

28
96

Señor

SUPERINTENDENTE DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

E. _____ S. _____ D. _____

SUPERINDUSTRIA Y COMERCIO
Raditacion : 00026091 00000001
Fecha (AMD): 2000-05-19 16:29:17
Tramite : 032 PATENTES D 1 REGISTRO/ 329 COMPLETEN
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios: 66

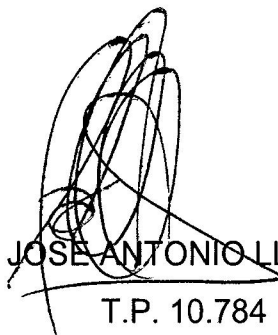
Re: P1.-UNILEVER N.V..-Solicitud de Patente de Invención para
"COMPOSICIONES COSMETICAS".-Clase A.61K.-Expediente
número 00-026.091.-

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 de la primera solicitud de patente presentadas para el invento arriba nombrado **respecto de la cual reclamo prioridad**, a saber la solicitud británica número 9908212.5 de 12 de Abril de 1999, junto con su traducción oficial, correspondiente a las legalizaciones y reivindicaciones de dicho documento;
 - (2) Copia debidamente autenticada por el Notario Sexto del Circulo de Bogotá, del documento que acredita la calidad de Traductor Oficial del señor Eduardo Calado Noguera quien elaboró la traducción oficial No. 0247 de la solicitud número 9908212.5, respecto de la cual se reivindica prioridad en el presente caso.
 - (3) Documento que acredita el traspaso que los autores del invento de la referencia hacen a favor de mi poderdante, de sus derechos sobre el mismo, debidamente legalizado hasta por el Ministerio de Relaciones Exteriores de Colombia bajo el número 065342 de 22 de Mayo de 2000.
 - (4) Traducción Oficial No. 105, debidamente legalizada hasta por el Ministerio de Relaciones Exteriores de Colombia bajo el número 066628 de 24 de Mayo de 2000, correspondiente a las legalizaciones de dicho documento de traspaso.

~~92~~
97

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

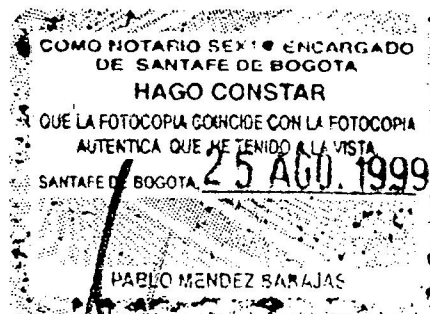
EL SUSCRITO JEFE DEL AREA DE
LEGALIZACIONES DEL MINISTERIO DE
RELACIONES EXTERIORES

CERTIFICA

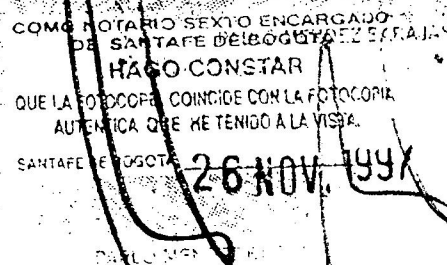
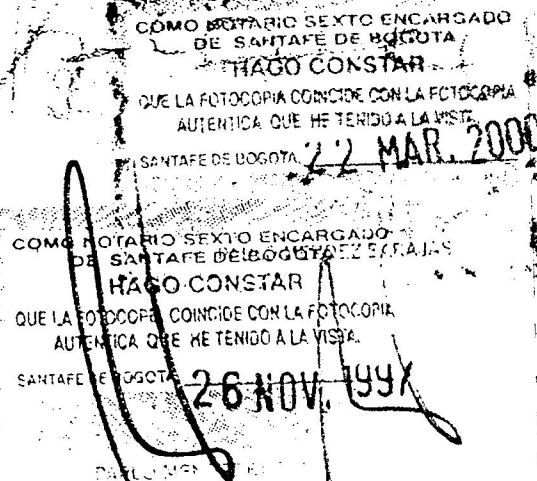
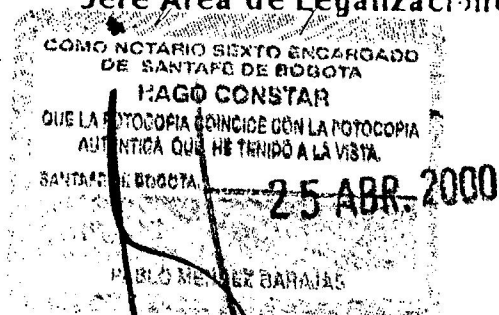
Que revisados los registros que se llevan en la oficina de Legalizaciones aparece la firma del señor **EDUARDO CALADO NOGUERA**, como traductor e intérprete oficial para los idiomas INGLES- ESPAÑOL, ESPAÑOL- INGLES, según resolución 541 del 27 de febrero de 1976.

La anterior certificación se expide a solicitud del interesado quien se identificó con cédula de ciudadanía 17.177.588 expedida en Bogotá.

Dada en Santa Fe de Bogotá, D.C., a los seis (6) de noviembre de 1997.



Blanca Acosta de García
BLANCA ACOSTA DE GARCIA
Jefe Area de Legalizaciones (e)



101
99

República de Colombia



Ministerio de Justicia y del Derecho

EL SECRETARIO GENERAL (E) DEL MINISTERIO DE
JUSTICIA Y DEL DERECHO

CERTIFICA:

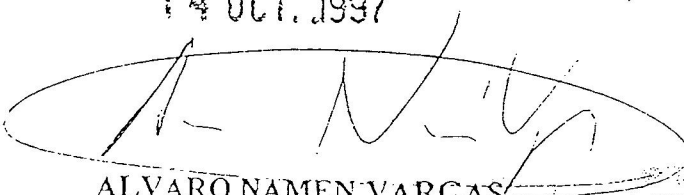
Que por Resolución 541 del 27 de febrero de 1976, le fue expedida licencia para ejercer funciones de Traductor e Intérprete Oficial en los idiomas INGLÉS y ESPAÑOL al señor EDUARDO CALADO NOGUERA, identificado con la cédula de ciudadanía No. 17.177.588 expedida en Bogotá.

Que dicha Resolución se encuentra vigente en la fecha.

Se expide la presente certificación a solicitud del interesado.

Dada en Santa Fe de Bogotá, D.C., a

14 OCT. 1997


ALVARO NAMEN VARGAS

COMO NOTARIO SEÑALADO ENCARGADO
DE SANTA FE DE BOGOTA
HAGO CONSTAR
QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA
AUTENTICA QUE HE TENIDO A LA VISTA.
SANTA FE DE BOGOTA 25 AGO 1999
PABLO MENDEZ BARRALES

COMO NOTARIO SEÑALADO ENCARGADO
DE SANTA FE DE BOGOTA
HAGO CONSTAR
QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA
AUTENTICA QUE HE TENIDO A LA VISTA.
SANTA FE DE BOGOTA 26 NOV. 1997

COMO NOTARIO SEÑALADO ENCARGADO
DE SANTA FE DE BOGOTA
HAGO CONSTAR
QUE LA FOTOCOPIA COINCIDE CON LA FOTOCOPIA
AUTENTICA QUE HE TENIDO A LA VISTA.
SANTA FE DE BOGOTA 25 ABR. 2000
PABLO MENDEZ BARRALES

Hago constar que esta copia coincide con documento original
solicito para la verificación que la fotocopia coincide con la fotocopia
SANTA FE DE BOGOTA 04 NOV. 1997
PABLO MENDEZ BARRALES

ICM/mmc

Abril 14, 2000
Traducción Oficial No.0247
REF:UNILEVER N.V.
Patente No.9908212.5

Caso: Uni q/P2248/co
UNILEVER N. V.

La Oficina de Patentes
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

LA OFICINA DE PATENTES

Yo, el abajo firmante, funcionario debidamente autorizado de acuerdo a la sección 74(1) y (4) de Actos de Patentes y Diseños 1994, otorgado para firmar y expedir certificados a nombre de Comptroller- General, por la presente certifico que la copia anexada aquí es una fiel copia de los documentos originales tal y como fueron registrados en relación con la solicitud de Patentes identificadas en el presente documento.

De acuerdo con las regulaciones de 1982 de Patentes (re-registro de compañías) , si una empresa es mencionada en este certificado o cualquiera de los documentos anexos, ha sido esta re-registrada en el Acta de Compañías bajo el mismo nombre con el cuál fué registrado inmediatamente en ese momento antes de tal re- registro, salvo a sustición tal como, inclusión tal como, la última parte del nombre con las palabras "Compañía Pública Limitada" o su equivalente en Galés, referencias al

Edwards Caladog

103
101

nombre de la compañía en este certificado o cualquier otros documento anexado debe ser tratado como referencias con el nombre con el cual fué re-registrados.

De acuerdo a los reglamentos, las palabras "Compañía Pública Limitada" puede ser remplazados con las siglas Cia. Ltda, C.Ltada, C.P.L. o CPL.

El re-registro bajo el Acta de Compañías no constituye una nueva empresa legal sino que solamente sujeta a la compañía a ciertas reglas adicionales legales impuestas por la compañía.

HAY FIRMA : R. Mahoney

FECHA: Abril 6, 2000

Hay sello de "The Patent Office" plastificado de color rojo

Edwardo Calado

102
~~104~~

LA OFICINA DE PATENTES

PETICION PARA OTORGAR UNA PATENTE

Actas de Patentes 1977

(Regulación 16)

Cardiff Road

Newport

Gwent NP9 1RH

Hay sello de la Oficina de Patente

Fecha: Abril 12/1999

1. Su referencia : MFF/LP5770367
2. Número de solicitud de patente: No.9908212.5
Fecha -Abril 12, 1999
3. Nombre completo de cada solicitante, dirección y código postal

UNILEVER PLC

UNILEVER HOUSE,
BLACKFRIARS
LONDON, EC4P 4BQ

Número de ADP de Patente 1628002

Hay sello de la Oficina de Patentes de Londres con fecha: Abril 12/99

Si el solicitante es una empresa escriba el
nombre del pais/estado de su incorporación. REINO UNIDO.

4. Título de la invención: Composiciones Cosméticas

Edwardo Delgado

5. Nombre de su suplente (si tiene uno)

MEWBURNS ELLIS

"Dirección para detalles de servicio" en el
Reino Unido para toda correspondencia:

YORK HOUSE
23 KINGSWAY
LONDRES
WC2B 6HP

Número de ADP de Patente

109006

8. Si existe una declaración del inventor o un derecho para otorgar una patente y sea necesario confirmar esta petición ? Si

Responda s "Si" en el cado de que:

- a) cualquier solicitante mencionado en la parte 3 no sea un inventor, o
 - b) hay un inventor que no aparece mencionado como solicitante, o
 - c) cualquier solicitante mencionado forma parte de la empresa;
- Ver nota (d)

9. Favor llenar los números de páginas por cada de los siguientes item incluidos en esta solicitud.

Hojas continuadas de esta forma. 0

Descripción 71

Reivindicación (es) 7

Resumen 0

Gráficas 0

Hay firma (ilegible)

11. Yo/Nosotros solicitamos la otorgación de una patente en base a esta solicitud. Firmado por: MICHAEL FORD, Funcionario autorizado.
Fecha: Abril 9, 1999.

