

58  
Señor

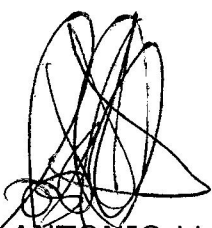
SUPERINTENDENTE DE INDUSTRIA Y COMERCIO  
DIVISION DE NUEVAS CREACIONES

E. \_\_\_\_\_ S \_\_\_\_\_ D. \_\_\_\_\_

Re: P1.-UNILEVER NV .- Solicitud de Patente de Invención para  
"COMPOSICIONES ANTITRANSPIRANTES".-Clase A61K.-  
Expediente número 00-026.094 .-

1. Me refiero a mi solicitud de patente arriba nombrada de fecha 10 de Abril de 2000.
2. Anexos me permito presentar a usted:
  - (1) Copia autentica, debidamente certificada de la solicitud de patente presentada para el invento arriba nombrado **respecto de la cual reclamo prioridad**, a saber la solicitud británica número 9908208.3 de 12 de Abril de 1999, junto con su traducción correspondiente a las legalizaciones y reivindicaciones de dicho documento; y
  - (2) Copia debidamente autenticada por el Notario Sexto del Circulo de Bogotá, de los documentos que acreditan la calidad de Traductor Oficial de la señora María Mercedes Uricoechea quien elaboró la traducción de la legalizaciones de la solicitud británica número 9908208.3 de 12 de Abril de 1999.
3. Ruego a usted tomar atenta nota de lo anterior y proceder de conformidad.

Señor Superintendente,

  
JOSE ANTONIO LLOREDA  
T.P. 10.784  
Código 231



REPUBLICA DE COLOMBIA  
MINISTERIO DE RELACIONES EXTERIORES.

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CERTIFICACION

Se hace constar que el Señor(a) MARIA MERCEDES URICOECHEA TORRÉS

se encuentra debidamente registrado(a) ante el Ministerio de Relaciones

Exteriores, como traductor e interprete oficial para los idiomas

Inglés - Español - Inglés según resolución N° 10607

de fecha 31 de Diciembre de 1981 del Ministerio de Justicia.

Se expide a los 6 dias del mes de Abril de 1983.

Atentamente,

  
RAFAEL HUMBERTO PEÑA FLOREZ

JEFE DE NEGOCIOS GENERALES

COMO NOTARIO SEXTO ENCARGADO  
DE SANTA FE DE BOGOTÁ

HAGO CONSTAR

QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA  
AUTENTICA QUE HE TENIDO A LA VISTA.

SANTA FE DE BOGOTÁ

21 ABR. 1998

COMO NOTARIO SEXTO ENCARGADO  
DE SANTA FE DE BOGOTÁ

HAGO CONSTAR

QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA  
AUTENTICA QUE HE TENIDO A LA VISTA.

SANTA FE DE BOGOTÁ

25 ABR. 2000

PABLO GONZALEZ BARAJAS

COMO NOTARIO SEXTO DE  
SANTA FE DE BOGOTÁ

HAGO CONSTAR

QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA  
AUTENTICA QUE HE TENIDO A LA VISTA.

SANTA FE DE BOGOTÁ

29 JUL 1999

JUAN MANUEL BOTERO MEDINA  
NOTARIO

COMO NOTARIO SEXTO ENCARGADO  
DE BOGOTÁ. HAGÓ CONSTAR  
QUE LA FOTOCOPIA COINCIDE CON LA ORIGINAL QUE HE  
TENIDO A LA VISTA.

16 JUN 1998

COMO NOTARIO SEXTO ENCARGADO  
DE SANTA FE DE BOGOTÁ

HAGO CONSTAR

QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA  
AUTENTICA QUE HE TENIDO A LA VISTA.

SANTA FE DE BOGOTÁ

24 NOV 1998



Unitec  
00.026.0901  
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## OFICINA DE PATENTES

Concept House  
Cardiff Road  
Newport  
South Wales  
NP9 1RH

El suscrito, un funcionario debidamente autorizado conforme a los Artículos 74(1) y (4) de la Ley de Desreglamentación y Contratación de 1994 para firmar y expedir certificados en nombre del Contralor General, certifico que la copia adjunta es una copia correcta de los documentos archivados originalmente con respecto a la solicitud de patente que allí se identifica.

De acuerdo con las Reglamentaciones de Patentes de 1982 (Re-registro de Compañías), si una compañía nombrada en este certificado y en los documentos adjuntos se ha vuelto a registrar según la Ley de Compañías de 1980 con el mismo nombre con el que fue registrada inmediatamente antes del re-registro, salvo la sustitución o inclusión como la última parte del nombre de las palabras "sociedad anónima" o su equivalente en galés, las referencias al nombre de la compañía y sus documentos adjuntos serán tratadas como referencias al nombre con el cual fue re-registrada.

De acuerdo con las reglas, las palabras "sociedad anónima" (o en inglés *public limited company*) pueden ser reemplazadas por las letras p.l.c, plc. P.L.C ó PLC.

El re-registro bajo la Ley de Compañías no constituye una nueva entidad legal sino simplemente somete a la compañía a ciertas normas de ley adicionales.

(FIRMA) ANDREW CRESSEY

FECHA: 1 de marzo de 2000.

(SELLO DE LACRE)

*Maria Mercedes*  
Maria Mercedes Uricoechea  
Res. No. 10007 Alipusilla  
Traductora Juramentada

**OFICINA DE PATENTES****SOLICITUD DE PATENTE**

1. Su referencia: **MFF/LP5770391 – J3460**

2. Solicitud No. **9908208.3** 12 de abril de 1999

3. Nombre completo y código postal de cada solicitante:

Dirección: UNILEVER PLC  
UNILEVER HOUSE, BLACKFRIARS  
BLACKFRIARS  
LONDON, EC4P 4BQ  
REINO UNIDO

Si el solicitante es una entidad, indique el país/estado de constitución:

REINO UNIDO

ADP No. 1628002

---

**TITULO DEL INVENTO:****COMPOSICIÓN ANTIPERSPIRANTE**

5. NOMBRE DE SU AGENTE:

Nombre del Agente: MEWBURN ELLIS

Dirección para notificaciones: YORK HOUSE  
23 KINGSWAY  
LONDON  
WC2B 6HP

NO. ADP Patentes 109006

6. Si declara prioridad de una o más patentes anteriores, indique el país y la fecha de radicación de cada una de ellas: N/A

7. N/A

8. SI

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9. Número de hojas radicadas (En inglés). Descripción: 38 Reivindicaciones: 5

Resumen : 1 Dibujos:

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10. Solicitud de examen preliminar y búsqueda : N/A

*Maria Mercedes Uricoechea*  
Maria Mercedes Uricoechea  
Res. No. 10007 Atequense  
Traductora Juramentada

11. Solicitamos se nos adjudique una patente con base en esta solicitud.

MICHAEL F. FORD, 9 de abril de 1999

12. Nombre y teléfono del contacto en el Reino Unido Nombre y teléfono del contacto  
en el Reino Unido (FIRMA) SR. MICHAEL F. FORD 0171-240 4405

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Harid Khosla  
[Signature]

## COMPOSICIONES ANTIPERSPIRANTES

## REIVINDICACIONES:

1. Una composición antiperspirante que comprende un antiperspirante activo, un vehículo líquido y un estructurante que incluye un esteroL para espesar o solidificar la composición, **caracterizada** en que el estructurante comprende una concentración efectiva de una combinación de al menos un esteroL y al menos un esteroL éster.
2. Una composición según la reivindicación 1, caracterizada en que el estructurante comprende esteroL y esteroL éster en una relación molecular de entre 6:1 a 1:4; preferiblemente, 3:1 a 1:2.
3. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que el peso combinado del esteroL y del esteroL éster es de 0.5 a 20%, y preferiblemente, de 1 a 15%.

*Maria Ullrich*  
Maria Ullrich  
Asesora  
Traducción J. L. L.

4. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que el esteroide comprende 4 anillos fusionados sustituidos por un grupo alifático, cicloalifático o aromático.
5. Una composición según la reivindicación 4, caracterizada en que el estero es sustituido por hidrocarburo alifático, saturado o insaturado, lineal o ramificado, que contiene hasta 20, preferiblemente de 4 a 14 átomos de carbono.
6. Una composición según la reivindicación 5 caracterizada en que el estero es  $\beta$  sitosterol o campesterol o colesterol, un derivado hidrogenado de lo mismo.
7. Una composición según la reivindicación 6, caracterizada en que el estero es  $\beta$  sitosterol.
8. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que el esteroide éster es un éster de ácido fenólico.
9. Una composición según la reivindicación 8, caracterizada en que la estructura de anillo del

*Maria Mercedes*  
María Mercedes Urcoche  
Res. No. 1007/1990  
Traductora Juramentada

esterol éster concuerda con la estructura de anillo del estero.

10. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que el estero ester es sustituido por un hidrocarburo alifático satura o insaturado, lineal o ramificado que contiene hasta 20 y preferiblemente, de 4 a 14 átomos de carbono.
11. Una composición según la reivindicación 10, caracterizada en que el sustituyente de hidrocarburo alifático es un sustituyente insaturado ramificado que contiene de 5 a 10 átomos.
12. Una composición según la reivindicación 11, caracterizada en que el estero ester es ester es y orizanol.
13. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que contiene de 1 a 10% por peso del peso combinado de  $\beta$  sitosterol y orizanol en una relación molecular de 3:1 a 1:2.

*Uad Urucho*  
Marta Mamede Leonche  
E. N. 1975  
Teléfono 1975 1975

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14. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que el antiperspirante activo comprende un halohidrato de aluminio, circonio o aluminio/circonio, un aluminio, circonio o halohidrato de aluminio/circonio activado, o un complejo de aluminio, circonio o aluminio/circonio o un complejo activado de aluminio/circonio.
15. Una composición según la reivindicación 14, caracterizada en que el antiperspirante es seleccionado de aluminio, circonio o mezcla de circonio y aluminio, y complejos de dichos clorhidratos, cualquiera clorhidrato o complejo de los cuales es activado de manera opcional.
16. Una composición según la reivindicación 14 o 15, caracterizada en que el antiperspirante activo es un clorhidrato mezclado de circonio-aluminio, o un clorhidrato o complejo de aluminio activado, o un complejo de un clorhidrato de aluminio más circonio con glicina, activado de manera opcional.

Haris Ahmed



17. Una composición según cualquiera de las reivndicaciones anteriores, caracterizada en que la proporción del antiperspirante activo es de 5 a 40% por peso.
18. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que contiene una silicona volátil y opcionalmente, una silicona no volátil y/o un vehículo líquido orgánico hidrofóbico de no silicona, seleccionado de hidrocarburos, ésteres alifáticos hidrofóbicos, ésteres aromáticos, alcoholes hidrofóbicos y éteres hidrofóbicos.
19. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que es anhidrida y contiene antiperspirante activo suspendido en partículas.
20. Una composición según cualquiera de las reivindicaciones 1 a 17, caracterizada en que el vehículo comprende una fase acuosa que contiene al menos una fracción del antiperspirante activo.

