immiscible carrier oils together with an emulsifier, Abil EM 90, were heated to 85°C in an oil bath whilst being shear mixed at 2500 rpm. The solution of antiperspirant active was heated to 80°C and introduced gradually into the oil/emulsifier mixture, and the resultant mixture was kept constant by heating at 85°C and sheared at 7500 rpm for 5 minutes. The emulsion was then mixed into the solution of the structurant solution which had been allowed to cool to ~ 90°C. The resultant mixture was stirred briefly to achieve complete mixing, poured into commercial 50g stick barrels at approximately 80°C and allowed to cool.

The formulations and properties of the sticks are summarised in Table 9 below.

Table 9

Example No	Ex 5.1	Ex 5.2
Ingredient	% by weight	
Ex 1.1 Product	1.5	
Ex 1.2 Product		1.5
GP-1		4
ISA	29.0	27.0
Finsolv TN	29.0	27.0
Zirconal 50	40.0	40.0
Abil EM90	0.5	0.5
Properties		
Hardness (mm)	27.8	17.1
pay-off (g) at t _o on wool	0.66	0.80
whiteness t=24hr on wool	17	18

From Table 9, it can be seen that even though the stick in Example 5.1 was comparatively soft for a stick, it had acceptable pay-off and only a low visible deposit. Visually it was slightly translucent. The somewhat harder stick of Example 5.2 also gave an acceptable pay-off and low visible deposits.

10 **Example 6 - Clear Emulsion Stick**

In this Example, the general method of making emulsion sticks described in Example 5 was followed, preceded by a preparatory step for refractive index matching in order to obtain a translucent emulsion stick.

15

In the preparatory step, the refractive indices of the ingredients of the organic and aqueous phases in the emulsion were obtained or measured, and proportions of those

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ingredients estimated, based on calculation and measurement, such that the two phases had roughly matched refractive indices. The two phases containing the estimated proportions of ingredients were prepared, their refractive indices measured and the proportions of the carrier oils in the continuous (water-immiscible) phase were adjusted to the extent necessary to more closely match the RI of the disperse aqueous phase.

10 The Versamid polymer when employed was dissolved simultaneously with the DOPAD. Any silica was incorporated in suspension in a fraction of the water-immiscible oil(s) and any antiperspirant active supplied as a solid was first dissolved in the specified weight of water.

15

In Examples 6.10 and 6.11, a fraction of ISA (7.4 parts for 6.10 and 5.9 parts for 6.11), all of the DC245 and the Arlacel P135™ were combined in a beaker and warmed to about 40°C to dissolve the Arlacel. The preformed aqueous

20 solution of Reach 908 was then poured into the Arlacel P135 solution while stirring with an overhead mixer. The speed of the mixer was increased to 1500 rpm for two minutes to form an emulsion whereupon the aqueous solution forms the internal phase. The emulsion was covered and warmed to 55-
25 58°C. The DOPAD and the remaining ISA were combined in a beaker together with the propane-1,2-diol, di-(propane-1,2-diol), Dowanol TPnB™ and Finsolv TN™ (as appropriate) and heated to 135-140°C on a hotplate with stirred to dissolve the DOPAD. The hotplate was then removed and the solution
30 allowed to cool to 65-70°C without stirring. The resultant solution was then poured into the emulsion and the mixture

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stirred briefly to ensure complete mixing. The mixture was then poured into a stick barrel and allowed to cool under ambient conditions. The formulation and its properties are summarised in Table 10 below.

5

Table 10

Example No	6.1	6.2	6.3	6.4	6.5	6.6
Ingredients	% by weight					
Ex 1.2	1.5	2.0	2.0	1.5	2.0	2.0
ISA	21.14	12.84	18.51	20.92	43.45	42.66
Finsolv TN	5.71	8.22	5.05	5.65		
DC245	21.14	26.83	20.44	20.93	11.77	11.56
Glycerol	10.0	17.0	10.0	10.0		
Benzyl Alcohol		4.61				
Zirconal 50	40.0	40.0	40.0	40.0		
water					16.52	17.58
Rezal 36GP					24.77	
Reach 908						23.71
Abil EM90	0.5	0.5	1.0	1.0	0.49	0.49
Fragrance					1.0	
Versamid 930						1.0
HDK H30RX						1.0
Properties						
Hardness (mm)	18.6	n/d	13.4	11.9	17.2	14.4
Clarity (% T)	6.7	n/d	n/d	n/d	n/d	42.0
Clarity (visual score)	1	n/d	n/d	n/d	n/d	4
pay-off (g) at t ₀ on wool)	1.39	n/d	n/d	n/d	n/d	n/d