12. Nombre de persona que se pueda contactar en el Reino Unido y número telefónico: Michael Ford Tel: 0171 240 4405

Edoardo

106
104

REIVINDICACIONES:

1. Una composición cosmética que consta de un portador líquido de agua inmiscible y un estructurante por el cual es eficaz a la composición de gelatina cuando la temperatura se enfría, en la cual la solución móvil es estructural en el portador líquido, y se caracteriza en que lo estructural tiene una gelatinidad enthalpy en el portador líquido con una magnitud de al menos 45 kJ/mole.

2. Una composición cosmética que consta de un portador líquido de agua inmiscible y estructural por el cual es eficaz a la composición de gelatina cuando la temperatura se enfría en la cual la solución móvil estructural en el portador líquido se caracteriza en que el el estructural es capaz de congelar uno o más

18) decametilo ciclopentasiloxano

19) Una mezcla de un 80:20 % del peso de decametilo ciclopentasiloxano y C12-15 linear alquilo benzoato

20) Una mezcla de un 80:20 % del peso de decametilo ciclopentasiloxano y alcohol de isosteárido.

Edwards Calado

~~107~~
105

21) Alcohol isostearilo

con una congelación en por lo menos uno de los líquidos con una magnitud de al menos 45 kJ/mole.

3. Una composición de acuerdo a la reivindicación 2 en el cual el estructural es capaz de congelar en un 80:20 % del peso una mezcla de decametilo ciclopentasiloxano y alcohol de isostearilo con una congelación de enthalpy, el cual tiene una magnitud de al menos 45 kJ/mole.

4. Una composición de acuerdo a cualquiera de las reivindicaciones anteriores en el cual la composición es una emulsión con un hidrofílico, preferiblemente miscible en agua, en una fase dispersa adicionalmente a dicho líquido de agua inmiscible en la fase continua.

5. Una composición cosmética la cual es una emulsión estructurada que consta de

Eduardo Caladoh

~~108~~
106

i) Una fase continua que contiene un portador líquido de agua inmiscible y un estructural presente en una fase continua, la cual es eficaz para que la composición se torne gelatinosa durante el enfriamiento a una temperatura en el cual el estructural se encuentra en la solución del portador líquido y

ii) Una fase dispersa la cual es una solución de desodorante activo en agua, solvente soluble en agua y mezcla de estas.

se caracterizan en que el estructurante tiene una congelación de enthalpy en un portador líquido con una magnitud de por lo menos 30 kJ/mole.

6. Una composición cosmética la cual es una emulsión estructurada que consta de:

i) Una fase continua que contiene un portador líquido de agua inmiscible y un estructurante presente en una fase continua, la cual es eficaz para que la composición se torne gelatinosa durante el enfriamiento a una temperatura en el cual el estructural se encuentra en una solución en el portador líquido y

Edwardo Calado

109
107

ii) Una fase dispersa la cual es una solución de desodorante activo en agua, solvente soluble en agua y mezcla de estas.

se caracterizan en que el estructural tiene capacidad de congelar uno o más de:

22) decametil ciclopentasiloxano

23) Una mezcla de un 80:20 % del peso de decametilo ciclopentasiloxane y C12-15 linear alquilo benzoato

24) Una mezcla de un 80:20 % del peso de decametilo ciclopentasiloxane y alcohol de isostearilo.

25) Alcohol isostearilo

con una congelación en por lo menos uno de los líquidos con una magnitud de al menos 30 kJ/mole.

Eduardo Caludo H.

140
108

7. Una composición de acuerdo a la reivindicación 6 en la cual el estructural es capaz de congelar a un 80:20% del peso de una mezcla de decametilo ciclopentasiloxano y alcohol isostearilo con una congelación de enthalpy la cual tiene una magnitud de por lo menos 30 kJ/mole.

8. Una composición de acuerdo a cualquiera de las reivindicaciones de la 4 hasta la 7 en el cual la fase dispersa contiene un diol y un poliol.

9. Una composición de acuerdo a cualquiera de las reivindicaciones desde la 4 hasta la 8 la cual contiene desde 0.1% hasta 10 % del peso de una emulsión no ionica.

10. Una composición de acuerdo a cualquiera de las reivindicaciones desde la 4 hasta la 9 la cual no contiene más de 8% del peso de etano o de cualquier alcohol monohídrico con una presión de vapor superior de 1.3 kPa a 22 grados centígrados.

11. Una composición de acuerdo a cualquiera de las reivindicaciones desde la 1 hasta la 3 en la cual la composición es una

Edwards

suspensión con un material particulado sólido disperso en dicho portador líquido.

12. Una composición de cosmético de acuerdo a cualquiera de las reivindicaciones anteriores en el cual el portador líquido de agua inmiscible contiene una silicona volátil y opcionalmente una silicona no volátil y/o una no silicona hidrofóbica líquida orgánica seleccionada de hidrocarburos, ésteres alifáticos hidrofóbicos, ésteres aromáticos, alcoholes hidrofóbicos y ésteres hidrofóbicos.

13. Una composición de acuerdo a cualquiera de reivindicaciones anteriores en el cual el portador líquido de agua inmiscible contiene aceite de silicona en una cantidad como mínimo de por lo menos un 10% del peso de la composición.

14. Una composición de acuerdo a cualquiera de las reivindicaciones anteriores que contienen desde 0.1 hasta 12% del peso del estructural.

15. Una composición de acuerdo a cualquiera de las reivindicaciones anteriores la cual contienen más de un 5% del

Edmundo Salas

11
109

peso de alcoholes grasos el cual se vuelve sólido a 20 grados centígrados.

112
110

16. Una composición de acuerdo a cualquiera de las reivindicaciones anteriores la cual sea un compuesto de desodorante la cual consiste de un desodorante activo.

17. Una composición de acuerdo a la reivindicación 1 la cual es un compuesto desodorante la cual consiste de un desodorante activo en partículas en suspensión de dicho portador líquido de agua inmisible.

18. Una composición de acuerdo a cualquiera de las reivindicaciones desde la 4 hasta la 10 la cual es un compuesto de desodorante que consiste de un desodorante activo disuelto en dicha fase dispersa.

19. Una composición de acuerdo a cualquiera de las reivindicaciones desde la 16 hasta la 18 en la cual el desodorante activo consiste de un aluminio y/o un halohidrato de circonio, un aluminio activo y/o un halohidrato de circonio o un aluminio y/o un complejo de circonio.

Edw. Salas

113
111

20. Una composición de acuerdo a la reivindicación 19 la cual es un halohidrato o complejo en el cual tanto el aluminio como el circonio se encuentran ambos presentes.

21. Una composición de acuerdo a la reivindicación de cualquiera de las reivindicaciones desde la 16 hasta 20 en la cual la proporción del desodorante activo es desde 5 hasta 40 % del peso de la composición.

22. Una composición de acuerdo a cualquiera de las reivindicaciones anteriores en la cual una gelatina firme en cuanto a que una aguja penetrometrica penetre con un ángulo a cono de unos 9 grados y 20 minutos no más de 30 mm cuando se permite que penetre bajo un peso total de 50 gramos por 5 segundos.

23. Una composición de acuerdo a cualquiera de las reivindicaciones anteriores la cual es translúcida o transparente.

24. Una composición de acuerdo a la reivindicación 24 la cual tiene por lo menos un 1% y preferiblemente un 3%, transmisión de

Edwardo Paludo

114
112
luz a 580 nm a través de 1 cm de espesor de la composición a 22 grados centígrados.

25. Un producto desodorante el cual consiste en distribuir el recipiente que tenga una apertura para despachar el contenido del recipiente, medio para empujar el contenido por dicha apertura , y una composición de acuerdo a cualquiera de las reivindicaciones anteriores acomodadas dentro del recipiente.

26. Un producto de acuerdo a la reivindicación 25 en la cual la composición se encuentra en la forma de bastón y el recipiente tiene un final con una apertura en el cual la parte final del bastón de la composición se encuentra expuesta para uso.

27. Un proceso para la producción de un composición de acuerdo a cualquiera de las reivindicaciones de 1 hasta la 20 las cuales constan de los siguientes pasos que necesariamente no tienen que estar en este orden:

- incorporar un estructural en un portador líquido de agua inmiscible

Edmundo Calasch

415
113

- mezclar de manera opcional el portador líquido con un sólido disperso o una fase líquida,
- calentar el portador líquido o una mezcla que lo mantenga a una temperatura elevada en el cual el estructural es soluble en el portador líquido de agua inmiscible,

es soluble en el portado líquido de agua inmiscible seguido por un enfriamiento o permitir que la mezcla se enfríe a una temperatura en la que se solidifique o espesen.

28. Un proceso de acuerdo a la reivindicación 27 en la cual se incluye el paso de verter la mezcla a una temperatura elevada en un recipiente y permitir que se enfríe allí mismo como para producir un producto de acuerdo a la reivindicación 25 o reivindicación 26.

29. Un método para prevenir o reducir el sudor en la piel humana el cual consiste en aplicar tópicamente a la piel una composición de acuerdo a cualquiera de las reivindicaciones entre la 16 y 20.

Edwards Calado N.



The
Patent
Office



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

L. Mahoney

Dated 6 April 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/LP5770367

112 APR 1999

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

9908212.5

12APR99 E439054-1 002823
P01/7700 0.00 - 9908212.5

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 COSMETIC COMPOSITIONS

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:

NO 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))

20
Patents Form 1/77

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 71

Claim(s) 7

Abstract 0

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

Michael F. Ford

Date

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

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) 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.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

COSMETIC COMPOSITIONS418
DUPLICATE
716

73463

FIELD OF THE INVENTION

5 The present invention relates to cosmetic compositions for application to human skin. Significant forms of the invention are concerned with antiperspirant compositions for application to human skin, especially the axilla. However, the invention can also be applied
10 to other forms of cosmetic composition.

BACKGROUND OF THE INVENTION AND SUMMARY OF PRIOR ART

 A wide variety of cosmetic compositions for
15 application to human skin make use of a thickened or structured liquid carrier to deliver colour or some other active material to the surface of the skin. A significant example of such cosmetic compositions are antiperspirant compositions which are widely used in
20 order to enable their users to avoid or minimise wet patches on their skin, especially in axillary regions.