21. Una composición según la reivindicación 20, caracterizada en que la fase acuosa contiene un di o poliol.
22. Una composición según la reivindicación 20 o 21, caracterizada en que es en la forma de una emulsión.
23. Una composición según la reivindicación 22, caracterizada en que la fase dispersa en la emulsión es de 5 a 80% por peso y la fase continua es de 95 a 20% por peso.
24. Una composición según cualquiera de las reivindicaciones 20 a 23, caracterizada en que contiene de 0.1 a 10% por peso del emulsificante.
25. Una composición según cualquiera de las reivindicaciones anteriores, caracterizada en que contiene un humectante seleccionado de glicerol y sorbitol.
26. Un proceso para la producción de una barra antiperspirante que comprende los pasos de

1. incorporar en un vehículo líquido un estructurante a una concentración efectiva y en una cantidad suficiente para espesar o estructurar el vehículo para producir un sólido o un sólido suave,
2. hacer móvil la mezcla que contiene el estructurante o uno o más de sus constituyentes a una temperatura elevada.
3. mezclar el vehículo líquido con un antiperspirante aactivo para formar una mezcla que contenga antiperspirante, realizando los pasos 2 y 3 bien sea antes, después o simultáneamente con el paso 1,
4. Introducir la mezcla móvil en un molde que preferiblemente sea un contenedor de dispensión, y
5. enfriar o permitir que la mezcla móvil se enfríe a una temperatura a la que se espese o estructure,

*Maria Mercedes*  
Maria Mercedes Chicoechea  
Res. No. 10997 a. 1999  
Traductora Juramentada

caracterizado en que el estructurante comprende una combinación de al menos un estero1 y al menos un estero1 éester.

27. Un proceso según la reivindicación 26, caracterizado en que el estero1 y el estero1 éster son introducidos de manera simultánea o secuencial en una fracción hidrofóbica del vehículo fracciones separadas del mismo, a temperatura elevada y mezclados hasta lograr su disolución, y la solución o soluciones que resulten son mezcladas en corte con el antiperspirante activo y con cualquier constituyente acuoso.

28. Un método para prevenir o reducir la perspiración en piel humana que consiste en aplicar tópicamente a la piel una composición antiperspirante que contenga un antiperspirante activo, un vehículo líquido y un estructurante que comprende una concentración eficaz de una combinación de al menos un estero1 y a menos un estero1 éster.

Usado en el  
Módulo de  
Módulo de  
Módulo de  
Módulo de



The  
Patent  
Office

JOSE LLOREDA CAMACHO & CO



INVESTOR IN PEOPLE

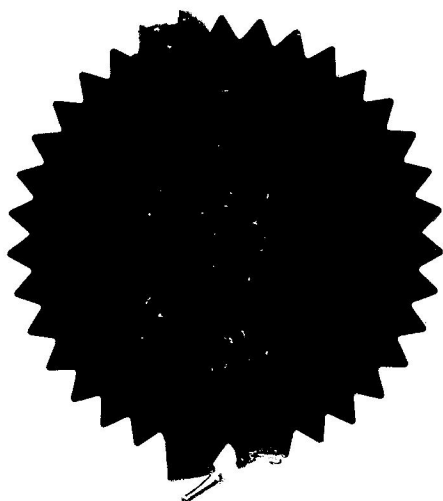
The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

*Andrew Gensey*

Dated 1 March 2000

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference MFF/LP5770391 - J3460

12 APR 1999

2. Patent application number  
(The Patent Office will fill in this part)

9908208.3

124PR99 E439049-1 002823  
F01/7700 0.00 - 9908208.3

3. Full name, address and postcode of the or of each applicant (underline all surnames)

UNILEVER PLC  
UNILEVER HOUSE  
BLACKFRIARS  
LONDON EC4P 4BQ

Patents ADP number (if you know it)

1628002

If the applicant is a corporate body, give the country/state of its incorporation

GB



4. Title of the invention ANTIPERSPIRANT COMPOSITION

5. Name of your agent (if you have one) MEWBURN ELLIS

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

YORK HOUSE  
23 KINGSWAY  
LONDON  
WC2B 6HP

Patents ADP number (if you know it)

109006

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form 0

Description 38

Claim(s) 5

Abstract 1

Drawing(s) 0

10. If you are also filing any of the following, state

Priority documents 0

Translations of priority documents 0

Statement of inventorship and right 0

Request for preliminary examination 0

Request for substantive examination 0  
(Patents Form 10/77)

Any other documents 0  
(Please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

Michael Ford

9 April 1999

12. Name and daytime telephone number of person to contact in the United Kingdom MICHAEL F. FORD 0171 240 4405

### Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

### Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

## Antiperspirant Compositions

### Technical field

The present invention relates to antiperspirant  
5 compositions and in particular to thickened or structured compositions.

### Background and prior art

Topically applied antiperspirant compositions are in  
10 widespread use throughout much of the world, in order to enable their users to avoid or minimise visible wet patches on their skin, especially in axillary regions. Antiperspirant formulations have been applied using a range of different applicators, including aerosols, roll-  
15 ons, pump sprays, sticks and mushroom applicators, in accordance with the individual preferences of consumers. In some parts of the world, sticks are especially popular. The term stick traditionally indicates a bar of solid material which was usually housed within a dispensing  
20 container and which retains its integrity whilst being applied, a firm stick. When a portion of a firm stick is drawn across the skin surface, a film of the stick composition is transferred onto the skin surface. Although the stick has the appearance of a solid article,  
25 the material forming the stick usually comprises a structured liquid phase such that a film of the material is readily transferred onto another surface upon contact under pressure.

30 More recently, the term has been applied to soft solids, which have an apparent solid form during storage, but which flow under mild pressure or shear, so that in use they can be extruded through an aperture or apertures onto a dispensing surface. Soft solids retain their shape for  
35 at least 30 seconds if removed under non-shear/stress conditions from a container, but if subjected to shear or stress, their structure is destroyed and no more than a



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minor fraction of the structure can be reformed within a period of about 24 hours when the shear/stress is removed.

There are typically three classes of antiperspirant sticks, namely suspension sticks, emulsion sticks and solution sticks. Suspension sticks contain a particulate antiperspirant active material suspended in a structured carrier. Emulsion sticks normally comprise an emulsion of an oil phase and a hydrophilic phase containing the antiperspirant active in solution, the continuous phase being structured. In some emulsion sticks, the continuous phase is an oil phase. In solution sticks, the antiperspirant is typically dissolved in the liquid carrier phase which is structured. The liquid phase can comprise water and/or a water-miscible organic solvent. The three categories can be applied to sticks of both firm and soft solids compositions.

Conventionally, many sticks have been structured using naturally-occurring or synthetic waxes, of which typical examples include stearyl alcohol, and hydrocarbon waxes or silicone waxes. Waxes are widely available, and by suitable selection of the waxes themselves and their concentrations in the formulation can effectively obtain either a soft solid or a firm solid. Thus for example, wax-structured sticks are described in an article in Cosmetics and Toiletries, 1990, vol 105, p75-78. However, fatty alcohol or wax structured sticks tend to leave visible white deposits on application to human skin, and the deposits can also be transferred onto clothing by physical contact with the skin. A significant, and possibly growing, proportion of consumers of antiperspirants have indicated displeasure at visible deposits. Accordingly, the antiperspirant industry, including the instant inventors, is devoting considerable time and resources to finding means to ameliorate or overcome the customer perception of whiteness deposits.

A number of alternative structurants to waxes have been proposed. The term "gellant" is often employed instead of "structurant". Where the resultant product is a liquid of increased viscosity rather than a solid or gel, the term "thickener" can also be used. For example, the use of dibenzylidene sorbitol (DBS) or derivatives thereof has been proposed as gellant in a number of publications, such as EP 0512770, WO 92/19222, USP 4822 602 and USP 4725430. Formulations containing such gellants can suffer from a number of disadvantages, including instability in the presence of acidic antiperspirants, and comparatively high processing temperatures needed in the production of sticks. Some of such formulations containing such gellants are sticky or tacky.

A combination of an n-acylaminoacid amide and 12-hydroxystearic acid to gel a non-aqueous formulation is described in WO 93/23008 and USP 3989087. However, high processing temperatures are needed to dissolve the gellants and prevent premature gelling. When applied to the skin the formulation can be difficult to wash off, reformulation to overcome the latter problem can be made impossible by the need for high processing temperature.

In WO 97/11678 to Helene Curtis, Inc, there is described the use of a sterol and particularly lanosterol as gellant, sometimes in conjunction with a starch hydrolyzate derivative for antiperspirant compositions.

In WO 98/34588 to Lancaster Group GmbH, there is described the use of lanesterol as a gellant for oil-based cosmetic compositions, containing a cosmetic active material, of which one listed material is a deodorant, though not exemplified.

**Objects of the invention**

It is an object of the present invention to ameliorate or overcome one or more of the foregoing disadvantages of structured sticks. A particular object of the invention, in at least one aspect, comprises providing a stick exhibiting low visible deposits gelled by a non-wax system.

**Summary of the invention**

According to the present invention there is provided an antiperspirant composition comprising an antiperspirant active, a liquid carrier and a structurant including a sterol to thicken or solidify the composition characterised in that the structurant comprises an effective concentration of a combination of at least one sterol and at least one sterol ester.

The combination of the sterol and the sterol ester in a suitable mole ratio enables the hydrophobic liquid carrier in the antiperspirant formulation to be structured effectively and in a readily controllable manner. The invention combination of gellants, a twin gellant system, has demonstrated superior gelation in comparison with either constituent. Without being bound to any specific theory or explanation as to why the combination is so effective, it is believed that the sterol and sterol ester constituents stack with each other to form a network of strands, the stacking possibly being regular. The presence of both constituents in the stacking appears to encourage the growth of the strands and result in a network which is superior to that from either constituent alone.

The employment of the twin gellant system can avoid or at least ameliorate a potential problem of premature gelation which can sometimes arise if a single gellant system is employed, for example by controlling the manner and timing

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in which the two components of the twin gellant system are mixed with the phase to be gelled.

#### Detailed Description of the Invention

5 The invention formulation comprises as essential constituents

- a) a sterol/sterol ester gellant system in addition to;
- b) an antiperspirant active and
- c) a liquid carrier

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The sterol/sterol ester gellant system comprises the sterol and sterol ester in a mole ratio that is normally selected in the range of from 10:1 to 1:10, especially from 6:1 to 1:4 and preferably in the range of from 3:1 to 1:2. Employment of the two system constituents within such a mole ratio range, and especially within the preferred range facilitates the co-stacking of the constituents and consequently facilitates the formation of a network that is readily able to structure the formulation.

20

The invention twin gellant system is desirably present at a concentration of greater than 0.5%, and preferably greater than 1%. It is normally present at a concentration of up to 20%, and in many preferred embodiments of not more than 15%. Concentrations herein are expressed by weight based on the formulations, unless explicitly otherwise stated, be they for the gellant system or some other constituent. Except in operative or comparative examples, all numbers herein indicating amounts or ratios of materials, such as limits of ranges are to be understood as modified by about, unless expressly stated otherwise.