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Example No	6.7	6.8	6.9	6.10	6.11	6.12
Ingredients	% by weight					
Ex 1.2	2.0	2.0	1.5	1.5	1.9	2.0
ISA	41.08	43.05	20.6	21.65	42.7	32.5
Finsolv TN			5.55	3.95		7.4
DC245	11.14	11.67	20.60	21.65	10.6	15.1
Glycerol			10.0	10.0		
propane-1,2- diol					4.6	2.1
di (propane-1,2- diol)						4.1
Dowanol TPnB					4.6	
Zirconal 50			40.0	40.0		
water	17.78	17.78			13.9	14.0
Reach 908	23.71	23.71			20.7	20.8
Abil EM90	0.49	0.49	0.75	0.75		
Arlacel P135					1.0	1.0
Fragrance						1.0
Versamid 930	2.0	1.0	1.0			
HDK H30		0.50				
HDK H30RX	2.0					
HDK H18				0.5		
Properties						
Hardness (mm)	19.9	17.2	14.8	14.7	17.6	17.1
Clarity (% T)	19.0	58.4	0.82	0.74	n/d	n/d
Clarity (visual score)	-1	7	n/d	n/d	n/d	n/d

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Stick Characterisation - Measurement of Properties

i) Stick hardness - Penetrometer

The hardness and rigidity of a composition which is a firm solid can be determined by penetrometry. If the composition
5 is a softer solid, this will be observed as a substantial lack of any resistance to the penetrometer probe.
A suitable procedure is to utilise a lab plant PNT penetrometer equipped with a Seta wax needle (weight 2.5 grams) which has a cone angle at the point of the needle
10 specified to be $9^{\circ}10' \pm 15'$. A sample of the composition with a flat upper surface is used. The needle is lowered onto the surface of the composition and then a penetration hardness measurement is conducted by allowing the needle with its holder to drop under a total weight, (i.e. the combined
15 weight of needle and holder) of 50 grams for a period of five seconds after which the depth of penetration is noted. Desirably the test is carried out at a number of points on each sample and the results are averaged. Utilising a test of this nature, an appropriate hardness for use in an open-
20 ended dispensing container is a penetration of less than 30 mm in this test, for example in a range from 2 to 30 mm. Preferably the penetration is in a range from 5mm to 20 mm.

In a specific protocol for this test measurements on a stick
25 were performed in the stick barrel. The stick was wound up to project from the open end of the barrel, and then cut off to leave a flat, uniform surface. The needle was carefully lowered to the stick surface, and then a penetration hardness measurement was conducted. This process was
30 carried out at six different points on the stick surface.

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The hardness reading quoted is the average value of the 6 measurements.

ii) Deposition by firm sticks (pay-off)

5 Another property of a composition is the amount of it which is delivered onto a surface when the composition is drawn across that surface (representing the application of a stick product to human skin), sometimes called the pay-off. To carry out this test of deposition when the composition is a
10 firm stick, able to sustain its own shape, a sample of the composition with standardised shape and size is fitted to apparatus which draws the sample across a test surface under standardised conditions. The amount transferred to the surface is determined as an increase in the weight of the
15 substrate to which it is applied. If desired the colour, opacity or clarity of the deposit may subsequently be determined. A specific procedure for such tests of deposition and whiteness applicable to a firm solid stick used apparatus to apply a deposit from a stick onto a
20 substrate under standardised conditions and then measures the mean level of white deposits using image analysis.

The substrates used were:

- a: 12 x 28cm strip of grey abrasive paper (3M™ P800
25 WetorDry™ Carborundum paper)
- b: 12 x 28cm strip of black Worsted wool fabric.