 Cosmetic compositions have been made in a variety of product forms. One of these is a so-called "stick" which
25 is usually a bar of an apparently firm solid material held within a dispensing container and which retains its structural integrity and shape whilst being applied.

When a portion of the stick is drawn across the skin surface a film of the stick composition is transferred to the skin surface. Although the stick has the appearance of a solid article capable of retaining its own shape for a period of time, the material usually has a structured liquid phase so that a film of the composition is readily transferred from the stick to another surface upon contact. Examples of cosmetic compositions which are, or can be, marketed in a stick form are lipsticks, lip salves and eyebrow pencils. The stick form has been used in particular for deodorant and antiperspirant compositions where the composition includes a deodorant active material or an antiperspirant active material respectively.

Another possibility is that a stick is a softer solid composition accommodated in a dispensing container which in use extrudes the composition through one or more apertures.

Antiperspirant sticks and other cosmetic compositions can be divided into three categories. Suspension sticks contain a particulate material, notably a particulate antiperspirant active material, suspended in a structured carrier liquid phase. Emulsion sticks normally have a hydrophilic phase forming an emulsion with a second, more hydrophobic, liquid phase. One of

119
117

the phases contains an active material. Solution sticks typically have the active material dissolved in a structured liquid phase; this phase may be organic solvent or may be a mixture of water and a water-miscible organic solvent. This classification into suspension, emulsion and solution types can be applied to both firm and soft solid compositions.

Besides firm and soft sticks, a number of cosmetic compositions have taken the form of liquids which are formulated to be somewhat viscous and hence pour and flow more slowly than water. One example is antiperspirant compositions in liquid form, such as applied using a roll-on applicator.

There is substantial literature on the structuring or thickening of cosmetic compositions which is frequently accomplished using some form of thickening agent as part of the composition.

Some compositions have a substantial viscosity, which may even make them capable of retaining their own shape for a time, because of transient interactions between molecules of a thickening agent in the liquid.

This is characteristic of compositions which are thickened with polymers. Thickening can be attributed to

interactions between polymer molecules.

It is characteristic of such thickened compositions that their viscosity can be achieved or recovered on standing at room temperature. If subjected to shear their viscosity reduces (hence they are described as shear thinning but the viscosity recovers [to its original value] if the composition is subsequently allowed to stand at room temperature.

Compositions which have two phases, i.e. compositions which are an emulsion or a suspension may also have substantial viscosity, even to the extent of being able to sustain their own shape.

Here too it is characteristic of the composition that - provided the composition is stable - its viscosity will recover spontaneously if it is reduced by subjecting the composition to shear.

Compositions have also been given structure and an enhanced viscosity or rigidity by the incorporation of a structurant (also referred to as a gellant or gelling agent) which causes the liquid to gel upon cooling from an elevated temperature.

Gel formation takes place as an exothermic event.

120
118

within a temperature range referred to as the gel point or gel temperature. Upon reheating, melting of the gel takes place as an endothermic event within a temperature range. When the gel melts, the structurant goes into solution in the liquid. Such gels can be disrupted by shearing and do not recover their viscosity for a long time, if at all unless remelted, although a small partial recovery may be observed.

10 One material which is well known to form gels is 12-hydroxy stearic acid which is discussed in Terech et al "Organogels and Aerogels of Racemic and Chiral 12-hydroxy octadecanoic Acid", Langmuir Vol 10, 3406-3418, 1994. The material is commercially available from
15 Ajinomoto and from Caschem.

US-A-5750096 is one of several documents which teaches that gelation can be brought about using esters or amides of 12-hydroxy stearic acid. The alcohol used
20 to form such an ester or the amine used to form such an amide may contain an aliphatic, cycloaliphatic or aromatic group with up to 22 carbons therein. If the group is aliphatic it preferably contains at least three carbon atoms. A cycloaliphatic group preferably contains
25 at least five carbon atoms and may be a fixed ring system such as adamantyl.

N-acyl amino acid amides and esters are also known to structure liquids. We have established that they do so by forming fibrous networks. They are described in US patent 3969087. N-Lauroyl-L-glutamic acid di-n-butylamide is commercially available from Ajinomoto under their designation GP-1.

Further materials which have been disclosed as gelling agents are the amide derivatives of di and tribasic carboxylic acids set forth in WO 98/27954 notably alkyl N,N'dialkyl succinamides.

Yet another example of material which can be used to bring about gelation of a hydrophobic carrier liquid is lanosterol, as described in WO 97/11678 where it is used in the preparation of soft, opaque gels as antiperspirant compositions WO 98/34588 also describes the use of lanosterol as a gellant for oil-based cosmetic compositions.

SUMMARY OF THE INVENTION

We have recognised that when a gel is formed, the solution of the structurant in a liquid may supercool before gelling commences, and in consequence the gel-melting temperature may be higher than the gel-formation temperature. If gel-formation takes place in a quiescent

solution of the structurant the extent of supercooling may be substantial. We have observed that it varies from one structurant to another.

5 However, if the structurant is being used to prepare a product where a constituent such as a disperse phase is mixed into the hot liquid before gel formation, we have found that it is likely to be necessary to carry out this mixing operation at a temperature at which the
10 structurant is fully soluble in the liquid. If an attempt is made to mix the composition at a temperature at which there is some supercooling, it is likely that the mixing will induce gelation to commence.

15 It is a consequence of this that when preparing structured liquid compositions containing a structurant to gel the liquid, all constituents of the composition must be subjected to a temperature high enough to dissolve the structuring agent.

20 We have now found that gelling agents, in particular gelling agents of moderate molecular weight, give advantageous properties if the enthalpy of gelation is at least 45 kiloJoule per mole.

25 According to a first aspect of this invention there is provided a cosmetic composition comprising a water-

immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant has an enthalpy of gelation in the carrier liquid of at least 45 kJ/mole, preferably at least 48 kJ/mole or 50 kJ/mole.

The enthalpy of gelation can be determined by differential scanning calorimetry (DSC).

We have found that if the enthalpy of gelation is high (45 kJ per mole or more) compositions can be prepared with two advantages. One is that a composition can be prepared using moderate processing temperatures (which we have found to be important). The other is that the resulting gel is stable. By contrast, if the enthalpy of gelation is low, one or both of two disadvantages are observed. Rather high processing temperatures may be needed and/or a gel may be formed but then undergo unwanted progressive transformation during storage, such as crystals appearing and growing, softening of the composition or leakage of liquid from it.

Although the enthalpy of gelation is a property of the structurant and carrier liquid jointly, we have found

122
120

that it is predominantly a property of the structurant. Consequently, the measurement of enthalpy of gelation in one or several representative liquids is valuable as technique (which can be carried out with a small sample and a standard instrument) to assess the suitability of a potential structurant. It may be desirable to take a measurement in any one of several representative liquids, since some structurants do not gel all hydrophobic carrier liquids.

Therefore in a second aspect this invention provides a cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant is able to gel one or more of

1. decamethyl cyclopentasiloxane
2. an 80:20 wt% mixture of decamethyl cyclopentasiloxane and C₁₂ - 15 linear alkyl benzoate
3. an 80:20 wt% mixture of decamethyl cyclopentasiloxane and isostearyl alcohol
4. isostearyl alcohol

with an enthalpy of gelation in one or more of those liquids of at least 45 kJ/mole, preferably at least 48 or 50 kJ/mole.

As defined above, an enthalpy of gel-formation of at least 45 kJ/mole is called for. It should be noted, however, that partial advantage can be obtained with an enthalpy of gelation of at least 30 or 35 kJ/mole. In particular, a gelling agent giving an enthalpy of gelation in this range of at least 30 or 35 kJ/mole upwards can give the advantage of allowing processing without requiring the entire composition to be subjected to high temperature. This can be valuable in preparing a composition which is an emulsion with a hydrophilic disperse phase.

Therefore further aspects of this invention provide compositions as defined earlier but with an enthalpy of gelation in a range from at least 30kJ/mole, where the composition contains a dispersed hydrophilic (eg aqueous) liquid phase.

A composition of this invention may be a structured solution with active ingredient or colourant dissolved in the carrier liquid, or it may be a composition with a dispersed second phase, either a suspension with a solid active ingredient dispersed in the carrier liquid or an emulsion with a second liquid phase dispersed in the carrier liquid. The second liquid phase may then be a solution of an antiperspirant active in a hydrophilic solvent.

A composition according to this invention may take the form of a firm gel with apparent rigidity, or a soft solid which is able to retain its own shape for a time (for example if it is taken out of a mould without being subjected to shear) but which is easily deformed by hand pressure. Preferred within this invention are compositions which have sufficient rigidity that they can be regarded as firm solids. The hardness of such compositions can be measured with a penetrometer, in a manner which will be described in greater detail below.

Certain preferred forms of this invention are concerned with compositions which are translucent or transparent. As is already known, translucent or transparent compositions can be obtained if it is possible to match the refractive indices of the different constituent phases present in the composition.

We have found that compositions within this invention which are a novel transparent or translucent emulsion can be obtained by formulating the composition to meet two criteria. Firstly the disperse phase and the continuous phase (consisting of the water-immiscible carrier liquid and the structurant contained within that liquid) should be formulated so that their refractive indices match. The refractive index of the continuous phase will be close to the refractive index of the water-

immiscible carrier liquid in it. In order to achieve good light transmission through a composition, the refractive index of the water-immiscible continuous phase and the refractive index of the disperse phase should match within 0.003 units preferably 0.002 units.

Secondly, the matched refractive indices of these two phases should lie in a range which is an approximate match to the refractive index of the structurant. The closeness of match required will depend on the structurant which is used. The refractive index of a structurant can be determined by making trial compositions as explained in more detail below. Such investigation will also show how closely the refractive index of the liquid must be matched to the structurant.

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

Another aspect of the invention therefore provides a cosmetic composition comprising a dispensing container having at least one aperture for delivery of the contents of the container, means for urging the contents of the container to the said aperture or apertures, and a composition of either of the previous aspects of the

invention in the container. Preferred is that a composition of this invention is sufficiently rigid to be accommodated as a stick product in a dispensing container having an open end at which an end portion of the stick
5 of composition is exposed for use.

The compositions of this invention can be produced by processes in which the composition is produced as a mobile liquid at an elevated temperature and allowed to
10 cool to permit gel-formation.

Thus, according to a further aspect of the present invention there is provided a process for the production of an antiperspirant composition comprising, not
15 necessarily in any order, the steps of

- incorporating at structurant into a water-immiscible liquid carrier
- optionally mixing the liquid carrier with a disperse solid or liquid phase,
- 20 • heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,

suitably followed by

- 25 • introducing the mixture into a mould which preferably is a dispensing container, and then
- cooling or permitting the mixture to cool to a

temperature at which it is thickened or solidified.