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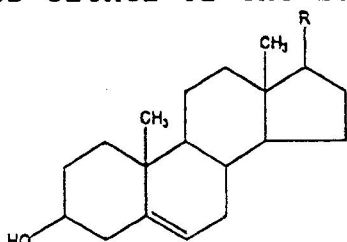
The hardness of the stick or viscosity of the formulation varies depending, amongst other parameters, on both the concentration of the twin gellant system and the choice of mole ratio of the two constituents of the system. For

18  
preparing a soft solid, it is preferable to employ the system at a concentration in the range of from 1.2 to 2.75% and a higher concentration to prepare a solid, particularly from 3.5 to 9%. The formulation tends to demonstrate greater hardness as the ratio of sterol to sterol ester increases. This property is of notable benefit, since it enables the hardness of the product formulation can be fined tuned whilst allowing the overall concentrations of the gellant system and the remaining constituents of the formulation to remain unchanged.

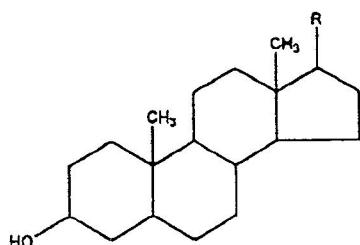
Herein, the sterol comprises a polycyclic alcohol containing at least 24 carbon atoms and contains at least 4 condensed rings, each ring having at least 3 carbon atoms and preferably from 3 to 6 carbon atoms, and especially 5 or 6 carbon atoms. The ring system can be saturated or may contain at least one degree of unsaturation. In a number of desirable sterols, the rings are approximately planar and in yet other desirable sterols the hydroxyl substituent is equatorial. Preferably, the sterol does not comprise lanesterol.

In particularly preferred embodiments, the sterol satisfies either of the formulae

25 (1)



(2)



in which R represents an aliphatic, cycloaliphatic or aromatic group, and preferably a linear or branched aliphatic saturated or unsaturated hydrocarbon group. R

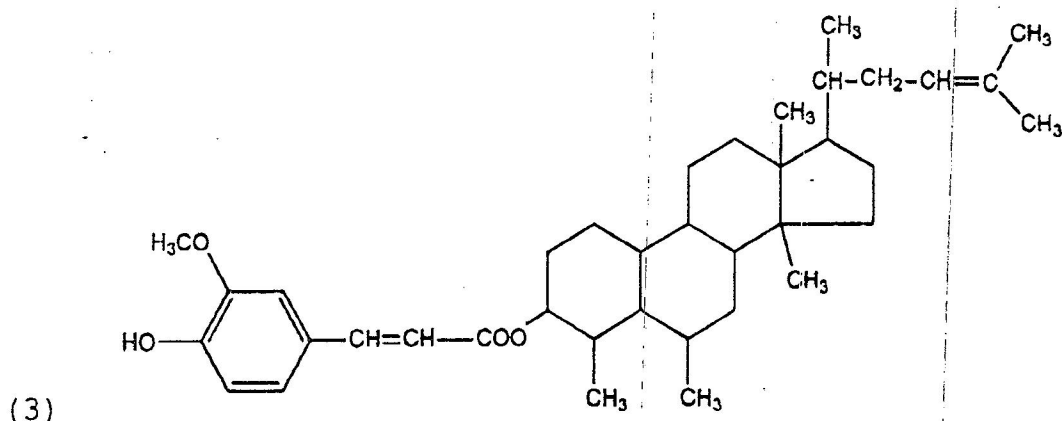
desirably contains from 1 to 20 carbons and preferably from 4 to 14 carbons.

It is particularly suitable to employ  $\beta$  sitosterol or campesterol or cholesterol, or a hydrogenated derivative thereof, such as dihydrocholesterol, or a mixture of two or more of them. An especially preferred sterol is  $\beta$  sitosterol.

- 10 The sterol ester employed herein is advantageously an ester of the sterols described hereinabove with a phenolic acid. The term phenolic acid as employed herein relates to the family of cinnamic acid, such as caffeic acid and ferulic acid. Beneficial results have been obtained when
- 15 the ring structure of the sterol ester matches the ring structure of the sterol, for example in terms of the number, size and relative positioning of the fused rings. The sterol ester preferably is substituted by an aliphatic, cycloaliphatic or aromatic group at a ring
- 20 carbon remote from the ester substituent, and most preferably the relative spacing of the ester group from that aliphatic, cycloaliphatic or aromatic group in the sterol ester is the same as the spacing of the hydroxyl group from that aliphatic, cycloaliphatic or aromatic
- 25 group in the sterol. It is highly desirable to employ a hydrocarbon substituent which may be linear or branched and saturated or unsaturated, containing from 2 to 20 and particularly 4 to 14 carbons. A convenient subclass of substituent comprises branched hydrocarbons containing
- 30 from 5 to 10 carbon atoms and one degree of unsaturation.

It is particularly suitable to employ as the sterol ester, oryzanol, sometimes referred to as  $\gamma$  oryzanol which consists of a mixture ferulic acid esters of unsaturated

35 triterpene alcohols, contains material satisfying the following formula (3):-



An especially preferred twin gellant system comprises  $\beta$  sitosterol and  $\gamma$  oryzanol, advantageously within the  
 5 ranges of mole ratios described hereinbefore.

The invention combination of sterol plus sterol ester forms a network of interconnected strands or fibres extending throughout the hydrophobic carrier liquid or  
 10 hydrophobic phase if the carrier liquid further comprises a dispersed polar phase. The interconnecting fibres are generally thin, a diameter typically less than  $0.5\mu\text{m}$  and often less than  $0.2\mu\text{m}$  and has numerous branches or interconnections.

15

For use in an unrelated field, there is described in WO 97/42830 to Unilever NV the addition of two different specific sterols, preferably phytosterols to increase the firmness of liquid fats, such as edible fats, without any  
 20 suggestion that such sterols be contemplated to gel a liquid carrier in antiperspirant compositions.

The second essential constituent of the invention compositions is an antiperspirant active. Antiperspirant  
 25 actives, are preferably incorporated in an amount of from 0.5-60%, particularly from 5 to 30 or 40% and especially from 10 to 30 or 35%.

Antiperspirant actives for use herein are often selected  
 30 from astringent active salts, including in particular aluminium salts, zirconium salts and mixed aluminium-

zirconium salts, including for each both inorganic salts and organic salts and complexes. Preferred astringent salts include aluminium, zirconium and aluminium-zirconium halides and halohydrate salts, such as chlorohydrates.

5

Preferred aluminium salts include aluminium halohydrates having the general formula  $Al_2(OH)_xQ_y \cdot wH_2O$  in which Q represents chlorine, bromine or iodine, x is from 2 to 5 and  $x + y = 6$ , x and y being either integers or non-integers and w represents a variable amount of hydration, which may be zero. Some especially preferred halohydrate salts comprise activated aluminium chlorohydrates such as those described in EP-A-6739 (Unilever NV et al), the contents of which specification is incorporated herein by reference. Activated salts retain their enhanced activity and are advantageously employed in substantially anhydrous formulations, i.e. formulations which do not contain a distinct aqueous phase. Some activated salts can also retain their enhanced activity in hydrous formulations too.

A range of zirconium salts which can be employed desirably in antiperspirant compositions herein is represented by the following empirical general formula:  $ZrO(OH)_{2n-nz}B_z \cdot wH_2O$  in which z is an integer or non-integer in the range of from 0.9 to 2.0, n is the valency of B,  $2 - nZ$  is at least 0, B is selected from the group consisting of halides, including chloride, sulphamate, sulphate and mixtures thereof and w represents a variable amount of hydration, which may be zero. In preferred zirconium salts B represents chloride and z lies in the range of 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, the aluminium component normally being selected in accordance with the above-mentioned formula for halohydrates. Especially desirable salts comprise mixed aluminium-zirconium chlorohydrates, optionally activated.



It will be recognised that the above-identified formulae for aluminium, zirconium and aluminium-zirconium salts are empirical and encompass compounds having co-ordinated and/or bound water in various quantities as well as polymeric species and mixtures and complexes. In particular, zirconium hydroxy salts often represent a range of salts having various amounts of the hydroxy group.

10

Antiperspirant complexes based on the above-mentioned astringent aluminium, zirconium and aluminium-zirconium salts can desirably be employed in the present invention. Preferably, aluminium halohydrate and/or zirconium chlorohydrate materials are complexed. The complex often employs a carboxylic acid or carboxylate group, and advantageously an aminoacid. Examples of suitable aminoacids include dl-tryptophane, dl- $\beta$ -phenylalanine, dl-valine, dl-methionine and  $\beta$ -aniline, and preferably glycine which satisfies the formula  $\text{CH}_2(\text{NH}_2)\text{COOH}$ .

It is highly desirable to employ complexes of a combination of aluminium halohydrates and zirconium chlorohydrates together with aminoacids such as glycine, such as those disclosed in US-A3792068 (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 the range of 2 to 10, especially 2 to 6, a ratio of (Al-Zr) / Cl in the range of 2.1 to 0.9 and a variable amount of an amino acid, particularly glycine. Actives of this preferred type are available from Westwood, Summit and Reheis.

In some formulations, it is particularly preferably to employ activated ZAG complexes which can be produced by the process disclosed in USP 5486347 (Callaghan et al).

Other actives which can be utilised comprise aluminium lactates, borate cross-linked aluminium salts, and astringent titanium salts, for example those described in GB 2299506A. Yet other actives includes chlorlinergenic, antihistamines and antiandrenics.

The proportion of solid antiperspirant salt in the composition normally includes the weight of any water of hydration and any complexing agent that may also be present. However, when the antiperspirant salt is dissolved in aqueous solution, it's weight excludes any water present..

In some embodiments of the present invention, the antiperspirant salts is employed herein in particulate form, and particularly in compositions which do not comprise an aqueous or hydrophilic phase. Such compositions are conveniently referred to as anhydrous or substantially anhydrous. The particle size of antiperspirant salts in such compositions often falls within the range of 1 to 200  $\mu\text{m}$  with a mean particle sizes often from 3 to 20 $\mu\text{m}$ , such as when conventional barrels are filled using conventional cast processes. Both larger and smaller mean particle sizes can also be contemplated such as from 20 to 50  $\mu\text{m}$  or 0.1 to 3  $\mu\text{m}$ .

In other embodiments, the antiperspirant active can be employed in solution form, for example where the composition comprises a polar phase, normally comprising water and/or a water-miscible solvent. In such embodiments, the concentration of antiperspirant active in solution (in the disperse polar phase) is often in the range of from 3 to 60%, based on solely the polar phase, particularly from 10% or 20% up to 55% or 60% of that phase.

21

The third essential constituent of the composition is a liquid carrier, often in a proportion of from 20 to 95% of the composition, and particularly from 40 to 90%.

- 5 The carrier that is incorporated in compositions herein comprises one or more materials that is liquid at which the composition is used and can be gelled or otherwise structured by the structurant to provide a firm or extrudable solid at that use temperature, which
- 10 conventionally is residential ambient, which is usually below 40°C and in many instances below 30°C and often at least 15°C. The carrier can be hydrophobic or a mixture of both hydrophobic and hydrophilic, the latter normally being in the form of an emulsion. It is particularly
- 15 desirable that the carrier herein contains sufficient hydrophobic material to produce a continuous phase in which a discontinuous hydrophilic phase or particulate phase can be dispersed. The twin gellant system of the present invention is suited especially to gelling a
- 20 hydrophobic medium and can also structure a dispersed oil phase, should that be present.