The substrates were weighed before use. The sticks were previously unused and with domed top surface unaltered.

30 The apparatus comprised a flat base to which a flat substrate was attached by a clip at each end. A pillar

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having a mounting to receive a standard size stick barrel was mounted on an arm that was moveable horizontally across the substrate by means of a pneumatic piston.

5 Each stick was kept at ambient laboratory temperature overnight before the measurement was made. The stick was advanced to project a measured amount from the barrel. The barrel was then placed in the apparatus and a spring was positioned to biased the stick against the substrate with a
10 standardised force. The apparatus was operated to pass the stick laterally across the substrate eight times. The substrate was carefully removed from the rig and reweighed. The whiteness of the deposit could subsequently be measured as described at (v) below.

15

(iii) Whiteness of Deposit

The deposits from the at test (ii) above, were assessed for their whiteness shortly after application (ie within 30 minutes) or after an interval of 24 hours approximately.

20

This was done using a Sony XC77 monochrome video camera with a Cosmicar 16mm focal length lens positioned vertically above a black table illuminated from a high angle using fluorescent tubes to remove shadowing. The apparatus was
25 initially calibrated using a reference white card, after the fluorescent tubes had been turned on for long enough to give a steady light output. A cloth or Carborundum paper with a deposit thereon from the previous test was placed on the table and the camera was used to capture an image. An area
30 of the image of the deposit was selected and analysed using a Kontron IBAS™ image analyser. This notionally divided the

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image into a large array of pixels and measured the grey level of each pixel on a scale of 0 (black) to 255 (white). The average of the grey intensity was calculated. This was a measure of the whiteness of the deposit, with higher numbers indicating a whiter deposit. It was assumed that low numbers show a clear deposit allowing the substrate colour to be seen.

iv Clarity of formulation - Light transmission

10 The translucency of a composition may be measured by placing a sample of standardised thickness in the light path of a spectrophotometer and measuring transmittance, as a percentage of light transmitted in the absence of the gel.

15 This test was carried out using a dual-beam Perkin Elmer Lambda 40 spectrophotometer. The sample of composition was poured hot into a 4.5 ml cuvette made of poly(methyl-methacrylate) (PMMA) and allowed to cool to an ambient temperature of 20-25°C. Such a cuvette gives a 1 cm
20 thickness of composition. Measurement was carried out at 580 nm, with an identical but empty cuvette in the reference beam of the spectrophotometer, after the sample in the cuvette had been held for 24 hours. A transmittance measured at any temperature in the range from 20-25°C is
25 usually adequately accurate, but measurement is made at 22°C if more precision is required.

v) Clarity of Formulation - Visual assessment score

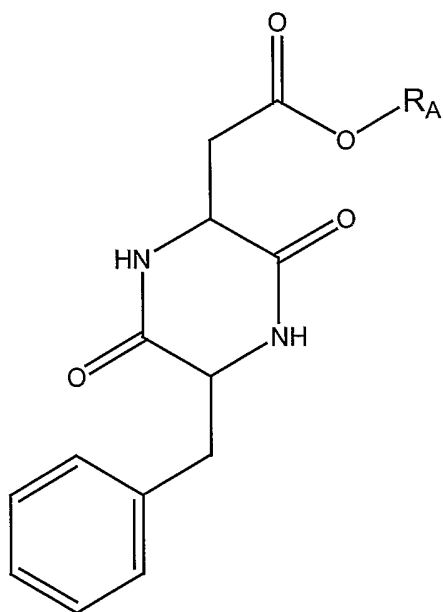
A gel contained within a 1cm thick cuvette was placed
30 directly on to a sheet of white paper on which 21 sets of figures where printed in black. The size and thickness of

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the figures varied systematically and were numbered from -12 (the largest, thickest set) through 0 to 8 (the smallest thinnest set) The score given to each gel was the highest numbered set which could be read clearly through the gel, 5 the higher the number, the higher the clarity.