In this invention it is possible and indeed preferred that the step of mixing with a disperse phase, and any subsequent steps, are carried out at a temperature not exceeding 90°C and possibly not exceeding 85°C.

It may be possible to keep below these temperatures throughout the process.

According to a yet further aspect of the present invention, there is provided a method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition as set forth earlier comprising an antiperspirant active, a water-immiscible liquid carrier and a structurant therefor.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

Measurement of enthalpy of gelation can be carried out using a small sample and standard DSC techniques.

Measurement should be carried out at a slow cooling rate and to promote consistency in measurement, it should, if possible, be carried out with the concentration in a standardised range or approximating to

125
123

a standard value.

We have preferred to carry out measurement at a concentration of structurant in the liquid which is not over 8% by weight, preferably from 3%, better 6%, up to 8% by weight. Results at such concentrations are generally a close approximation to results at a standardised concentration of 7.5% by weight.

For any structurant which cannot dissolve at such a concentration, an alternative standardised concentration would be 3% by weight.

A gel may first be made by heating and cooling, and a sample of gel sealed in a calorimeter capsule. Alternatively the appropriate weights of liquid and structurant could be sealed in a calorimeter capsule, heated and allowed to cool to a gel in the capsule.

In a preferred procedure a gel is prepared containing from 7 to 7.5% by weight of structuring agent. Approximately 20mg of the gel (for example between 18 and 22 mg) is weighed into a calorimeter capsule and sealed. It is then heated at 10K/minute to a temperature at which the structuring agent is known to be fully soluble in the liquid, held for one minute at this temperature and then a DSC scan is taken while cooling at 2K/minute.

The scan is repeated with a capsule containing approximately 20mg of decamethyl cyclopentadisiloxane and in accordance with normal DSC technique, data collected with the liquid alone (multiplied by a scaling factor if necessary) is subtracted from the data collected with the gel, so that the gel-formation exotherm appears as a departure from a flat baseline. The enthalpy is the area between the peak and the baseline.

For calculation it is assumed that the exotherm (heat given out during gel formation) comes from the whole quantity of structuring agent present.

Structurant

A number of organic compounds are known to possess the ability to gel hydrophobic organic liquids such as water-immiscible hydrocarbon and/or silicone oils. Such materials are generally monomers or dimers with molecular weight below 10,000 rather than polymers with more than 8 repeat units or with molecular weight above 10,000.

Materials with this property have been reviewed by Terech and Weiss in "Low Molecular Mass Gelators of Organic Liquids and the Properties of their Gels" Chem. Rev 97, 3133-3159 [1997] and by Terech in Chapter 8, "Low-molecular weight Organogelators" of the book

"Specialist surfactants" edited by I D Robb, Blackie Academic Professional, 1997.

It is characteristic of such structurants that

- 5 • they are able to gel the organic liquid in the absence of any disperse phase
- the structured liquids are obtainable by cooling from an elevated temperature at which the structurant is in solution in the liquid - this
- 10 solution being mobile and pourable
- the structured liquid becomes more mobile if subjected to shear or stress
- the structure does not spontaneously recover within 24 hours if the sheared liquid is left to stand at
- 15 room temperature even though a small partial recovery may be observed
- the structure can be recovered by reheating to a temperature at which the structurant is in solution in the liquid, and allowing it to cool back to room
- 20 temperature.

It appears that such structurants operate by interactions which are permanent unless disrupted by shear or heating. It is believed that such structurants

25 operate by forming a network of interconnected strands or fibres extending throughout the gelled liquid. In some cases these fibres can be observed by electron

microscopy, although in other cases the observation of the fibres which are believed to be present is prevented by practical difficulties in preparing a suitable specimen.

5

From our observations made using differential scanning calorimetry we believe that fibrous networks consist of crystalline material. The crystalline fibres may or may not be the same polymorph as macroscopic crystals obtained by conventional crystallization from a solvent.

10

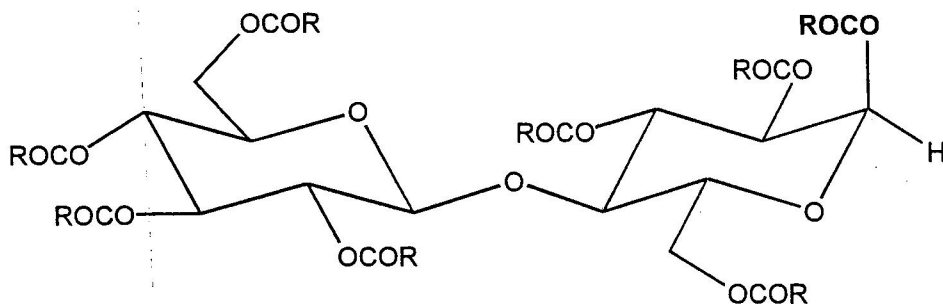
A novel structurant which is the subject of a co-pending application and which may be used in this invention is an ester of cellobiose and a fatty acid, preferably of 6 to 13 carbon atoms especially 8 to 10 carbon atoms. Preferably the cellobiose is fully esterified, or nearly so, and is in the α -anomeric form.

15

20

The structure of such a compound in its α -anomeric form is:

127
125



where R is an alkyl or alkenyl chain of 5 to 12 carbon atoms so that the acyl group contains 6 to 13 carbon atoms. Particularly preferred acyl groups incorporate a linear alkyl chain of 7 to 9 carbon atoms and are thus octanoyl, nonanoyl or decanoyl.

The acyl groups may have a mixture of chain lengths but it is preferred that they are similar in size and structure. Thus it is preferred that all of the acyl groups are aliphatic and at least 90% of the acyl groups have a chain length within a range such that the shorter and longer chain lengths in the range differ by no more than two carbon atoms, i.e. length in a range from $m - 1$ to $m + 1$ carbon atoms where m has a value in a range from 7 to 10.

Linear aliphatic acyl groups may be obtained from natural sources, in which case the number of carbon atoms

in the acyl group is likely to be an even number or may be derived synthetically from petroleum as the raw material in which case both odd and even numbered chain lengths are available.

5

Synthetic methods for the esterification of saccharides are well known. The esterification of cellobiose has been reported by Takada et al in *Liquid Crystals*, (1995) Volume 19, pages 441-448. This article gives a procedure for the production of the alpha anomers of cellobiose octa-alkanoates by esterification of β -cellobiose using an alkanoic acid together with trifluoroacetic anhydride.

10

15

For this invention the structurant is a material from this category discussed above but selected so that it also satisfies the criterion of an enthalpy of gelation exceeding 45 kilojoule per mole.

20

Carrier liquid

25

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

128
126

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

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

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

Volatile polyorganosiloxanes can be linear or cyclic or mixtures thereof. Preferred cyclic siloxanes include polydimethsiloxanes 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 10^{-5} m²/sec (10 centistokes), and particularly above 10^{-7} m²/sec (0.1 centistokes), the linear siloxanes normally exhibiting a viscosity of below 5×10^{-6} m²/sec (5 centistokes). The volatile silicones can also comprise branched linear or cyclic siloxanes such as the aforementioned linear or cyclic siloxanes substituted by one or more pendant -O-Si(CH₃)₃ groups. Examples of commercially available silicone oils include oils having grade designations 344, 345, 244, 245 and 246 from Dow Corning Corporation; Silicone 7207 and Silicone 7158 from Union Carbide Corporation; and SF1202 from General Electric.

The hydrophobic carrier employed in compositions herein can alternatively or additionally comprise non-volatile silicone oils, which include polyalkyl siloxanes, polyalkylaryl siloxanes and polyethersiloxane copolymers. These can suitably be selected from dimethicone and dimethicone copolyols. Commercially available non-volatile silicone oils include Dow Corning 556 and Dow Corning 200 series.

The water-immiscible liquid carrier may contain from

128
127

0 to 100% by weight of one or more liquid silicones.

Preferably, there is sufficient liquid silicone to provide at least 10%, better at least 15%, by weight of the whole composition. If silicone oil is used, volatile silicone preferably lies in a range from 20% possibly from 30 or 40% up to 100% of the weight of the water-immiscible carrier liquid. 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 liquids can be used instead of, or more preferably in addition to liquid silicones. Silicon-free hydrophobic organic liquids which can be incorporated include liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected to exhibit a low viscosity. Further examples of liquid hydrocarbons are polydecene and paraffins and isoparaffins of at least 10 carbon atoms.

Other hydrophobic carriers are liquid aliphatic or aromatic esters.

Suitable aliphatic esters contain at least one long chain alkyl group, such as esters derived from C_1 to C_{20} alkanols esterified with a C_8 to C_{22} alkanolic acid or C_6 to C_{10} alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they

each have a melting point of below 20°C. These esters include isopropyl myristate, lauryl myristate, isopropyl palmitate, diisopropyl sebacate and diisopropyl adipate.

5

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl benzoates. Examples of such esters include suitable C₈ to C₁₈ alkyl benzoates or mixtures thereof.

10

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

15

Aliphatic alcohols which are solid at 20°C, such as stearyl alcohol are preferably absent or present in low concentration such as less than 5% by weight of the whole composition since these lead to visible white deposits when a composition is used.

20

However, aliphatic alcohols which are liquid at 20°C may be employed. These include branched chain alcohols of at least 10 carbon atoms such as isostearyl alcohol and octyl dodecanol.

25

130
128

Very polar materials are preferably excluded or present in only small quantity in the water-immiscible carrier liquid. Preferably therefore, this liquid or mixture of liquids contains not more than 10% of its own weight, better not more than 5%, of any constituent which is a water-miscible compound.

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

If any oxygen-containing silicon-free organic liquids are included in the hydrophobic carrier liquid, the amount of them is likely to be not over 70% by weight of the carrier liquid. Smaller amounts, ranging up to 20, 30 or 35% by weight are likely.

The carrier liquid must be compatible with the structurant. If the structurant is too soluble or conversely is very insoluble in the carrier liquid it may fail to form a gel and the carrier liquid should be modified to alter its polarity.

Liquid Disperse Phase

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

The hydrophilic disperse phase in an emulsion normally comprises water as solvent and can comprise one or more water soluble or water miscible 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 60%, and particularly from 10% up to 40% or 50% of the whole formulation.

One class of water soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C₁ to C₄ and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further class of hydrophilic liquids comprises diols or polyols preferably having a melting point of below 40°C, or which are water miscible. Examples of water-soluble or water-miscible liquids with at least one free hydroxy group include ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, hexylene glycol, diethylene glycol,

135
129

dipropylene glycol, 2-ethoxyethanol, diethylene glycol monomethylether, triethyleneglycol monomethylether and sorbitol. Especially preferred are propylene glycol and glycerol.