The hydrophobic carrier liquid may have some volatility or contain volatile constituents but generally its vapour

25 pressure will be less than 4 kPa at 25°C, so that it can be described 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 having a vapour pressure not above 4 kPa at

30 25°C.

One class of carriers that is particularly desirable herein is hydrophobic and comprises liquid silicones, in order to promote good sensory properties at the time of

35 use of the formulation. Preferably at least a major fraction of the silicone carrier is constituted by at least one volatile polyorganosiloxane, i.e. liquid materials having a measurable vapour pressure at ambient

conditions (about 20 to 25°C). Typically the vapour pressure of volatile silicones lies in the range of from 1 or 10Pa to 2kPa at 25°C. 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 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  $1 \times 10^{-5}$  m<sup>2</sup>/sec (10 centistokes), and particularly above  $1 \times 10^{-7}$  m<sup>2</sup>/sec (0.1 centistokes), the linear siloxanes normally exhibiting a viscosity of below  $5 \times 10^{-6}$  m<sup>2</sup>/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(CH<sub>3</sub>)<sub>3</sub> 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 [US]). Volatile silicones are often present in the composition in a proportion of up to 80% particularly from 10 to 70% and in a number of instances from 20 to 60%.

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 Dow Corning 556 and Dow Corning 200 series. Non-volatile silicones are often present in not more than about 30% by weight of the composition, and preferably from 1 to 15% by weight. In many instances, when a non-volatile silicone oil is

present, its weight ratio to volatile silicone oil is chosen in the range of from 1:3 to 1:40.

- Silicon-free hydrophobic organic carriers can be incorporated in the invention compositions in addition to or instead of liquid silicones, i.e. from 0 to 100% of the hydrophobic carrier liquids. Such silicon-free hydrophobic organic carrier materials can include liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected to exhibit a low viscosity. Further examples of liquid hydrocarbons comprise polydecene and isoparaffins containing at least 10 carbon atoms.
- Other suitable hydrophobic carriers comprise liquid aliphatic or aromatic esters, as a fraction of the water-immiscible carrier, desirably not more than 20% and in many instances less than 10% of the weight of the water-immiscible carrier.
- Suitable aliphatic esters contains at least one long chain alkyl group, such as esters derivable from C<sub>1</sub>-C<sub>20</sub> alkanols esterified with a C<sub>6</sub> to C<sub>22</sub> alkanolic acid or C<sub>6</sub> to C<sub>10</sub> alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they have a melting point of below 20°C. Suitable 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, including fatty alkyl benzoates. Examples of such esters include suitable C<sub>8</sub> to C<sub>18</sub> alkyl benzoates or mixtures thereof.
- Further instances of suitable hydrophobic carriers comprise liquid aliphatic ethers derivable 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 PPG-14 butyl ether. The proportion of ether in a formulation according to the present invention is often selected in the range of from 0 to 40% w/w and in some formulations particularly from 1 to 30% w/w.

5

Yet other suitable hydrophobic carriers comprise liquid aliphatic alcohols containing at least 10 carbon atoms which are liquid at 20°C. Examples of such alcohols include branched chain alcohols such as ethylhexyl

10

alcohol, octyldodecanol and isostearyl alcohol. The proportion of the alcohol in a formulation according to the present invention is often selected in the range of from 0 to 40% w/w and particularly from 1 to 30% w/w.

15

Aliphatic alcohols which are solid at 20°C are preferably absent or present at a low concentration such as less than 5% w/w of the whole composition, since such alcohols can lead to visible white deposits from topical employment of the composition.

20

The total proportion of non-silicone hydrophobic carrier(s) is often chosen in the range of from 0 to 80% and particularly from 5 to 70% by weight. Mixtures of hydrophobic non-silicone organic carriers can be employed.

25

If oxygen-containing silicon-free hydrophobic organic liquids are employed, they desirably constitute not more than 70% by weight of the hydrophobic carrier. Lower proportions of the hydrophobic phase, ranging up to for example 20, 30 or 35% in total by weight are more likely.

30

Mixtures of silicone and non-silicone carriers can suitably be employed herein, in any weight ratio, and in a number of tested embodiments the ratio lies in the range of from 20:1 to 1:20.

35

The carrier or mixture of carrier employed in the present invention can be and in many effective compositions is anhydrous, i.e. contain no free water, by employing solely one or more hydrophobic carriers. Alternatively, if

desired, the composition can comprise a hydrophilic carrier, such as in particular water and/or a water-miscible organic solvent such as an alcoholic water-miscible solvent, in addition to a hydrophobic carrier, such as those indicated hereinbefore. Compositions containing both a hydrophobic and a hydrophylic carrier normally have one of them as a disperse phase. Formulations containing a disperse phase in practice would often further comprise an emulsifying surfactant, such as an anionic, cationic, zwitterionic and/or nonionic surfactant.

In emulsions herein, the polar disperse phase, including any material dissolved therein, normally constitutes from 5 to 80% of the weight of the composition and in many embodiments up to 50 or 60% by weight and such or other embodiments preferably at least 25% by weight by weight. The continuous phase containing structurant therefor provides the weight balance of the composition, such as from 20 to 95% by weight. The emulsions herein normally comprises a water in oil emulsion, i.e. the disperse phase is the hydrophilic phase. Where an emulsion is employed, it can be convenient to prepare an emulsion in a separate step before it is mixed with the remaining constituents of the composition to produce the complete formulation.

The emulsion in many instances incorporates one or more emulsifiers, which often are non-ionic. The proportion of emulsifier or emulsifier system, i.e. combination of emulsifiers, in the emulsion is often selected in the range of from 0.1 to 10% w/w, and in many instances from 0.25 to 5% w/w. Most preferred is an amount of from 0.1 or 0.25% up to 3% w/w. It is desirable to employ an emulsifier or emulsifier system providing an overall HLB value in a range of from 2 to 10 and preferably from 3 to 8.



It may be convenient to employ an emulsifier system employing in combination an emulsifier having an HLB value above a desired overall value and one having an HLB value below the desired value. By employing the two  
5 emulsifiers together in appropriate ratios, it is readily feasible to attain a weighted average HLB value that promotes the formation of an emulsion.

Many suitable emulsifiers are nonionic ester or ether  
10 emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often containing from about 2 to 80, and especially 5 to 60 oxyethylene units, and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditols as hydrophilic moiety. The  
15 hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a hydrophobic alkyl, alkenyl or aralkyl moiety, normally containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched  
20 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 tallow, lard, palm oil sunflower seed oil or soya bean oil. Such non-ionic surfactants can also be  
25 derived from a polyhydroxy compound such as glycerol or sorbitol or other alditols. Examples of emulsifiers include cetareth-10 to -25, ceteth-10-25, steareth-10-25, and PEG-15-25 stearate or distearate. Other suitable examples include C10-C20 fatty acid mono, di or tri-  
30 glycerides. Further examples include C18-C22 fatty alcohol ethers of polyethylene oxides (8 to 12 EO). The co-emulsifiers, which typically have a low HLB value, and often of from 2 to often comprise mono or possibly fatty acid diesters of polyhydric alcohols such as  
35 glycerol, sorbitol, erythritol or trimethylolpropane. The fatty 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.

- 5 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  
10 in C1 to C12 alkyl groups.

Suitable emulsifiers are widely available under many tradenames including Abil <sup>TM</sup>, Arlacel <sup>TM</sup>, Brij <sup>TM</sup>, Cremophor <sup>TM</sup>, Dehydrol <sup>TM</sup>, Emerest <sup>TM</sup>, Lameform <sup>TM</sup>, Quest  
15 PGPH <sup>TM</sup>, Pluronic <sup>TM</sup>, Prosorine <sup>TM</sup>, Span <sup>TM</sup>, Tween <sup>TM</sup>, SF 1228, DC3225C and Q2-5200.

The hydrophilic carrier normally comprises water and can comprise one or more water soluble or water miscible  
20 liquids in addition to or replacement for water. The proportion of water in an emulsion according to the present invention is often selected in the range of up to 50%, and particularly from 5 to 40%. Some of the water may be introduced as a solvent for the antiperspirant  
25 active.

One class of water soluble or water-miscible solvents comprises short chain monohydric alcohols, e.g. C1 to C4, and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further  
30 class of hydrophilic liquids comprises di or polyols, preferably having a melting point of below 40°C, or which are water miscible. Examples of di or polyols include glycol, 1,2 propylene glycol, 1,3 butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol 2-  
35 ethoxyethanol, diethylene glycol monoethylether and triethyleneglycol monomethylether. Especially preferred polyols comprise glycerol or sorbitol and related

compounds which are capable also of acting as a humectant. The proportion of a mono, di or polyol in the formulation is often selected in the range of up to 15%, and in a number of instances from 0.5 to 12%. conveniently up to  
5 about 5% and preferably from about 0.2 to 3%.

Optional ingredients in the invention compositions can include disinfectants, for example at a concentration of up to about 10% w/w. Suitable deodorant actives can  
10 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 Irgasan DP300™, Triclosan™,  
15 Triclorban™ and Chlorhexidine warrant specific mention. A yet another class comprises biguanide salts such as available under the trademark Cosmosil™.

Other optional ingredients include wash-off agents, often  
20 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 non-ionic surfactants such as esters or ethers containing a C8 to C22 alkyl moiety and a hydrophilic moiety which can comprise a  
25 polyoxyalkylene group (POE or POP) and/or a polyol.

A further optional constituent of the formulation comprises one or more secondary structurants which can be employed in addition to the primary structurant system,  
30 i.e. the sterol plus sterol ester. The amount of such secondary structurants in the formulation is often 0, and usually not more than 15% of the formulation. It is normally not greater than the amount of the primary structurant.

35 The secondary structurants employable herein can be non-polymeric or polymeric. Non-polymeric structurants, sometimes referred to as gellants, can be selected from

fatty acids or salts thereof, such as stearic acid or sodium stearate or 12-hydroxystearic acid. Other suitable gellants can comprise dibenzylidene alditols, e.g. dibenzylidene sorbitol. Further suitable gellants can  
5 comprise lanosterol, selected n-acyl amino acid derivatives, including ester and amide derivatives, such as N-lauroyl glutamate dibutylamide, which gellants can be contemplated in conjunction with hydroxystearic acid or an ester or amide derivative thereof. Still further gellants  
10 include amide derivatives of di or tribasic carboxylic acids, such as alkyl N,N' dialkylsuccinamides, e.g. dodecyl N,N'-dibutylsuccinamide. Stearyl alcohol and/or a natural plant or animal derived wax or similar synthetic waxes can be employed, if desired, as secondary  
15 structurant but are currently not preferred.

Polymeric structurants which can be employed can comprise organo polysiloxane elastomers such as reaction products of a vinyl terminated polysiloxane and a cross linking  
20 agent or alkyl or alkyl polyoxyalkylene-terminated poly(methyl 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  
25 groups have been disclosed in WO 97/36572 and WO 99/06473. If the composition comprises an aqueous phase, this phase can be structured or thickened by polyacrylamides, polyacrylates or polyalkylene oxides.