CLAIMS:

1. An antiperspirant composition comprising:
- i) an antiperspirant active material
 - ii) a continuous phase which comprises water-immiscible liquid carrier, and
 - iii) a structurant therein which comprises a cyclodipeptide derivative, hereinafter DOPAD, having the general formula



in which R_A represents a carbocyclic or heterocyclic group containing not more than 2 rings, other than unsubstituted cyclohexyl.

2. A composition according to claim 1 in which the carbocyclic or heterocyclic group in R_A is substituted by at least one alkyl, alkenyl, ether or ester substituent and/or contains at least one degree of ring unsaturation.

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3. A composition according to claim 1 or 2 in which R_A in DOPAD represents a six membered ring, optionally bridged, other than unsubstituted cyclohexyl.
4. A composition according to any preceding claim in which R_A in DOPAD represents a substituted carbocyclic saturated, unsaturated non-aromatic or aromatic ring.
5. A composition according to claim 4 in which R_A in DOPAD represents a single ring.
6. A composition according to any one of claims 1 to 5 in which the ring in R_A is a substituted cyclohexyl group.
7. A composition according to any one of claims 1 to 5 in which the ring in R_A is a cyclohexenyl group, optionally substituted.
8. A composition according to any one of claims 1 to 5 in which the ring in R_A is a phenyl group, optionally substituted.
9. A composition according to any one of claims 1 to 4 in which the ring in R_A is a naphthenyl group, optionally substituted.
10. A composition according to claim 1 2 or 3 in which R_A in DOPAD represents a saturated heterocyclic ring.
11. A composition according to claim 5 in which the hetero atom in the ring in R_A is nitrogen.

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12. A composition according to any preceding claim in which the ring in R_A is substituted by at least one alkyl group.
13. A composition according to claim 12 in which the alkyl group is methyl or isopropyl.
14. A composition according to claim 12 or 13 in which the ring in R_A is substituted by two to four alkyl groups.
15. A composition according to claim 12, 13 or 14 in which at least one of the alkyl groups is methyl.
16. A composition according to claim 15 in which the ring in R_A is also substituted by an isopropyl group.
17. A composition according to claim 16 in which the ring in R_A is a cyclohexane or benzene ring substituted by a methyl and an isopropyl group that are para to each other.
18. A composition according to any preceding claim in which the ring in R_A is substituted by an hydroxyl, ether or ester substituent.
19. A composition according to claim 15 in which the DOPAD is derivable from methyl substituted piperidinol.
20. A composition according to claim 13 in which the residue R_A is derivable from thymol, isopinocampheol and a 3,5-dialkyl cyclohexanol.

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21. A composition according to claim 20 in which the 3,5-dialkyl cyclohexanol is 3,5-dimethyl cyclohexanol.
22. A composition according to claim 20 in which the residue R_A is derivable from thymol.
23. A composition according to claim 7 in which the residue R_A is derivable from carveol.
24. A composition according to claim 8 in which the residue R_A is derivable from carvacrol.
25. A composition according to any preceding claim in which the DOPAD is present at a concentration of from 0.1 to 15% by weight of the composition.
26. A composition according to claim 25 in which the DOPAD is present at a concentration of from 0.3 to 10% by weight of the composition.
27. A composition according to claim 26 in which the DOPAD is present at a concentration of from 0.5 to 3.5% by weight of the composition.
28. A composition according to claim 27 in which the DOPAD is present at a concentration of from 0.4 to 8% by weight of the continuous phase.
29. A composition according to claim 28 in which the DOPAD is present at a concentration of from 1.5 to 2.5% by weight of the continuous phase.

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30. A composition according to any one of the preceding claims characterised in that the water-immiscible liquid carrier contains a silicone oil and/or a non-silicone hydrophobic organic liquid selected from hydrocarbons, hydrophobic aliphatic esters, aromatic esters, hydrophobic alcohols and hydrophobic ethers.
31. A composition according to any one of the preceding claims wherein the water-immiscible carrier liquid contains silicone oil in an amount which is at least 10% by weight of the composition.
32. A composition according to any one of the preceding claims which contains not more than 3% by weight of any fatty alcohol which is solid at 20°C.
33. A composition according to any one of the preceding claims which does not contain more than 3% of any wax material which is solid at 30°C, softens and is molten and soluble in the water-immiscible liquid at 95°C.
34. A composition according to any preceding claim in which the DOPAD is employed in conjunction with a further structurant.
35. A composition according to claim 34 in which the further structurant is an N-acyl amino acid derivative, and/or an hydroxystearic acid and/or a dibenzylidene alditol.
36. A composition according to claim 35 in which the further structurant is N-lauroyl glutamic acid dibutylamide.