5

In an emulsion the disperse phase is likely to constitute from 5 to 80 or 85% of the weight of the composition preferably from 5 to 50 or 65% more preferably from 25 or 35% up to 50 or 65%, while the continuous phase with the structurant therein provides the balance from 15 or 35% up to 95% of the weight of the composition. Compositions with a high proportion of disperse phase i.e. from 65 to 85% disperse phase may be advantageous because the large proportion of disperse phase can make a contribution to hardness.

15

An emulsion composition will generally include one or more emulsifying surfactants which may be anionic, cationic, zwitterionic and/or nonionic surfactants. The proportion of emulsifier in the composition is often selected in the range up to 10% by weight and in many instances from 0.1 or 0.25 up to 5% by weight of the composition. Most preferred is an amount from 0.1 or 0.25 up to 3% by weight. Nonionic emulsifiers are frequently classified by HLB value. It is desirable to use an emulsifier or a mixture of emulsifiers with an overall HLB value in a range from 2 to 10 preferably from

20

25

3 to 8.

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

Many suitable emulsifiers of high HLB are nonionic ester or ether emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often containing from about 2 to 80, and especially 5 to 60 oxyethylene units, and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditol as hydrophilic moiety. The hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a hydrophobic alkyl, alkenyl or aralkyl moiety, normally containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched and is often saturated, though it can be unsaturated, and is optionally fluorinated. The hydrophobic moiety can comprise a mixture of chain lengths, for example those deriving from tallow, lard, palm oil, sunflower seed oil or soya bean oil. Such nonionic surfactants can also be 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 (i.e. C16 to C18 alcohols ethoxylated with 10 to 25 ethylene oxide residues) and PEG-15-25 stearate or distearate.

- 5 Other suitable examples include C₁₀-C₂₀ fatty acid mono, di or tri-glycerides. Further examples include C₁₈-C₂₂ fatty alcohol ethers of polyethylene oxides (8 to 12 EO).

- 10 Examples of emulsifiers, which typically have a low HLB value, often a value from 2 to 6 are fatty acid mono or possibly diesters of polyhydric alcohols such as glycerol, sorbitol, erythritol or trimethylolpropane. The fatty acyl moiety is often from C₁₄ to C₂₂ and is saturated in many instances, including cetyl, stearyl, 15 arachidyl and behenyl. Examples include monoglycerides of palmitic or stearic acid, sorbitol mono or diesters of myristic, palmitic or stearic acid, and trimethylolpropane monoesters of stearic acid.

- 20 A particularly desirable class of emulsifiers comprises dimethicone copolymers, namely polyoxyalkylene modified dimethylpolysiloxanes. The polyoxyalkylene group is often a polyoxyethylene (POE) or polyoxypropylene (POP) or a copolymer of POE and POP. 25 The copolymers often terminate in C₁ to C₁₂ alkyl groups.

Suitable emulsifiers and co-emulsifiers are widely

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

Antiperspirant Actives

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

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

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

133
131

salts, known as activated aluminium chlorohydrates, are described in EP-A-6739 (Unilever NV et al), the contents of which specification is incorporated herein by reference. Some activated salts do not retain their enhanced activity in the presence of water but are useful in substantially anhydrous formulations, i.e. formulations which do not contain a distinct aqueous phase.

Zirconium actives can usually be represented by the empirical general formula: $\text{ZrO}(\text{OH})_{2n-nz}\text{B}_z \cdot w\text{H}_2\text{O}$ in which z is a variable in the range of from 0.9 to 2.0 so that the value $2n-nz$ is zero or positive, n is the valency of B, and B is selected from the group consisting of chloride, other halide, sulphamate, sulphate and mixtures thereof. Possible hydration to a variable extent is represented by $w\text{H}_2\text{O}$. Preferable is that B represents chloride and the variable z lies in the range from 1.5 to 1.87. In practice, such zirconium salts are usually not employed by themselves, but as a component of a combined aluminium and zirconium-based antiperspirant.

The above aluminium and zirconium salts may have coordinated and/or bound water in various quantities and/or may be present as polymeric species, mixtures or complexes. In particular, zirconium hydroxy salts often represent a range of salts having various amounts of the

hydroxy group. Zirconium aluminium chlorohydrate may be particularly preferred.

Antiperspirant complexes based on the above-mentioned astringent aluminium and/or zirconium salts can be employed. The complex often employs a compound with a carboxylate group, and advantageously this is an amino acid. Examples of suitable amino acids include dl-tryptophan, dl- β -phenylalanine, dl-valine, dl-methionine and β -alanine, and preferably glycine which has 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 amino acids such as glycine, which are disclosed in US-A-3792068 (Luedders et al). Certain of those Al/Zr complexes are commonly called ZAG in the literature. ZAG actives generally contain aluminium, zirconium and chloride with an Al/Zr ratio in a range from 2 to 10, especially 2 to 6, an Al/Cl ratio from 2.1 to 0.9 and a variable amount of glycine. Actives of this preferred type are available from Westwood, from Summit and from Reheis.

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

134
132

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

If the composition is in the form of an emulsion the antiperspirant active will be dissolved in the disperse phase. In this case, the antiperspirant active will
10 often provide from 3 to 60% by weight of the aqueous disperse phase, particularly from 10% or 20% up to 55% or 60% of that phase.

Alternatively, the composition may take the form of
15 a suspension in which antiperspirant active in particulate form is suspended in the water-immiscible liquid carrier. Such a composition will probably not have any separate aqueous phase present and may conveniently be referred to as "substantially anhydrous"
20 although it should be understood that some water may be present bound to the antiperspirant active or as a small amount of solute within the water-immiscible liquid phase. In such compositions, the particle size of the antiperspirant salts often falls within the range of 0.1
25 to 200 μm with a mean particle size often from 3 to 20 μm . Both larger and smaller mean particle sizes can also be contemplated such as from 20 to 50 μm or 0.1 to 1 μm .

Optional ingredients

Optional ingredients in compositions of this invention can include disinfectants, for example at a concentration of up to about 10% w/w. Suitable deodorant actives can comprise deodorant effective concentrations of antiperspirant metal salts, deoperfumes, and/or microbicides, including particularly bactericides, such as chlorinated aromatics, including biguanide derivatives, of which materials known as Irgasan DP300 TM, Triclosan TM, Tricloban TM, and Chlorhexidine warrant specific mention. A yet another class comprises biguanide salts such as available under the trade mark Cosmosil TM.

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

A further optional constituent of the formulation comprises one or more secondary structurants which can be employed in addition to the esterified saccharide which is the primary structurant. The amount of such secondary

135
133

structurants in the formulation is often zero, and usually not more than 15% of the formulation. It is normally not greater than the amount of the primary structurant.

5

The secondary structurants employable herein can be non-polymeric or polymeric. Solid linear fatty alcohol and/or a wax may be included but are not preferred. Non-polymeric secondary structurants, perhaps gelling agents of lower gel formation enthalpy, can be included. Gellants can comprise dibenzylidene alditols, e.g. dibenzylidene sorbitol. Further suitable gellants can comprise lanosterol, selected N-acyl amino acid derivatives, including ester and amide derivatives, such as N-lauroyl glutamic acid dibutylamide, which gellants can be contemplated in conjunction with 12-hydroxy stearic acid or an ester or amide derivative thereof. Still further gellants include amide derivatives of di or tribasic carboxylic acids, such as alkyl N,N'-dialkylsuccinamides, e.g. dodecyl N,N'-dibutylsuccinamide.

15
20

Polymeric structurants which can be employed can comprise organo polysiloxane elastomers such as reaction products of a vinyl terminated polysiloxane and a cross linking agent or alkyl or alkyl polyoxyalkylene-terminated poly (methyl substituted) or poly (phenyl

25

substituted) siloxanes. A number of polyamides have also been disclosed as structurants for hydrophobic liquids. Polymers containing both siloxane and hydrogen bonding groups, which might be used as secondary structurants, have been disclosed in WO 97/36572 and WO 99/06473. If an aqueous disperse phase is present, Polyacrylamides, polyacrylates or polyalkylene oxides may be used to structure or thicken this aqueous phase.

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 up to about 10%; skin benefit agents such as allantoin or lipids, for example in an amount of up to 5%; colours; skin cooling agents other than the already mentioned alcohols, such as menthol and menthol derivatives, often in an amount of up to 2%, all of these percentages being by weight of the composition. A commonly employed adjunct is a perfume, which is normally present at a concentration of from 0 to 4% and in many formulations from 0.25 to 2% by weight of the composition.

Translucent/Transparent Compositions

If a composition of this invention is formulated as

136
134

an emulsion it is possible to construct the formulation such that the emulsion is translucent or transparent. In order to do this the refractive indices of the water-immiscible continuous phase and the polar or aqueous disperse phase must be matched to each other and the value of refractive index at which they are matched must also approximately match the refractive index of the structurant.

The refractive index of a fibrous network of a structurant can be determined by using that structurant to gel a number of oils or oil mixtures of differing refractive index. When the resulting gel is transparent, the refractive index of the oil or oil mixture (which can be determined by conventional measurement) is a good approximation to the refractive index of the structurant. The oils or mixtures or oils should be chosen from these which are gelled well by the structurant to avoid interfering effects. When the gel is not transparent, but is translucent, it will indicate a refractive index which is not precisely matched to the refractive index of the structurant, and thus indicate an amount of mismatch which can be tolerated without loss of translucency. It is likely that the matched refractive indices of the liquid phases will be not over 0.07 units below and not over 0.04 units above the refractive index of the structurant.

below even if the active is partially hydrated to lower its refractive index.

For this reason, a feature within this invention is to prefer the emulsion form of antiperspirant stick when seeking to achieve a transparent or translucent product.

Mechanical Properties and Product Packages

The compositions of this invention are structured liquids and may be firm or soft in appearance. Even a soft solid has an ability to sustain its own shape, for instance if it is removed from a mould without being subjected to shear it will retain its shape for at least 30 seconds, usually longer.

A composition of this invention will usually be marketed as a product comprising a container with a quantity of the composition therein, where the container has at least one aperture for the delivery of composition, and means for urging the composition in the container towards the delivery aperture. Conventional containers take the form of a barrel of oval cross section with the delivery aperture(s) at one end of the barrel.

A composition of this invention may be sufficiently

~~138~~
136

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

Generally the container will include a cap for its open end and a component part which is sometimes referred to as an elevator or piston fitting within the barrel and capable of relative axial movement along it. The stick of composition is accommodated in the barrel between the piston and the open end of the barrel. The piston is used to urge the stick of composition along the barrel. The piston and stick of composition may be moved axially along the barrel by manual pressure on the underside of the piston using a finger or rod inserted within the barrel. Another possibility is that a rod attached to the piston projects through a slot or slots in the barrel and is used to move the piston and stick. Preferably the container also includes a transport mechanism for moving the piston comprising a threaded rod which extends axially into the stick through a correspondingly threaded aperture in the piston, and means mounted on the barrel for rotating the rod. Conveniently the rod is rotated by means of a handwheel mounted on the barrel at its closed

end, i.e. the opposite end to the delivery opening.