30 The compositions herein can incorporate one or more cosmetic adjuncts conventionally contemplatable for antiperspirant 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  
35 up to about 10% w/w; skin benefit agents such as allantoin or lipids, for example in an amount of up to 5% w/w;

colours; skin cooling agents other than the already mentioned alcohols, such as menthol and menthol derivatives, often in an amount of up to 2% w/w. A commonly employed adjunct comprises a perfume, which is normally present at a concentration of from 0 to 4% and in many formulations from 0.25 to 2%.

The compositions described herein can be produced by conventional processes for making suspension or emulsion solids or soft-solids.

Thus, according to a second aspect of the present invention there is provided process for the production of an antiperspirant stick comprising the steps of

- 1 incorporating into a liquid carrier a structurant comprising an effective concentration of a combination of at least one sterol and at least one sterol ester in an amount sufficient to thicken or structure the carrier to produce a solid or soft solid,
- 2 rendering the structurant-containing mixture or one or more of its constituents mobile at an elevated temperature
- 3 mixing the liquid carrier with an antiperspirant active to form an antiperspirant-containing mixture, steps 2 and 3 being conducted either before, after or simultaneously with step 1
- 4 introducing the mobile mixture into a mould which preferably is a dispensing container and
- 5 cooling or permitting the mobile mixture to cool to a temperature at which it is thickened or structured.

A convenient process sequence for suspension formulations comprises first forming a solution of the sterol and sterol ester in the carrier or mixture of carriers. This is normally carried out by agitating the mixture at an elevated temperature, such as selected within the range of from 50 to 120°C. Both the sterol ester and the sterol can be introduced simultaneously or sequentially into the

carrier, at an appropriate temperature and agitation, for example the sterol ester followed by the sterol, or the sterol ester and sterol can be dissolved in aliquots of the carrier which are subsequently blended. Thereafter, particulate antiperspirant active can be blended with the carrier solution and the blend introduced, at a temperature that is often 5 to 10°C above its setting temperature into its dispensing container, such as a barrel using suitable filling processes and is cooled or allowed to cool to ambient.

In a suitable process for making emulsion formulations, a solution of sterol ester and sterol is formed in the hydrophobic carrier in the manner as for preparation of a suspension stick, and separately an aqueous or hydrophilic phase is prepared, by introduction of antiperspirant active into the phase (if necessary, since such actives can conveniently be supplied in aqueous solution) preferably being heated to a temperature similar to that of the oil phase and thereafter mixed, or alternatively introduced into the oil phase at a rate which maintains the elevated temperature of the mixture and is thereafter filled in a similar manner to that for suspension sticks.

The compositions herein are suitable for applying topically to human skin, and particularly to axillae, thereby reducing observable perspiration.

Thus, according to a third aspect of the present invention, there is provided a method for preventing or reducing perspiration on human skin comprising topically applying to the skin an antiperspirant composition comprising an antiperspirant active, a liquid carrier and a structurant which comprises an effective concentration of a combination of at least one sterol except lanosterol and at least one sterol ester.

Having described the invention in general terms, specific embodiments thereof will be described more fully by way of example only.

- 5 In the Examples or Comparisons, the various constituents were as follows:-
- 1) vol sil = cyclomethicone blend DC345 (Dow Corning Inc)
  - 2) PPG-14 Butylether Fluid AP (Amercol).
  - 3) CAB = C<sub>12</sub>-C<sub>15</sub> alkyl benzoate Finsolv TN (Fintex).
  - 10 4) ISA = isostearyl alcohol Prisorine 3515 (Unichema).
  - 5a)  $\beta$  Sitosterol (D.R.T)
  - 5b) ultrasitosterol (Kaukas)
  - 5c)  $\beta$  Sitosterol (Acros)
  - 6)  $\gamma$  Oryzanol (Jan Dekker (UK) Ltd)
  - 15 7) Al/Zr Tetrachlorohydrex glycine complex AZAG 7167 (Summit)
  - 8) Cholesterol (Acros)
  - 9) Dihydro-cholesterol (Sigma)
  - 10) Polydecene Silkflo 364NF (Albemarle)
  - 20 11) Isopropyl Myristate Estol 1514 (Unichema)
  - 12) Cetyl Dimethicone Copolyol Abil EM90 (Th. Goldschmidt) [emulsifier]
  - 13) 50% aqueous solution of Al/Zr pentachlorohydrate Zirconal 50 (Giulini)
  - 25 14) Glycerol (Aldrich)
  - 15) Low refractive index AACH (Unilever)
  - 16) Superfino talc (Cyprus Minerals) 57.5% Rezal 36 GPSUF aqueous solution
  - 17) Aluminium zirconium tetrachlorohydrex glycine (fine
  - 30 particle size) Rezal 36 GPSUF aqueous solution
  - 18) Aluminium-Zirconium Glycine complex Summit AZG-375
  - 19) Propylene Glycol (Fisons)
  - 20) Polyglycerol-3 diisostearate Lamemform TGI
  - 21) Polyglycerol-2 dipolyhydroxystearate Dehymuls PGPH
  - 35 22) Polyglycerol-polyrincinolate Quest PGPR
  - 23) Polyglycerol-2 isostearate Prisorine 3791
  - 24) Polyglycerol-2 diisostearate Prisorine 3792
  - 25) Cyclomethicone blend DC245 (Dow Corning Inc)

## Comparisons C1-C10 and Examples 11 to 19

In these Comparisons and Examples, the capability of individual sterols or sterol esters and mixtures of sterol and sterol ester to gel representative hydrophobic solvents is demonstrated. The sterol and/or sterol ester was/were dissolved in the solvent in a glass bottle by heating and stirring. The resulting clear solution was allowed to cool to laboratory temperature without stirring. The product was assessed the following day. The results are summarised in Table 1 below.

Table 1

| Comp or Example | Sterol Sterol Ester                 | Solvent or mixture                                  | Product *                |
|-----------------|-------------------------------------|-----------------------------------------------------|--------------------------|
| C1              | 10% cholesterol                     | Polydecene <sup>(10)</sup>                          | crystal slush            |
| C2              | 10% dihydro-cholesterol             | Polydecene <sup>(10)</sup>                          | crystal slush            |
| C3              | 10% $\beta$ sitosterol              | Polydecene <sup>(10)</sup>                          | soft paste               |
| C4              | 10% oryzanol                        | Polydecene <sup>(10)</sup>                          | crystals + clear liquid  |
| Ex 11           | 5% cholesterol / 5% oryzanol        | Polydecene <sup>(10)</sup>                          | hard gel                 |
| Ex 12           | 5% dihydrocholesterol / 5% oryzanol | Polydecene <sup>(10)</sup>                          | hard gel                 |
| Ex 13           | 5% $\beta$ sitosterol / 5% oryzanol | Polydecene <sup>(10)</sup>                          | hard gel                 |
| C5              | 10% cholesterol                     | 70% volsil <sup>(1)</sup><br>30% ISA <sup>(2)</sup> | crystal slush            |
| C6              | 10% dihydrocholesterol              | 70% volsil <sup>(1)</sup><br>30% ISA <sup>(2)</sup> | crystals + clear liquid  |
| C7              | 10% $\beta$ sitosterol              | 70% volsil <sup>(1)</sup><br>30% ISA <sup>(2)</sup> | crystals + clear liquid  |
| C8              | 10% oryzanol                        | 70% volsil <sup>(1)</sup> 30% ISA <sup>(2)</sup>    | crystals + cloudy liquid |
| Ex 14           | 5% cholesterol / 5% oryzanol        | 70% volsil <sup>(1)</sup> 30% ISA <sup>(2)</sup>    | hard gel                 |

35

| Table 1 cont |                                     |                                                  |                         |
|--------------|-------------------------------------|--------------------------------------------------|-------------------------|
| Ex 15        | 5% dihydrocholesterol / 5% oryzanol | 70% volsil <sup>(1)</sup> 30% ISA <sup>(2)</sup> | hard gel                |
| Ex 16        | 5% $\beta$ sitosterol / 5% oryzanol | 70% volsil (1) 30% ISA 9"0                       | hard gel                |
| C9           | 10% $\beta$ sitosterol              | 60% volsil <sup>(1)</sup> 40% CAB <sup>(4)</sup> | crystal slush           |
| C10          | 10% oryzanol                        | 60% volsil <sup>(1)</sup> 40% CAB <sup>(4)</sup> | crystals + clear liquid |
| Ex 17        | 5% $\beta$ sitosterol / 5% oryzanol | 60% volsil <sup>(1)</sup> 40% CAB <sup>(4)</sup> | hard gel                |
| Ex 18        | 8% $\beta$ sitosterol / 2% oryzanol | 60% volsil <sup>(1)</sup> 40% CAB <sup>(4)</sup> | hard gel                |
| Ex 19        | 2% $\beta$ sitosterol / 8% oryzanol | 60% volsil <sup>(1)</sup> 40% CAB <sup>(4)</sup> | hard gel                |

From Table 1, it can be seen clearly by comparing the comparisons marked with a C and the Examples marked with Ex that the combination of sterol and sterol ester was capable of producing gelation superior to that from either the sterol or the sterol ester alone at the same overall concentration.

#### Examples 20 to 38

10 In these Examples, suspension sticks according to the formulations summarised in Table 2 below were made as follows:-

The carriers were first combined. The oryzanol (the sterol ester) was introduced into the carriers and dissolved by heating and stirring. Once the oryzanol had dissolved completely, the sterol was introduced and the mixture heated and stirred until a clear solution was obtained. The solution was then allowed to cool under gentle stirring until it had reached a temperature of about 5-10 degrees above its gelling point. The specified particulate antiperspirant active was then stirred in and fully dispersed. The mixture was then poured into stick barrels and allowed to cool and solidify. A number of the



sticks were analysed by the methods described hereinbelow and the results summarised in Table 2 below. The evaluations were made after the stick had been stored for at least 24 hours at laboratory room temperature.