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37. A composition according to any of claims 34 to 36 in which the further structurant is employed in a weight ratio to DOPAD of from 1:10 to 10:1.
38. A composition according to claims 37 in which the further structurant comprises N-lauroyl glutamic acid dibutylamide or 12-hydroxy stearic acid in a weight ratio to DOPAD of from 1:1 to 6:1.
39. A composition according to claim 37 in which the further structurant comprises dibenzylidene sorbitol in a weight ratio to DOPAD of from 1:3 to 1:10.
40. A composition according to any preceding claim in which the composition comprises a suspension of the cosmetic active in the structured hydrophylic carrier liquid.
41. A composition according to claim 40 in which the carrier liquid and the suspended cosmetic active have matched refractive indices and has a light transmission of at least 1%.
42. A composition according to any one of claims 1 to 39 wherein the composition is an emulsion with the cosmetic active in solution in a hydrophilic, preferably water-miscible, disperse phase.
43. A composition according to claim 42 wherein the disperse phase contains a diol or polyol.
44. A composition according to claim 43 wherein the disperse

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phase contains glycerol or 1,2-propane diol.

45. A composition according to any of claims 42 to 44 in which the composition contains from 0.1% to 10% by weight of a nonionic emulsifier.
46. A composition according to claim 45 in which the emulsifier is an alkyl dimethicone copolyol.
47. A composition according to any of claims 42 to 46 in which the refractive indices of the disperse and continuous phases of the emulsion are matched.
48. A cosmetic composition according to any preceding claim in which the cosmetic active is an antiperspirant or deodorant active.
49. A composition according to claim 48 in which the antiperspirant active comprises an aluminium and/or zirconium halohydrate, an activated aluminium and/or zirconium halohydrate, or an aluminium and/or zirconium complex or an activated aluminium and/or zirconium complex.
50. A composition according to claim 48 in which the complex contains both aluminium and zirconium.
51. A composition according to any one of the preceding claims which contains from 5 to 40% by weight of the antiperspirant active.

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52. An cosmetic product comprising a dispensing container having an aperture for delivery of a stick, means for urging the contents of the container to the said aperture or apertures, and a composition according to any one of the preceding claims accommodated within the container.
53. A product according to claim 52 wherein the composition is a firm gel such that a penetrometer needle with a cone angle of 9 degrees 10 minutes, drops into the gel for no more than 30mm when allowed to drop under a total weight of 50 grams for 5 seconds.
54. A process for the production of a composition according to any one of claims 1 to 51 comprising the steps of:-
ai) incorporating into a water-immiscible liquid carrier a structurant which is one or more structurant compounds as defined in claim 1,
a2) mixing the liquid carrier with a solid or a disperse liquid phase comprising cosmetic active in particulate or dissolved form to be suspended in the water-immiscible liquid,
a3) heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is dissolved or dispersed in the water-immiscible liquid carrier
steps a1) a2) and a3) being conducted in any order followed by:
b1) introducing the mixture into a mould which preferably is a dispensing container, and then
c1) cooling or permitting the mixture to cool to a

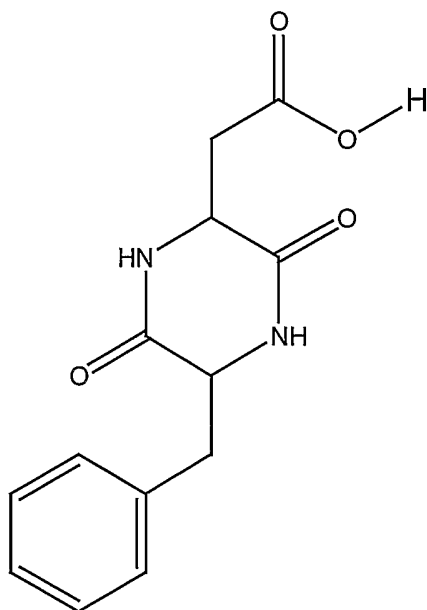
- 80 -

temperature at which the liquid carrier is solidified.