If a composition of this invention is softer, but still capable of sustaining its own shape it will be more suited for dispensing from a barrel with a closure instead of an open end, where the closure has one or more apertures through which composition from the barrel can be extruded. The number and design of such apertures is at the discretion of the designer of the package.

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

Measurement of Properties

i) Penetrometer

The hardness and rigidity of a composition which is a firm solid can be determined by penetrometry. If the composition is a softer solid, this will be observed as a substantial lack of any resistance to the penetrometer probe.

A suitable procedure is to utilise a lab plant PNT penetrometer equipped with a Seta wax needle (weight 2.5 grams) which has a cone angle at the point of the needle

138
137

specified to be $9^{\circ}10' \pm 15'$. A sample of the composition with a flat upper surface is used. The needle is lowered onto the surface of the composition and then a penetration hardness measurement is conducted by allowing the needle with its holder to drop under a total weight, (i.e. the combined weight of needle and holder) of 50 grams for a period of five seconds after which the depth of penetration is noted.

Desirably the test is carried out at a number of points on each sample and the results are averaged. Utilising a test of this nature, an appropriate hardness for use in an open-ended dispensing container is a penetration of less than 30 mm in this test, for example in a range from 2 to 30 mm. Preferably the penetration is in a range from 5mm to 20 mm.

In a specific protocol for this test measurements on a stick were performed in the stick barrel. The stick was wound up to project from the open end of the barrel, and then cut off to leave a flat, uniform surface. The needle was carefully lowered to the stick surface, and then a penetration hardness measurement was conducted. This process was carried out at six different points on the stick surface. The hardness reading quoted is the average value of the 6 measurements.

ii) Texture analyser

The hardness of a softer solid can be measured by using a texture analyser. This test apparatus can move a blunt probe into or out from a sample at a controlled speed and at the same time measure the applied force. The parameter which is determined as hardness is a function of the peak force and the projected area of indentation.

A specific test protocol used a Stable Micro systems TA.XT2i Texture Analyser. A metal sphere, of diameter 9.5mm, was attached to the underside of the Texture Analyser's 5 kg load cell such that it could be used for indenting a sample placed beneath it on the base plate of the instrument. After positioning the sample, the sphere position was adjusted until it was just above the sample surface. *Texture Expert Exceed* software was used to generate the subsequent motion profile used in the test method. This profile initially indented the sphere into the sample at an indentation speed of 0.05mm/s until a designated force was reached, which was chosen such that the distance of penetration into the sample was less than the radius of the sphere. At this load the direction of motion of the sphere was immediately reversed to withdraw the sphere from the sample at the same speed of 0.05mm/s. During the course of the test, the data acquired were time(s), distance (mm) and force (N) and the data

140
138

acquisition rate was 25 Hz.

Suitable samples for measurement were either contained in stick barrels, which had a screw mechanism, or in 15 ml glass jars. For the barrel samples, the stick was wound up until it protruded above the edges of the barrel and then a knife was used to skim the top of the barrel in such a way as to leave a flat uniform surface. The stick was then pushed back into the barrel as far as possible to minimise any mechanical interference resulting from the compliance of the screw mechanism in the pack. Two indents were generally made either side of the screw. The samples in the 15 ml jars needed no surface preparation but only had enough surface area for a single indentation test to be performed.

The data associated with each test were manipulated using standard spreadsheet software and used to calculate the hardness, H , using the following equation:

$$H[N/mm^2] = \frac{F_{max}[N]}{A_p[mm^2]}$$

where F_{max} is the peak load and A_p is the projected area of the indentation remaining on unloading. This area can be calculated geometrically from the plastic indentation depth. This is slightly less than the total penetration depth measured under load because of elastic deformation

of the sample. The plastic indentation depth is calculated from a graph of the unloading-force-versus-total-penetration-depth. The initial slope of this unloading data depends on the initial elastic recovery of the sample. The plastic indentation depth is estimated from an intercept between the zero force axis and a straight line drawn at a tangent to the initial part of the unloading slope.

Similar hardness measurements were also done using a desktop *Instron Universal Testing Machine* (Model 5566) fitted with a 10 N load cell, and the data analysis performed in the same way.

iii) Deposition and whiteness of deposit

Another test of the properties of a composition is the amount of the composition which is delivered onto a surface when the composition is drawn across that surface (representing the application of a stick product to human skin). To carry out this test of deposition, a sample of the composition with standardised shape and size is fitted to apparatus which draws the sample across a test surface under standardised conditions. The amount transferred to the surface is determined as an increase in the weight of the substrate to which it is applied. If desired the colour, opacity or clarity of the deposit may subsequently be determined.

141
139

A specific procedure for such tests used apparatus to apply a deposit from a stick onto a substrate under standardised conditions and then measures the mean level of white deposits using image analysis.

5

The substrates used were

a: 12 x 28cm strip of grey abrasive paper (3M™ P800 WetorDry™ Carborundum paper)

b: 12 x 28cm strip of black Worsted wool fabric.

10

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

15

The apparatus comprised a flat base to which a flat substrate was attached by a clip at each end. A pillar having a mounting to receive a standard size stick barrel was mounted on an arm that was moveable horizontally across the substrate by means of a pneumatic piston.

20

Each stick was kept at ambient laboratory temperature overnight before the measurement was made. The stick was advanced to project a measured amount from the barrel. The barrel was then placed in the apparatus and a spring was positioned to biased the stick against the substrate with a standardised force. The apparatus was operated to pass the stick laterally across the

25

substrate eight times. The substrate was carefully removed from the rig and reweighed.

Whiteness of Deposit

5 The deposits from the previous test were assessed for their whiteness after an interval of 24 hours approximately.

10 This was done using a Sony XC77 monochrome video camera with a Cosmocar 16mm focal length lens positioned vertically above a black table illuminated from a high angle using fluorescent tubes to remove shadowing. The apparatus was initially calibrated using a reference grey card, after the fluorescent tubes had been turned on for
15 long enough to give a steady light output. A cloth or Carborundum paper with a deposit thereon from the previous test was placed on the table and the camera was used to capture an image. An area of the image of the deposit was selected and analysed using a Kontron IBAS
20 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 0 (black) to 255 (white). The average of the grey intensity was calculated. This was a measure of the whiteness of the deposit, with higher
25 numbers indicating a whiter deposit. It was assumed that low numbers show a clear deposit allowing the substrate colour to be seen.

142
140

iv) Light transmission

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

We have carried out this test using a dual-beam spectrophotometer. The sample of composition was poured hot into a 4.5 ml cuvette made of polymethylmethacrylate (PMMA) and allowed to cool to an ambient temperature of 20-25°C. Such a cuvette gives a 1 cm thickness of composition. Measurement was carried out at 580 nm, with an identical but empty cuvette in the reference beam of the spectrophotometer, after the sample in the cuvette had been held for 24 hours. We have observed that a composition which gives a transmittance of as little as 1% in this test is perceived by eye as "translucent". If a stick is made from a composition with 3% transmittance, it is possible to see cavities made by boring beneath the surface of the sample. By contrast, a conventional stick structure with stearyl alcohol is so opaque that it is impossible to see beneath its surface. A transmittance measured at any temperature in the range from 20-25°C is usually adequately accurate, but measurement is made at 22°C if more precision is required. In a number of preferred examples we have achieved a transmittance of

20% or above.

Preparation

5 Compositions of this invention can be produced by conventional processes for making suspension or emulsion solids or soft-solids. Such processes involve forming a heated mixture of the composition at a temperature which is sufficiently elevated that all the esterified
10 saccharide structurant dissolves, pouring that mixture into a mould, which may take the form of a dispensing container, and then cooling the mixture whereupon the structurant solidifies into a network of interconnected fibres extending through the water-immiscible liquid
15 phase.

A convenient process sequence for a composition which is a suspension comprises first forming a solution of the esterified saccharide structurant in the water-
20 immiscible liquid. This is normally carried out by agitating the mixture at a temperature sufficiently high that all the structurant dissolves (the dissolution temperature) such as a temperature in a range from 50 to 120°C. Thereafter the particulate constituent, for
25 example particulate antiperspirant active, is blended with the hot mixture. This must be done slowly, or the particulate solid must be preheated, in order to avoid

43
141

premature gelation. The resulting blend is then introduced into a dispensing container such as a stick barrel. This is usually carried out at a temperature 5 to 30°C above the setting temperature of the composition. The container and contents are then cooled to ambient temperature. Cooling may be brought about by nothing more than allowing the container and contents to cool. Cooling may be assisted by blowing ambient or even refrigerated air over the containers and their contents.

In a suitable procedure for making emulsion formulations, a solution of the esterified structurant in the water-immiscible liquid phase is prepared at an elevated temperature just as for suspension sticks. If any emulsifier is being used, this is conveniently mixed into this liquid phase. Separately an aqueous or hydrophilic disperse phase is prepared by introduction of antiperspirant active into the liquid part of that phase (if this is necessary; antiperspirant actives can sometime be supplied in aqueous solution which can be utilised as is). This solution of antiperspirant active which will become the disperse phase is preferably heated to a temperature similar to that of the continuous phase with structurant therein, but without exceeding the boiling point of the solution, and then mixed with the continuous phase. Alternatively, the solution is introduced at a rate which maintains the temperature of

the mixture. If necessary a pressurised apparatus could be used to allow a higher temperature to be reached, but with the structurant materials of this invention this is usually unnecessary. After the two phases are mixed, the resulting mixture is filled into dispensing containers, typically at a temperature 5 to 30°C above the setting temperature of the composition, and allowed to cool as described above for suspension sticks.

10 EXAMPLES

The examples below were prepared using a number of materials set out with their proprietary names in the following list. All temperature are in degrees Celsius. Refractive indices were measured at 25°C.