5

Table 2

| Example No                                            | 20                      | 21   | 22   | 23   | 24   | 25   | 26   | 27   | 28   |
|-------------------------------------------------------|-------------------------|------|------|------|------|------|------|------|------|
| Constituent                                           | Weight % in formulation |      |      |      |      |      |      |      |      |
| cyclomethicones<br>( <sup>1</sup> )                   | 56.0                    | 56.0 | 56.0 | 56.0 | 56.0 | 52.0 | 53.0 | 53.0 | 55.5 |
| PPG-14<br>Butylether ( <sup>2</sup> )                 | 0.7                     | 2.8  | -    | 3.5  | -    | -    | -    | -    | -    |
| C <sub>12-15</sub> Alkyl<br>Benzoate ( <sup>3</sup> ) | 8.4                     | 8.4  | 10.5 | 10.5 | 15.0 | 15.0 | 15.0 | -    | 12.5 |
| Isostearyl<br>Alcohol ( <sup>4</sup> )                | 4.9                     | 2.8  | 3.5  | -    | -    | -    | -    | 15.0 | -    |
| $\beta$ Sitosterol<br>( <sup>5a</sup> )               | 3.0                     | 3.0  | 3.0  | 3.0  | 3.5  | 4.5  | 4.0  | 4.0  | 4.0  |
| Oryzanol ( <sup>6</sup> )                             | 3.0                     | 3.0  | 3.0  | 3.0  | 3.5  | 4.5  | 4.0  | 4.0  | 4.0  |
| AZAG 7167 ( <sup>7</sup> )                            | 24                      | 24   | 24   | 24   | 24   | 24   | 24   | 24   | 24   |
| Penetrometer<br>Hardness (mm)                         | 10.5                    | 10.3 | 10.5 | 10.5 | 9.2  | 7.7  | 9.3  | 8.2  | 10.7 |
| Deposits Score<br>Abrasive Paper                      | n/d                     | 43   | n/d  | 36   | 24   | 25   | 24   | n/d  | n/d  |
| Deposit Score<br>Black Wool                           | n/d                     | 60   | n/d  | 52   | 15   | 14   | 17   | n/d  | n/d  |

Table 2 (cont)

| EXAMPLE                                               | 29                      | 30   | 31   | 32   | 33   | 34   | 35   | 36   | 37   |
|-------------------------------------------------------|-------------------------|------|------|------|------|------|------|------|------|
| Constituent                                           | Weight % in formulation |      |      |      |      |      |      |      |      |
| Cyclomethicone<br>( <sup>1</sup> )                    | 53.0                    | 50.0 | 50.0 | 50.0 | 50.0 | 56.0 | 56.0 | 55.0 | 55.0 |
| PPG-14<br>Butylether ( <sup>2</sup> )                 | -                       | -    | 5.0  | 4.0  | 1.0  | 2.8  | 2.8  | 2.8  | 2.8  |
| C <sub>12-15</sub> Alkyl<br>Benzoate ( <sup>3</sup> ) | 7.5                     | 15.0 | 15.0 | 12.0 | 12.0 | 8.4  | 8.4  | 8.4  | 8.4  |
| Isostearyl<br>Alcohol ( <sup>4</sup> )                | 7.5                     | 5.0  | -    | 4.0  | 7.0  | 2.8  | 2.8  | 2.8  | 2.8  |
| $\beta$ Sitosterol<br>( <sup>5a</sup> )               | 4.0                     | 3.0  | 3.0  | 3.0  | 3.0  | 2.1  | 3.9  | -    | -    |
| Cholesterol ( <sup>8</sup> )                          | -                       | -    | -    | -    | -    | -    | -    | 3.5  | -    |
| Dihydro-<br>cholesterol ( <sup>9</sup> )              | -                       | -    | -    | -    | -    | -    | -    | -    | 3.5  |
| Oryzanol ( <sup>6</sup> )                             | 4.0                     | 3.0  | 3.0  | 3.0  | 3.0  | 3.9  | 2.1  | 3.5  | 3.5  |
| AZAG 7167 ( <sup>7</sup> )                            | 24                      | 24   | 24   | 24   | 24.0 | 24.0 | 24.0 | 24.0 | 24.0 |
| Penetrometer<br>Hardness (mm)                         | 8.4                     | 11.8 | 11.7 | 11.6 | 11.1 | 11.0 | 18.2 | 10.4 | 10.6 |
| Deposits Score<br>Abrasive Paper                      | n/d                     | 28   | n/d  | 26   | n/d  | 24   | n/d  | 36   | 24   |
| Deposit Score<br>Black Wool                           | n/d                     | 11   | n/d  | 29   | n/d  | 26   | n/d  | 63   | 15   |

Table 2 (cont)

|                                                  |                         |  |     |  |  |  |  |  |  |
|--------------------------------------------------|-------------------------|--|-----|--|--|--|--|--|--|
| EXAMPLE                                          | 38                      |  | CWS |  |  |  |  |  |  |
| Constituent                                      | Weight % in formulation |  |     |  |  |  |  |  |  |
| C <sub>12-15</sub> Alkyl Benzoate <sup>(3)</sup> | 62.0                    |  |     |  |  |  |  |  |  |
| $\beta$ Sitosterol <sup>(5a)</sup>               | 7.0                     |  |     |  |  |  |  |  |  |
| Oryzanol <sup>(6)</sup>                          | 7.0                     |  |     |  |  |  |  |  |  |
| AACH water modified <sup>(15)</sup>              | 24.0                    |  |     |  |  |  |  |  |  |
| Penetrometer Hardness (mm)                       | 15.1                    |  | 9.4 |  |  |  |  |  |  |
| Deposits Score Abrasive Paper                    | 22                      |  | 118 |  |  |  |  |  |  |
| Deposit Score Black Wool                         | 12                      |  | 186 |  |  |  |  |  |  |

CWS is a conventionally stearyl alcohol and wax-structured white suspension stick

5

Examples 20 to 34, 36 and 37 were hard opaque white sticks. Example 35 was a slightly softer white stick. Example 38 was a hard slightly translucent stick. Qualitative assessment showed that all gave lower white deposits on skin than a conventional opaque white solid stick.

10

From Table 2, it can be observed that suspension sticks having acceptable hardness and only low or very low deposits can be obtained using a combination of a sterol and a sterol ester according to the present invention.

15

#### Example 39 to 55

In these Examples, emulsion sticks according to the formulations summarised in Table 3 below were made as follows:-

20

In the first step, the hydrophobic phase was prepared by combining the cosmetic oils and solvents, the emulsifier introduced and dissolved in a Silverson mixer. The oryzanol (the sterol ester) was introduced and dissolved  
5 by heating and stirring at 5000 rpm. Once the oryzanol had dissolved completely, the sterol was added and the mixture again heated and stirred until a clear solution had been obtained. The solution was then allowed to cool under gentle stirring until it reached a temperature of  
10 about 5-10 degrees above its gelling point.

In the second step, the aqueous phase was prepared by combining the antiperspirant solution with the other aqueous phase components. This was heated to the same  
15 temperature as the continuous phase solution.

In the third step, the aqueous phase was introduced slowly into the hydrophobic phase was introduced in the Silverson mixer, and maintained at a constantly temperature and at  
20 constant shear conditions (8000rpm). The mixture was sheared for up to 10 minutes, until the aqueous phase had been evenly dispersed. The resulting emulsion was then left to stand and to de-aerate. It was then  
25 poured into stick barrels and allowed to cool to laboratory ambient temperature and solidify. A number of the resultant sticks were evaluated for penetration and hardness by the methods described below after the stick had been maintained for at least 24 hours at room  
30 temperature. The results are summarised in Table 3 below.

Table 3

| Example                                               | 39                      | 40   | 41   | 42   | 43   | 44   | 45   |
|-------------------------------------------------------|-------------------------|------|------|------|------|------|------|
| Constituent                                           | Weight % in formulation |      |      |      |      |      |      |
| Continuous phase                                      |                         |      |      |      |      |      |      |
| Cyclomethicone<br>( <sup>1</sup> )                    | 23.5                    | 32.4 | 40.0 | 40.0 | 40.0 | 40.0 | 35.0 |
| PPG-14 Butylether<br>( <sup>2</sup> )                 | -                       | 5.0  | -    | -    | -    | -    | -    |
| C <sub>12-15</sub> Alkyl<br>Benzoate ( <sup>3</sup> ) | 12.5                    | 12.7 | 10.0 | -    | -    | -    | -    |
| Isostearyl<br>Alcohol ( <sup>4</sup> )                | -                       | -    | -    | 10.0 | 10.0 | -    | -    |
| Polydecene ( <sup>10</sup> )                          | 11.3                    | -    | -    | -    | -    | -    | -    |
| Isopropyl<br>Myristate ( <sup>11</sup> )              | -                       | -    | -    | -    | -    | 10.0 | 15.0 |
| $\beta$ Sitosterol ( <sup>5a</sup> )                  | -                       | -    | -    | -    | -    | -    | -    |
| $\beta$ Sitosterol ( <sup>5b</sup> )                  | 2.4                     | 2.5  | -    | 2.5  | -    | 2.5  | 2.5  |
| $\beta$ Sitosterol ( <sup>5c</sup> )                  | -                       | -    | 2.5  | -    | -    | -    | -    |
| Dihydrocholesterol<br>( <sup>9</sup> )                | -                       | -    | -    | -    | 2.5  | -    | -    |
| Oryzanol ( <sup>6</sup> )                             | 2.4                     | 2.5  | 2.5  | 2.5  | 2.5  | 2.5  | 2.5  |
| Cetyl Dimethicone<br>Copolyol ( <sup>12</sup> )       | 0.9                     | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  |
| Aqueous phase                                         |                         |      |      |      |      |      |      |
| Zirkonal 50 ( <sup>13</sup> )                         | 37.6                    | 39.9 | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 |
| Glycerol ( <sup>14</sup> )                            | 9.4                     | 4.0  | 4.0  | -    | -    | 4.0  | 4.0  |
| water                                                 | -                       | -    | -    | 4.0  | 4.0  | -    | -    |
| Penetrometer<br>Hardness (mm)                         | 16.9                    | 17.8 | 17.1 | 22.4 | 26.7 | n/d  | 18.8 |
| Deposits Score<br>Abrasive Paper                      | 22                      | 28   | 26   | n/d  | 22   | n/d  | n/d  |
| Deposit Score<br>Black Wool                           |                         | 11   | 14   | n/d  | 29   | n/d  | n/d  |

Table 3 (cont)

| Example                                            | 46                      | 47   | 48   | 49   | 50   | 51   | 52   |
|----------------------------------------------------|-------------------------|------|------|------|------|------|------|
| Constituent                                        | Weight % in formulation |      |      |      |      |      |      |
| Continuous phase                                   |                         |      |      |      |      |      |      |
| Cyclomethicone ( <sup>1</sup> )                    | 35.0                    | 35.0 | 35.0 | 35.0 | 25.0 | 34.0 | 33.0 |
| PPG-14 Butylether ( <sup>2</sup> )                 | -                       | -    | -    | -    | -    | -    | -    |
| C <sub>12-15</sub> Alkyl Benzoate ( <sup>3</sup> ) | 7.5                     | -    | 15.0 | 7.5  | 25.0 | 7.5  | 7.5  |
| Isostearyl Alcohol ( <sup>4</sup> )                | -                       | -    | -    | -    | -    | 7.5  | 7.5  |
| Polydecene ( <sup>10</sup> )                       | -                       | -    | -    | -    | -    | -    | -    |
| Isopropyl Myristate ( <sup>11</sup> )              | 7.5                     | 15.0 | -    | 7.5  | -    | -    | -    |
| $\beta$ Sitosterol ( <sup>5a</sup> )               | -                       | -    | -    | -    | -    | -    | -    |
| $\beta$ Sitosterol ( <sup>5b</sup> )               | -                       | -    | -    | -    | -    | -    | -    |
| $\beta$ Sitosterol ( <sup>5c</sup> )               | 2.5                     | 2.5  | 2.5  | 2.5  | 2.5  | 3.0  | 3.5  |
| Dihydrocholesterol ( <sup>9</sup> )                | -                       | -    | -    | -    | -    | -    | -    |
| Oryzanol ( <sup>6</sup> )                          | 2.5                     | 2.5  | 2.5  | 2.5  | 2.5  | 3.0  | 3.5  |
| Cetyl Dimethicone Copolyol ( <sup>12</sup> )       | 1.0                     | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  |
| Aqueous Phase                                      |                         |      |      |      |      |      |      |
| Zirkonal 50 ( <sup>13</sup> )                      | 40.0                    | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 |
| Glycerol ( <sup>14</sup> )                         | 4.0                     | -    | -    | -    | -    | -    | -    |
| water                                              | -                       | 4.0  | 4.0  | 4.0  | 4.0  | 4.0  | 4.0  |
| Penetrometer Hardness (mm)                         | 17.0                    | 20.7 | 27.4 | 18.2 | 18.5 | 15.6 | 12.5 |
| Deposits Score Abrasive Paper                      | n/d                     | 29   | 30   | 31   | n/d  | 26   | 25   |
| Deposit Score Black Wool                           | n/d                     | 12   | 12   | 8    | n/d  | 12   | 12   |

Examples 39 to 52 were all translucent/opaque or opaque medium hard to hard white sticks. Qualitative assessment showed that all gave lower white deposits on skin than a conventional wax-structured white solid stick.