55. A process according to claim 54 in which the DOPAD structurant is dissolved in one component of the liquid hydrophobic carrier at a temperature that is higher than that attained by the remainder of hydrophobic carrier.
56. A process according to claim 54 or 55 which includes a step of pouring the mixture at elevated temperature into a dispensing container and allowing it to cool therein so as to produce a product according to claim 51 or 52.
57. A cosmetic method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition according to any one of claims 1 to 50.
58. As a new compound, a cyclodipeptide derivative (DOPAD) as described in any one of claims 1 to 24, excluding the compound in which R_A is the residue of menthol.
59. A cyclodipeptide according to claim 58 in which R_A comprises a saturated or unsaturated 6 membered carbocyclic ring substituted by two C1 to C3 alkyl or alkenyl substituents.
60. A cyclodipeptide according to claim 59 in which R_A is the residue from thymol.

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61. A process for making a cyclopeptide derivative comprising the step of reacting DOPA acid (DOPAA) having the formula



- with at least an equimolar amount of an alcohol of formula $R_A\text{OH}$ in which R_A is as defined in claim 58 in the presence of at least 0.5 moles of promoter per mole of DOPA acid in a reaction medium comprising dimethyl sulphoxide.
62. A process according to claim 61 in which the promoter is a carbonyldiimidazole.
63. A process according to claim 61 or 62 in which the mole ratio of DOPAA to the alcohol $R_A\text{OH}$ is from 2:1 to 7:1.
64. A process according to any of claims 61 to 63 employing from 0.5 to 2 moles of promoter per mole of DOPAA.

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65. A process according to any of claims 61 to 64 which is conducted at a temperature of from 40 to 60°C for a period of from 9 to 24 hours.
66. A gel comprising a water-immiscible oil gelled with an effective concentration of a cyclodipeptide derivative (DOPAD) described in any one of claims 1 to 24 other than the compound in which R_A is the residue of menthol, optionally in conjunction with a further structurant.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/14525

A. 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 C07D

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, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001 247451 A (POLA CHEM IND INC; NISSHIN OIL MILLS LTD:THE) 11 September 2001 (2001-09-11) cited in the application paragraph '0011!; claim 1 ---	1-66
A	JP 07 247475 A (NISSHIN OIL MILLS LTD:THE) 26 September 1995 (1995-09-26) paragraph '0005!; claim 1 ---	1-66
A	JP 10 226615 A (POLA CHEM IND INC) 25 August 1998 (1998-08-25) cited in the application paragraphs '0007!, '0008!; claim 1 ---	1-66
	-/--	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents:

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Date of the actual completion of the international search

24 April 2003

Date of mailing of the international search report

09/05/2003

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/14525

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>HANBUSA K ET AL: "Cyclo(dipeptide)s as Low-molecular-mass Gelling Agents to Harden Organic Fluids" JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, CHEMICAL SOCIETY. LETCHEWORTH, GB, 1994, pages 1401-1402, XP002191895 ISSN: 0022-4936 cited in the application abstract</p> <p style="text-align: center;">----</p>	1-66
A	<p>K. HANABUSA, M. MATSUMOTO ET AL.: "Low Molecular Weight Gelators for Organic Fluids: Gelation using a family of Cyclo(dipeptides)" JOURNAL OF COLLOID AND INTERFACE SCIENCE, vol. 224, 2000, pages 231-244, XP002237792 cited in the application abstract; figures 22-28; tables 1-3</p> <p style="text-align: center;">-----</p>	1-66

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/14525

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2001247451	A	11-09-2001	NONE	
JP 07247475	A	26-09-1995	JP 2921732 B2	19-07-1999
JP 10226615	A	25-08-1998	NONE	