- 1) octamethyl cyclotetrasiloxane (Volatile cyclic silicone also known as a cyclomethicone; DC 245 from Dow Corning)
- 20 2) decamethyl cyclopentasiloxane (Volatile cyclic silicone also known as a cyclomethicone; DC 345 from Dow Corning)
- 3 & 4) Non-volatile silicone fluids
DC 556 and DC 710 (Dow Corning)
- 25 5) Polydecene (Silkflo 364NF from Albemarle)
- 6) Isostearyl Alcohol (abbreviated to ISA -
Prisorine 3515 from Unichema)

144
142

- 7) C12-15 alkyl benzoate (Finsolv TN from Fintex)
- 8) Mineral Oil (Sirius M70 from Dalton)
- 9) Polypropyleneglycol 14 butylether (Fluid AP from Amercol)
- 5 10) Isopropyl myristate (abbreviated to IPM from Unichema)
- 11) Isohexadecane (Permethyl 101A from Presperse Inc)
- 12) Isoeicosane (Permethyl 102A from Presperse Inc).
- 10 13) Cetyl dimethicone copolyol (Abil EM90 emulsifier from Th. Goldschmidt)
- 14) Al/Zr Tetrachlorohydrex glycine complex (AZAG 7167 from Summit)
- 15 15) 50% aqueous solution of Al/Zr pentachlorohydrate (Zirkonal 50 from Giuliani)
- 16) Al/Zr Tetrachlorohydrex glycine complex 30% in propylene glycol (WA2Z 8106 from Westwood)
- 17) Al/Zr tetrachlorohydrex glycine complex (AZG 375 from Summit)
- 20 18) Glycerol (from Aldrich)
- 19) Propylene glycol (from Fisons)
- 20) N-lauryl-L-glutamic acid di-n-butylamide (GP1 from Ajinomoto)
- 25 21) 12-hydroxystearic acid (from Caschem)
- 22) Activated aluminium chlorhydrate abbreviated to AACH (A-418 from Summit)

Example 1

The enthalpy of gelation was measured for four structuring agents in three liquids. In each case the gels are made to contain 7 to 7½wt% of the structurant in the liquid.

A sample gel, weighing between 18 and 22 mg was placed in a stainless steel calorimeter capsule, which was sealed with an elastomeric O-ring. The capsule was placed in the DSC at room temperature and heated at 10K/minute to 150°C, held at 150°C for 60 seconds and cooled at 2K/minute to -50°C.

The procedure was repeated with DC 345 alone. The data recorded for DC 345 was subtracted from the data for the gel, so that the gel formation appears a departure from a flat baseline. The gelation enthalpy was calculated as the area between the peak and the baseline.

Values of enthalpy (in kJ/mole) were obtained as set out in the following table

145
143

5

10

Structurant	Liquid		
	DC 345	DC 345:ISA (80:20 ratio by weight)	Isostearyl alcohol (ISA)
cellobiose octa- nonanoate	65	58	77
12 -hydroxy stearic acid		40	
N-lauroyl glutamic acid di-n-butylamide (GP1)		11	
lanosterol	27	7	

Example 2 (Comparative)

15

20

Gels were prepared with lanosterol by a standard procedure in which the ingredients of the gel were placed in a 30ml glass bottle together with a magnetic stirrer bar. The mixture was stirred and heated until all the lanosterol had dissolved. The bottle was then removed from the heat, the stirrer bar taken out and the contents of the jar left to cool to room temperature.

25

The following was observed:

Lanosterol was found to dissolve at 10.0 wt% in Finsolv TN at 83°C. After cooling to room temperature for 1

hours a hard, transparent gel was obtained. However the gel was found to be unstable at room temperature: large crystalline lumps appeared within hours and spread throughout the entire gel leading to its collapse.

5

Lanosterol was found to dissolve at 5.0 wt% in 80:20 (wt%) DC 345: Finsolv TN at 85°C. After cooling to room temperature for 1 hour a hard, translucent gel was obtained. However the gel was found to be unstable at room temperature: large crystalline lumps developed after 1 week.

10

Example 3 (Comparative)

15

An unsuccessful attempt was made to prepare compositions as set out in the table below, using N-lauroyl glutamic acid di-n-butylamide (GPI) as structurant

20

Compositions 3.1 and 3.2 would have been suspensions of solid antiperspirant active.

25

Compositions 3.3 and 3.4 would have been emulsions where the disperse phase would be a solution of antiperspirant active in water (Zirkonal 50 is a 50% aqueous solution of antiperspirant active).

~~146~~
144

Example no	3.1	3.2	3.3	3.4
	Suspension	Suspension	Emulsion	Emulsion
5	Continuous phase			
	GP1 (20)	6%	5%	3.5%
	DC 345 (2)	30%	53%	39%
10	Isopropyl myristate (10)	44%		5%
	Isostearyl alcohol (6)			11%
	Finsolv TN (7)	22%	16.5%	
15	Abil EM 90 (13)		1%	1%
	Disperse Phase			
	AZAG 7167 (14)	20%	20%	
20	Zirkonal 50 (15)		40%	40%
	Continuous Phase Data			
25	Temp at which all the GP-1 had dissolved	113°C	123°C	122°C
30	Temperature at which the continuous phase gelled	108°C	115°C	116°C
				99°C

In each case the components of the continuous phase were placed in a beaker and the mixture heated with stirring on a hot plate until all the GP-1 structurant dissolved. The temperature at which it dissolved is shown in the table above.

The intention was then to cool the mixture, while still stirring gently to about 85-90°C in order to add the components of the disperse solid or liquid phase. In all cases the continuous phase gelled at a temperature (shown in the table) above or very close to 100°C, which was too high for safe addition of the disperse phase.

W7
145**Example 4 (Comparative)**

Suspension sticks were prepared containing 12-hydroxystearic acid as structurant. The compositions are given in the following table

Example No	4.1	4.2
Continuous Phase		
12-hydroxystearic acid (21)	5%	7.5%
Finsolv TN (7)	75%	72.5%
Disperse Phase		
AACH (A-418 from Summit) (22)	20%	11.24%
Data		
Temperature for dissolution of 12-Hydroxystearic acid in the Finsolv TN	58°C	63°C
Gelling temperature of stick	41°C	47°C
Stick Hardness after 24 hours (penetrometer [mm])	12.6	11.2
Stick Hardness after 1 week storage at 22°C (penetrometer [mm])	13.8	12.0

The components of the continuous phase were placed in a beaker and the mixture heated with stirring on a hot plate until all the 12-hydroxystearic acid structurant dissolved. The temperature at which it dissolved is shown in the table above.

The mixture was then allowed to cool slightly, to about 10°C above the gelling temperature shown in the table, while stirring gently. The solid antiperspirant active was mixed in under low shear.

5

The resulting mixture was poured into stick barrels and allowed to cool to ambient laboratory temperature. In each case the mixture gelled to a rigid stick.

10

The hardness of the stick was determined by penetrometer after 24 hours at ambient temperature and then after storage at ambient temperature for 1 week. The results, in the table above show slight softening during storage. After the period of storage the sticks were observed to have leaked some of the Finsolv TN solvent, which could be seen as free liquid on the stick surface.

15

20

Example 5

Cellobiose was esterified with nonanoic acid to yield the fully esterified product in the form of its α -anomer following a procedure generally as described in Takada et al, Liquid Crystals, Volume 19, page 441 (1995).

25

148
146

The following materials were used:

β -D-cellobiose, 20 grams, 0.058 moles

Nonanoic acid, 591.6 grams, 3.74 moles

Trifluoroacetic anhydride, 297.6 grams, 1.42 moles.

5

These materials were obtained from Acros Organics -
Fisher Scientific.

10 Into a 2 litre flange pot equipped with an overhead
stirrer, water condenser and addition inlet was placed
the nonanoic acid together with the trifluoroacetic
anhydride. The resultant clear mixture was stirred up
and heated to 100°C using a silicone oil bath and
temperature probe. During heating it was noted that the
15 colour of the reaction mixture darkened and developed a
dark brown tinge. After allowing the mixture to stir for
one hour at 100°C, the cellobiose was slowly added via a
solid powder funnel to the dark activated solution, and a
dirty brown suspension was formed which re-dissolved
20 forming a clear black solution within 10-20 minutes.

The reaction flask was then maintained at 100°C for
a total of 6 hours then cooled down to ambient laboratory
temperature. Next the contents of the flask were
25 transferred into 2 litres of methanol containing 10% de-
ionised water in an ice-cooled 5 litre beaker.
Immediately an off-white solid precipitate came out of

solution, this was filtered off and collected. The crude solid was recrystallised a total of 4 times from a tetrahydrofuran/methanol solution producing a white solid product.

5

The product was obtained in a quantity of 31.5 g which was a 37% yield. It had a melting point of 110°C. The infra-red spectrum showed an absorption peak at 1739 cm^{-1} for the ester carbonyl group. The amount of free acid could be determined from its absorption peak at 1705 cm^{-1} .

10

The n.m.r. spectrum showed the amount of cellobiose which was fully esterified to be 93.5% and showed the proportions of product which were the α - and β -anomers, (93.5% α -anomer).

15

Samples of esterified cellobiose prepared as above were used to gel various water-immiscible liquids and mixtures of liquids. The procedure was as follows:

20

0.5 grams esterified cellobiose and 9.5 grams of the liquid (or other proportions to give a total of 10 grams) were weighed directly into a 15 gram or 30 gram glass jar. A small magnetic follower was placed in the jar which was then placed on a hot plate. It was stirred and heated until all of the esterified cellobiose had

25

149
147

dissolved in the liquid. This "dissolution temperature" was noted. The jar was then removed from the hot plate, the stirrer was removed from the hot liquid in the jar. A thermometer was placed in the liquid and the contents of the jar were then left undisturbed to cool. The gelling temperature, i.e. the temperature at which the contents gelled, was noted. The jar was left to stand for 24 hours and then the contents of the jar were inspected visually, pressed with a probe and classified qualitatively according to their appearance as a soft, medium or hard gel. The clarity or otherwise of the gel was noted. In most instances the gel was remelted, the remelting temperature was noted, and some of the melt was poured into a plastic (polymethylmethacrylate) cuvette and allowed to cool back to ambient laboratory temperature so that the gel reformed in the cuvette. The transmittance of light through the 1cm thickness of gel in the cuvette was determined at a wave length of 580 nm using an ultraviolet/visible spectrophotometer.

The following tables show the water-immiscible liquids which were used, the percentage of esterified cellobiose structurant used to gel the liquid, the dissolution temperature, the gelling temperature, the visual appearance of the gel, the remelt temperature and the percentage light transmittance (denoted as %T) through 1cm of the gel at 580nm.

Gelling with α -cellobiose octa-nonanoate ("CB9")						
Liquid	% CB9	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	57	25	46	78	Medium/hard & transparent
DC 345 (2)	5	62	42	60	15	Hard & transparent/ translucent
DC 566 (3)	5	69	29	52	81	Hard & transparent
Silkflo 364NF (5)	5	71	40	55	78	Hard & transparent
Fluid AP	5	82	38	55	37	Soft/medium & transparent
DC 345 : Fluid AP 80 : 20 wt ratio	5	68	28	54	39	Soft/medium & transparent
DC 710 (4)	5	82	48	62	11	Medium & translucent
DC 710 : DC 345 60 : 40 wt ratio	5	74	33	60	4	Hard & translucent

It can be seen from the above table that the gelation temperatures were low. The remelt temperatures were well below 80°C and the compositions could be prepared without any need to exceed 85°C.