From Table 3, it can be observed that emulsion sticks having acceptable hardness and only low or very low deposits can be obtained using a combination of a sterol and a sterol ester according to the present invention.

5

**Examples 53 to 56**

In these Examples, soft solid or semi-solid sticks according to the present invention and having formulations summarised in Table 4 below were made by the following process:-

10

First, the sterol ester (oryzanol), and carrier fluid, wase introduced into a vessel, and heated to 110°C, whilst being sheared by a Silverson mixer at approximately 15 3000rpm until the sterol ester had dissolved. Then, the B-Sitosterol was introduced into the vessel, and sheared further until it had dissolved to a clear solution. The mixture was then allowed to cool to about 80°C and the powders (talc and AZAG) were introduced slowly with high 20 shear mixing in the mixer, at about 6500rpm until homogeneously mixed. The resultant mixture was then poured into glass jars at fill temperatures specified in Table 4.

25

Table 4

| Example                                            | 53                      | 54   | 55   | 56   |
|----------------------------------------------------|-------------------------|------|------|------|
| Constituent                                        | Weight % in formulation |      |      |      |
| AZAG 7167 ( <sup>7</sup> )                         | 24.0                    | 24.0 | 24.0 | 24.0 |
| Cyclomethicone ( <sup>1</sup> )                    | 54.0                    | 55.0 | 54.5 | 53.0 |
| Oryzanol ( <sup>6</sup> )                          | 1.0                     | 0.5  | 0.75 | 1.5  |
| β-Sitosterol ( <sup>5a</sup> )                     | 1.0                     | 0.5  | 0.75 | 1.5  |
| Talc ( <sup>16</sup> )                             | 6.0                     | 6.0  | 6.0  | 6.0  |
| C <sub>12-15</sub> Alkyl Benzoate ( <sup>3</sup> ) | 14.0                    | 14.0 | 14.0 | 14.0 |
| Hardness                                           | 22.7                    | n/d  | >30  | 17.1 |

From Table 4, it can be seen that the formulations in Examples 53 and 55 were soft solid formulations suitable for dispensing in conventional soft solid applicators in which the material is extruded through an aperture.

- 5 Example 57 was soft and leaked solvent. Example 56 was a semi-firm solid, possibly more suited to application via a traditional applicator for a solid.

#### Examples 57 to 73

- 10 Further Soft Solid and Solid Formulations were made by the general methods described in the respective previous Examples for such types of material.

Table 5

| Example No                                         | 57    | 58    | 59    | 60   | 61   | 62   |
|----------------------------------------------------|-------|-------|-------|------|------|------|
| cyclomethicone ( <sup>1</sup> )                    | 15.15 | 25.25 | 8.6   | 38.0 | 38.0 | 9.0  |
| C <sub>12-15</sub> alkyl benzoate ( <sup>3</sup> ) | 10.10 | 22.73 | 3.44  | 7.5  | 7.5  | 3.6  |
| Isopropyl myristate ( <sup>11</sup> )              |       |       |       |      |      |      |
| PPG-14 butyl ether ( <sup>2</sup> )                | 25.25 | 2.52  | 30.96 | 7.5  | 7.5  | 32.4 |
| Cetyl dimethicone copolyol ( <sup>12</sup> )       | 1.00  | 1.00  | 1.0   | 1.0  | 1.0  | 1.0  |
| Oryzanol ( <sup>6</sup> )                          | 2.50  | 2.50  | 3.0   | 3.0  | 3.0  | 7.0  |
| $\beta$ -Sitosterol ( <sup>5c</sup> )              | 2.50  | 2.50  | 3.0   | 3.0  | 3.0  | 7.0  |
| 57.5% Rezal 36 ( <sup>17</sup> )                   | 43.5  | 43.5  |       | 20.0 | 20.0 |      |
| Zirconal 50 ( <sup>13</sup> )                      |       |       | 50.0  |      |      | 40.0 |
| Summit AZG-375 ( <sup>18</sup> )                   |       |       |       |      |      |      |
| Water                                              |       |       |       | 9.0  | 5.0  |      |
| Propylene Glycol ( <sup>19</sup> )                 |       |       |       | 3.6  | 15.0 |      |
| Glycerol ( <sup>14</sup> )                         |       |       |       |      |      |      |
| Hardness (mm)                                      | >50   | >50   | >50   | 32.4 | 14.4 | 15.1 |



Table 5 cont

| Example No                                         | 63    | 64    | 65   | 66    | 67    | 68    |
|----------------------------------------------------|-------|-------|------|-------|-------|-------|
| cyclomethicone ( <sup>1</sup> )                    | 24.5  | 24.5  | 38.0 | 24.5  | 24.5  | 23.5  |
| C <sub>12-15</sub> alkyl benzoate ( <sup>3</sup> ) | 22.05 | 8.82  | 7.5  | 22.54 | 10.78 | 10.34 |
| Isopropyl myristate ( <sup>11</sup> )              |       |       | 7.5  | 1.96  | 13.72 | 13.16 |
| PPG-14 butyl ether ( <sup>2</sup> )                | 2.45  | 15.68 |      |       |       |       |
| Cetyl dimethicone copolyol ( <sup>12</sup> )       | 1.0   | 1.0   | 1.0  | 1.0   | 1.0   | 1.0   |
| Oryzanol ( <sup>6</sup> )                          | 5.0   | 5.0   | 3.0  | 5.0   | 5.0   | 4.0   |
| $\beta$ -Sitosterol ( <sup>5c</sup> )              | 5.0   | 5.0   | 3.0  | 5.0   | 5.0   | 4.0   |
| 57.5% Rezal 36 ( <sup>17</sup> )                   |       |       |      |       |       |       |
| Zirconal 50 ( <sup>13</sup> )                      | 40.0  | 40.0  |      | 40.0  | 40.0  | 40.0  |
| Summit AZG-375 ( <sup>18</sup> )                   |       |       | 20.0 |       |       |       |
| Water                                              |       |       | 15.0 |       |       | 4.0   |
| Propylene Glycol ( <sup>19</sup> )                 |       |       | 5.0  |       |       |       |
| Glycerol ( <sup>14</sup> )                         |       |       |      |       |       |       |
| Hardness (mm)                                      | 9.3   | 9.3   | 11.2 | 8.28  | 7.92  | 12.06 |

Table 5 cont

| Example No                                         | 69    | 70    | 71    | 72    | 73    |  |
|----------------------------------------------------|-------|-------|-------|-------|-------|--|
| cyclomethicone ( <sup>1</sup> )                    | 34.3  | 34.3  | 34.3  | 31.44 | 13.65 |  |
| C <sub>12-15</sub> alkyl benzoate ( <sup>3</sup> ) | 8.82  | 8.82  | 8.82  | 6.03  | 12.28 |  |
| Isopropyl myristate ( <sup>11</sup> )              | 5.88  | 5.88  | 5.88  | 6.03  | 19.57 |  |
| PPG-14 butyl ether ( <sup>2</sup> )                |       |       |       |       |       |  |
| Cetyl dimethicone copolyol ( <sup>12</sup> )       | 1.0   | 1.0   | 1.0   | 1.00  | 1.00  |  |
| Oryzanol ( <sup>6</sup> )                          | 3.0   | 3.0   | 3.0   | 2.75  | 5.7   |  |
| $\beta$ -Sitosterol ( <sup>5c</sup> )              | 3.0   | 3.0   | 3.0   | 2.75  | 3.8   |  |
| 57.5% Rezal 36 ( <sup>17</sup> )                   |       |       |       |       |       |  |
| Zirconal 50 ( <sup>13</sup> )                      |       |       |       | 40.0  | 40.0  |  |
| Summit AZG-375 ( <sup>18</sup> )                   | 22.0  | 22.0  | 22.0  |       |       |  |
| Water                                              | 16.5  | 11.0  | 11.0  | 10.0  | 4.0   |  |
| Propylene Glycol ( <sup>19</sup> )                 |       | 11.0  |       |       |       |  |
| Glycerol ( <sup>14</sup> )                         | 5.5   |       | 11.0  |       |       |  |
| Hardness (mm)                                      | 13.74 | 10.71 | 12.36 | 14.5  | 10.9  |  |

5

**Examples 74 to 81**

In these Examples, formulations according to the present invention were made by the general method employed for Examples 39-55 with other emulsifiers or without an explicit emulsifier.

10

Table 6

| Example No                               | 74    | 75    | 76    | 77    | 78    | 79    | 80    | 81    |
|------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| cyclomethicone<br>( <sup>1</sup> )       | 33.78 | 33.78 | 33.78 | 33.78 | 33.78 | 33.78 | 33.78 | 34.65 |
| Isopropyl<br>myristate ( <sup>11</sup> ) | 5.79  | 5.79  | 5.79  | 5.79  | 5.79  | 5.79  | 5.79  | 5.79  |
| Finsolve TN ( <sup>3</sup> )             | 8.69  | 8.69  | 8.69  | 8.69  | 8.69  | 8.69  | 8.69  | 8.69  |
| Abil EM90 ( <sup>12</sup> )              | 1.75  |       |       |       |       |       |       |       |
| Lamemform TGI<br>( <sup>20</sup> )       |       |       |       | 0.875 | 1.75  |       |       |       |
| Dehymuls PGPH<br>( <sup>21</sup> )       |       |       | 1.75  | 0.875 |       |       |       |       |
| Quest PGPR ( <sup>22</sup> )             |       | 1.75  |       |       |       |       |       |       |
| Prisorine 3791<br>( <sup>23</sup> )      |       |       |       |       |       | 1.75  | 0.875 |       |
| Prisorine 3792<br>( <sup>24</sup> )      |       |       |       |       |       |       | 0.875 |       |
| Oryzanol ( <sup>b</sup> )                | 3.0   | 3.0   | 3.0   | 3.0   | 3.0   | 3.0   | 3.0   | 3.03  |
| $\beta$ -Sitosterol<br>( <sup>5c</sup> ) | 3.0   | 3.0   | 3.0   | 3.0   | 3.0   | 3.0   | 3.0   | 3.03  |
| Zirconal 50 ( <sup>13</sup> )            | 40.0  | 40.0  | 40.0  | 40.0  | 40.0  | 40.0  | 40.0  | 40.04 |
| water                                    | 4.0   | 4.0   | 4.0   | 4.0   | 4.0   | 4.0   | 4.0   | 4.04  |
| Hardness (mm)                            | 12.8  | 13.1  | 12.2  | 11.8  | 12.8  | 16.2  | 12.2  | 11.6  |

**Examples 82 to 87**

In these Examples, the formulations were obtained by the  
5 following general method:-

A continuous oil phase was prepared by first introducing  
oryzanol into a mixture of the oils and the emulsifier.  
The mixture was heated to and then maintained at  
10 approximately 95-100°C, with gentle mixing in a Silverson  
mixer until the oryzanol had dissolved. The  $\beta$ -sitosterol  
was then introduced and allowed to dissolve under the  
same conditions. A disperse phase (also referred to as  
15 the internal phase) was prepared by heating a solution of  
aluminium zirconium active in water or a mixture of water  
and polyol to a similar temperature as the continuous oil  
phase. The disperse phase was then introduced slowly into  
the oil phase whilst progressively increasing the mixing  
speed of the Silverson mixer. When the disperse phase had  
20 been completely introduced, the formulation was mixed at  
higher speed for a further 5 minutes, then poured in the

stick barrels and allowed to cool naturally to ambient laboratory temperature.

Table 7

| Example No                            | 82          | 83    | 84    | 85    | 86    | 87    |
|---------------------------------------|-------------|-------|-------|-------|-------|-------|
| Constituent                           | % by Weight |       |       |       |       |       |
| DC245 ( <sup>23</sup> )               | 25.06       | 24.11 | 21.08 | 20.61 | 17.10 | 13.60 |
| Silkflo 364NF ( <sup>10</sup> )       | 31.67       | 30.46 | 26.65 | 26.04 | 21.62 | 17.20 |
| Fluid AP ( <sup>2</sup> )             | 6.27        | 6.03  | 5.27  | 5.15  | 4.28  | 3.40  |
| Abil EM90 ( <sup>12</sup> )           | 1           | 1     | 1     | 1     | 1     | 1     |
| Zirkonal 50 ( <sup>13</sup> )         | 24          | 24    | 40    | 40    | 40    | 40    |
| Glycerol ( <sup>14</sup> )            | 6           | 6     | -     | -     | 10    | 10    |
| water                                 | -           | -     | -     | -     | -     | 10    |
| $\beta$ -sitosterol ( <sup>5c</sup> ) | 3           | 4.2   | 3     | 3.6   | 3     | 2.4   |
| Oryzanol ( <sup>6</sup> )             | 3           | 4.2%  | 3     | 3.6   | 3     | 2.4   |
| Internal phase                        | 30          | 30    | 40    | 40    | 50    | 60    |
| Hardness (mm)                         | 12.9        | 11.2  | 11.8  | 10.7  | 10.4  | 14.1  |

## 5 Hardness Measurements by Penetrometer

### Equipment

Lab Plant PNR 10 penetrometer

- 10 Seta wax needle, mass = 2.5g cone angle at the point of the needle specified to be 9°10'  $\pm$  15' (ASTM D1321; IP376; DIN 51579)

### Conditions

- Depth limit = 50mm  
15 Drop time = 5 secs

### Operational

- 20 Penetration measurements on a stick were performed in the stick barrel. The stick was wound up to above the barrel surface, and then cut to leave a flat, uniform surface. The needle was carefully lowered to the stick surface, and then a penetration hardness measurement was conducted by allowing the needle in its holder to drop under its combined weight of 50g for a period of 5 seconds after

which the penetration depth is noted. This process was carried out at six different points on the stick surface. Each stick was then wound up a further 1cm, and a new surface was cut. Six more penetration hardness  
5 measurements were made.

The hardness reading quoted is the average value of the 12 measurements.

- 10 An appropriate hardness for antiperspirant material intended for use in an open-ended dispensing container is less than 30mm, particularly in the range of 5 to 20mm.

#### **Measurement of Deposits**

- 15 The procedure involves instrumentally applying a sample of an AP stick to a substrate using a pay-off rig under standardised conditions and then measuring the mean level of whiteness of the deposits using image analysis.

#### **20 I) Application of the Sample to the Substrate**

Substrates were

- a: 12x28cm strip of abrasive grey 3M™ P800 WetorDry™ carborundum paper  
b: 12x28cm strip of black Worsted wool fabric which is  
25 re-enforced with hypoallergenic surgical tape [3M™ Transpore (1527-2)] to give sufficient rigidity.

The AP sticks were previously unused and with domed top surface unaltered.

30

- The pay-off rig comprised a flat base on to which a flat substrate was attached by a clip at each end. The stick was wiped across the substrate under standard conditions - a spring biased standard downward force onto the substrate  
35 and speed of motion.

Each stick was temperature conditioned in the laboratory overnight before the measurement was made. The stick was

laterally passed across the substrate eight times. The substrate was carefully removed from the rig and the deposit score, i.e. assessment of whiteness, measured 24 hrs later using image analysis.

5

## II) Image analysis

The measurement was conducted using a Sony<sup>TM</sup> XC77 Monochrome video camera with a Cosmical<sup>TM</sup> 16mm focal length lens positioned vertically above a black table which was illuminated from a high angle using fluorescent tubes to remove shadowing.. The apparatus was initially calibrated using a reference grey card, after the fluorescence tubes had been turned on long enough for them to give a steady light output. The sample substrate with a deposit thereon from the deposit test was placed on the table and the camera used to capture an image. An area of the image was selected and analysed using a Kontron IBAS image analyser. This notionally divided the image into a large array of pixels and measured the grey level of each pixel on a scale of from 0 (black) through to 255 (white). The average of the grey intensity was calculated. This was an indication of the whiteness of the deposit, higher average numbers indicating a whiter deposit.

25

**Claims:**

1. An antiperspirant composition comprising an antiperspirant active, a liquid carrier and a structurant including a sterol to thicken or solidify the composition characterised in that the structurant comprises an effective concentration of a combination of at least one sterol and at least one sterol ester.
2. A composition according to claim 1 characterised in that the structurant comprises sterol and sterol ester in a mole ratio of from 6:1 to 1:4, preferably 3:1 to 1:2.
3. A composition according to either preceding claim characterised in that the combined weight of the sterol and sterol ester is from 0.5 to 20%, and preferably from 1 to 15%.
4. A composition according to any preceding claim characterised in that the sterol comprises 4 fused rings substituted by an aliphatic, cycloaliphatic or aromatic group.
5. A composition according to claim 4 characterised in that the sterol is substituted by a linear or branched saturated or unsaturated aliphatic hydrocarbon containing up to 20 and preferably from 4 to 14 carbon atoms.
6. A composition according to claim 5 characterised in that the sterol is  $\beta$  sitosterol or campesterol or cholesterol, or a hydrogenated derivative thereof.
7. A composition according to claim 6 characterised in that the sterol is  $\beta$  sitosterol.

8. A composition according to any preceding claim characterised in that the sterol ester is a phenolic acid ester.
9. A composition according to claim 8 characterised in that the ring structure of the sterol ester matches the ring structure of the sterol.
10. A composition according to any preceding claim characterised in that the sterol ester is substituted by a linear or branched saturated or unsaturated aliphatic hydrocarbon containing up to 20 and preferably from 4 to 14 carbon atoms.
11. A composition according to claim 10 characterised in that the aliphatic hydrocarbon substituent is a branched unsaturated substituent which contains from 5 to 10 carbons.
12. A composition according to claim 11 characterised in that the sterol ester is  $\gamma$  oryzanol.
13. A composition according to any preceding claim characterised in that it contains from 1 to 10% by weight of the combined weight of  $\beta$  sitosterol and oryzanol in a mole ratio of from 3:1 to 1:2.
14. A composition according to any preceding claim characterised in that the antiperspirant active comprises an aluminium, zirconium or aluminium/zirconium halohydrate, an activated aluminium, zirconium or aluminium/zirconium halohydrate, or an aluminium, zirconium or aluminium/zirconium complex or an activated aluminium, zirconium or aluminium/zirconium complex.
15. A composition according to claim 14 characterised in that the antiperspirant is selected from

chlorohydrates of aluminium, zirconium or mixed zirconium - aluminium, and complexes of such chlorohydrates, any of which chlorhydrate or complex is optionally activated.

16. A composition according to claim 14 or 15 characterised in that the antiperspirant active is a mixed zirconium - aluminium chlorohydrate, or an activated aluminium chlorohydrate or a complex of a chlorohydrate of aluminium plus zirconium with glycine, optionally activated.
17. A composition according to any preceding claim characterised in that the proportion of antiperspirant active is from 5 to 40% by weight.
18. A composition according to any preceding claim characterised in that contains a volatile silicone and optionally a non-volatile silicone and/or a liquid non-silicone hydrophobic organic carrier selected from hydrocarbons, hydrophobic aliphatic esters, aromatic esters, hydrophobic alcohols and hydrophobic ethers.
19. A composition according to any preceding claim characterised in that it is anhydrous and contains suspended particulate antiperspirant active.
20. A composition according to any of claims 1 to 17 characterised in that the carrier comprises an aqueous phase containing at least a fraction of the antiperspirant active.
21. A composition according to claim 20 characterised in that the aqueous phase contains a di or polyol.



22. A composition according to claim 20 or 21 characterised in that it is in the form of an emulsion
23. A composition according to claim 22 characterised in that the dispersed phase in the emulsion is from 5 to 80% by weight and the continuous phase from 95 to 20% by weight.
24. A composition according to any of claims 20 to 23 characterised in that it contains from 0.1 to 10% by weight of an emulsifier.
25. A composition according to any preceding claim characterised in that it contains a humectant selected from glycerol and sorbitol.
26. A process for the production of an antiperspirant stick comprising the steps of
- 1 incorporating into a liquid carrier a structurant at an effective concentration and in an amount sufficient to thicken or structure the carrier to produce a solid or soft solid,
  - 2 rendering the structurant-containing mixture or one or more of its constituents mobile at an elevated temperature
  - 3 mixing the liquid carrier with an antiperspirant active to form an antiperspirant-containing mixture, steps 2 and 3 being conducted either before, after or simultaneously with step 1
  - 4 introducing the mobile mixture into a mould which preferably is a dispensing container and
  - 5 cooling or permitting the mobile mixture to cool to a temperature at which it is thickened or structured.
- characterised in that the structurant comprises a combination of at least one sterol and at least one sterol ester.

27. A process according to claim 26 characterised in that the sterol and sterol ester are introduced into simultaneously or sequentially into a hydrophobic fraction of the carrier or separate fractions thereof at elevated temperature and mixed until dissolved, and the resultant solution or solutions is shear mixed with the antiperspirant active and any aqueous constituent.
28. A method for preventing or reducing perspiration on human skin comprising topically applying to the skin an antiperspirant composition comprising an antiperspirant active, a liquid carrier and a structurant which comprises an effective concentration of a combination of at least one sterol and at least one sterol ester.

**Abstract****Antiperspirant Compositions.**

Antiperspirant compositions herein comprise an  
5 antiperspirant active, a carrier and a structurant for the  
carrier which comprises an effective concentration of a  
combination of at least one sterol and at least one sterol  
ester, to form a solid or a soft solid. The compositions  
can be anhydrous and in the form of a suspension of  
10 antiperspirant active, or can comprise aqueous emulsions.

A particularly suitable sterol comprises  $\beta$  sitosterol and  
a particularly preferred sterol ester comprises oryzanol.  
Preferably the mole ratio of sterol to sterol ester is in  
15 the range of 3:1 to 1:2.