150.
148

Example 6

An antiperspirant suspension stick is prepared with the following formulation, using the same procedure as in Example 3

5

	Parts by weight
Cyclomethicone, DC 245 (1)	54.8
Polydecene (5)	13.7
Cellobiose octa-nonanoate	7.5
AZAG 7167 (14)	24

10

Example 7

Opaque emulsion sticks were prepared with formulations as set out in the table below.

5 To prepare these sticks, the cyclomethicone was mixed with the other organic liquids (if any) including the cetyl dimethicone copolyol which functioned as an emulsifier (silicone surfactant) and the mixture was heated with gentle stirring to a temperature 5 to 10°C
10 above the temperature at which the structurant had been found to dissolve in a preliminary test. The esterified cellobiose was then added and allowed to dissolve.

The disperse phase (also referred to as internal
15 phase) was an aluminium zirconium active dissolved in water or in a mixture of a polyol and water. This disperse phase was pre-heated to the same temperature as the organic oils containing the esterified cellobiose and added slowly to them over a period of one minute while
20 mixing with a Silverson mixer. After addition was complete the formulation was mixed at higher speed for five minutes. Stirring speed was then reduced for a further one minute after which the mixture was poured into stick barrels and allowed to cool undisturbed to ambient
25 laboratory temperature. The sticks were tested by penetrometer, by texture analyser and for whiteness of deposits, in each instance by the test procedures given earlier. All of the sticks were opaque although without the chalky white appearance of a commercial white stick
30 (CWS) structured with stearyl alcohol and castor wax whose

151
149

test results are given at the right of the table.

Examples		7.1	7.2	7.3	CWS
		% by weight			
5	Cyclomethicone DC 245 (1)	18	22.25	21.7	
	Cyclomethicone DC 345 (2)	-	-	-	
	Mineral Oil (7)	-	-	-	
10	Polydecene (5)	22.75	27.5	27.4	
	PPG-14 Butyl Ether (9)	4.5	5.5	5.4	
	Cellobiose octa- nonanoate	3.75	3.75	4.5	
15	Cetyl Dimethicone Copolyol (13)	1	1	1	
	Zirkonal 50 (15)	40	40	40	40
	Glycerol (18)	-	-	-	-
	Water	10			10
20		Properties			
	penetration depth (mm)	16.8	17.5	15.7	9.8
	Hardness by texture analyser (N/mm ²)	0.11	0.10	0.12	-
25	Whiteness on grey paper 24 hours after deposition	19	16	16	118
30	Whiteness on black wool 24 hours after deposition	28	28.5	27	186

Example 8

The procedure of Example 7 was repeated to prepare a number of emulsion sticks with formulations set out in the following tables. The continuous and disperse phases were formulated to have refractive indices which matched closely at the value given in the tables. These sticks were tested as before and the properties are also given in these tables.

182
150

	Examples	8.1	8.2	8.3	8.4	8.5	8.6
		% by weight					
5	Cyclomethicone DC245 (1)	22.625	18.75	25.5	19	26	17.75
	Mineral Oil (8)	22.625	-	-	-	-	-
	Polydecene (5)	-	22.5	15.75	22	15	22
	PPG-14 Butyl Ether (9)	-	4	4	-	-	4.25
	Isostearyl Alcohol (6)	-	-	-	4.25	4.25	-
10	Cellobiose octa-nonoate	3.75	3.75	3.75	3.75	3.75	5
	Cetyl Dimethicone Copolyol (13)	1	1	1	1	1	1
	Zirkonal 50 (15)	40	40	40	40	40	40
15	Glycerol (18)	10	10	7.5	10	7.5	10
	Water	-	-	2.5	-	2.5	-
	Propylene glycol (19)	-	-	-	-	-	-
	AZG 375 (17)	-	-	-	-	-	-
20	Properties						
	Matched RI of phases	1.43	1.43	1.425	1.435	1.425	1.43
	penetration depth (mm)	19.3	18.5	17.3	24.7	23.6	12.4
	Hardness by texture analyser (N/mm ²)	0.11	0.12	0.08	0.07	0.06	0.17
	Whiteness on grey paper 24 hours after deposition	-	15	16	18	19	16
25	Whiteness on black wool 24 hours after deposition	-	24	28	25	30	26
	Transmittance at 580nm	-	38%	33%	41%	35%	51%
30							

5

10

15

20

25

Examples	8.7	8.8	8.9	8.10	8.11
	% by weight				
Cyclomethicone DC245 (1)	16.75	18	14.02	28.4	4.5
Cyclomethicone DC345 (2)					
Mineral Oil (8)	-	-	-	-	
Polydecene (5)	20.75	22.75	17.72	13.1	50.75
PPG-14 Butyl Ether (9)	4	4.5	3.51	3.75	-
Isostearyl Alcohol (6)	-	-	-	-	-
Cellobiose octa-nonanoate	7.5	3.75	3.75	3.75	3.75
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
Zirkonal 50 (15)	40	-	40	40	-
Glycerol (18)	10	4	17.5	6.25	12
Water	-	14	2.5	3.75	8
Propylene glycol (19)	-	12	-	-	-
AZG 375 (17)	-	20	-	-	20
	Properties				
Matched RI of phases	1.43	1.43	1.43	1.42	1.45
penetration depth (mm)	11	14.5	14.9	15.1	14.8
Hardness by texture analyser (N/mm ²)	0.29	0.11	0.14	0.13	0.11
Whiteness on grey paper 24 hours after deposition	17	20	18	21	16
Whiteness on black wool 24 hours after deposition	25	28	25	31	19
Transmittance at 580nm	48%	82%	65%	30%	72%

152
151

Examples	8.12	8.13	8.14	8.15	8.16
	% by weight				
Cyclomethicone DC245 (1)	41.85	35.4	10.04	10.64	6.96
Permethyl 101A (11)	2.15				
Permethyl 102A (12)	-	8.6			
Polydecene (5)			12.7	13.45	8.8
PPG-14 Butyl Ether (9)			2.51	2.66	1.74
Isostearyl Alcohol (6)	-	-			
Cellobiose octa-nonanoate	5	5	3.75	2.25	1.5
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
Zirkonal 50 (15)	40	40	52.71	52.71	60.24
Glycerol (18)	0.75	4.5	17.29	17.29	19.76
Water	9.25	5.5	-	-	-
	Properties				
Matched RI of phases	1.40	1.41	1.43	1.43	
penetration depth (mm)	13.5	13.2	12.0	16.8	
Hardness by texture analyser (N/mm ²)	0.16	0.15	0.13	0.07	
Whiteness on grey paper 24 hours after deposition	59	61	24	24	
Whiteness on black wool 24 hours after deposition	122	24	14.9	16.2	
Transmittance at 580nm	2.7%	5%	33%	73%	

CLAIMS:

1. A cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant has an enthalpy of gelation in the carrier liquid with a magnitude of at least 45 kJ/mole.
2. A cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant is able to gel one or more of
- 18) decamethyl cyclopentasiloxane
 - 19) an 80:20 wt% mixture of decamethyl cyclopentasiloxane and C₁₂ - 15 linear alkyl benzoate
 - 20) an 80:20 wt% mixture of decamethyl cyclopentasiloxane and isostearyl alcohol
 - 21) isostearyl alcohol
- with an enthalpy of gelation in at least one of the liquids with a magnitude of at least 45 kJ/mole.
3. A composition according to claim 2 wherein the structurant is able to gel an 80:20 wt% mixture of decamethyl cyclopentasiloxane and isostearyl alcohol with

154
152

an enthalpy of gelation having a magnitude of at least 45 kJ/mole.

4. A composition according to any one of the preceding claims wherein the composition is an emulsion with a hydrophilic, preferably water-miscible, disperse phase in addition to said water-immiscible liquid continuous phase.

5. A cosmetic composition which is a structured emulsion comprising

- i) a continuous phase containing water-immiscible liquid carrier and a structurant present in the continuous phase, which is effective to gel the composition upon cooling from a temperature at which the structurant is in solution in the carrier liquid, and
- ii) a disperse phase which is a solution of antiperspirant active in water, water-soluble solvent or a mixture of them.

characterised in that the structurant has an enthalpy of gelation in the carrier liquid with a magnitude of at least 30 kJ/mole.

6. A cosmetic composition which is a structured emulsion comprising

- i) a continuous phase containing water-immiscible liquid carrier and a structurant present in the continuous phase, which is effective to gel the composition upon cooling from a temperature at which the structurant

is in solution in the carrier liquid, and

- ii) a disperse phase which is a solution of antiperspirant active in water, water-soluble solvent or a mixture of them

5 characterised in that the structurant is able to gel one or more of

22) decamethyl cyclopentasiloxane

23) an 80:20 wt% mixture of decamethyl cyclopentasiloxane and C₁₂ - 15 linear alkyl benzoate

10 24) an 80:20 wt% mixture of decamethyl cyclopentasiloxane and isostearyl alcohol

25) isostearyl alcohol

with an enthalpy of gelation in at least one of the liquids with a magnitude of at least 30 kJ/mole.

15

7. A composition according to claim 6 wherein the structurant is able to gel an 80:20 wt% mixture of decamethyl cyclopentasiloxane and isostearyl alcohol with an enthalpy of gelation having a magnitude of at least 30 kJ/mole.

20

8. A composition according to any one of claims 4 to 7 wherein the disperse phase contains a diol or polyol.

25

9. A composition according to any one of claims 4 to 8 which contains from 0.1% to 10% by weight of a nonionic emulsifier.

185
153

10. A composition according to any one of claims 4 to 9 which does not contain more than 8% by weight of ethanol or any monohydric alcohol with a vapour pressure above 1.3 kPa at 22°C.

5

11. A composition according to any one of claims 1 to 3 wherein the composition is a suspension with a particulate solid material dispersed in said liquid carrier.

10

12. A cosmetic according to any one of the preceding claims wherein the water-immiscible liquid carrier contains a volatile silicone and optionally a non-volatile silicone and/or a non-silicone hydrophobic organic liquid selected from hydrocarbons, hydrophobic aliphatic esters, aromatic esters, hydrophobic alcohols and hydrophobic ethers.

15

13. A composition according to any one of the preceding claims wherein the water-immiscible carrier liquid contains silicone oil in an amount which is at least 10% by weight of the composition.

20

14. A composition according to any one of the preceding claims containing from 0.1 to 12% by weight of the structurant.

25

15. A composition according to any one of the preceding claims which contains not more than 5% by weight of any

fatty alcohol which is solid at 20°C.

16. A composition according to any one of the preceding claims which is an antiperspirant composition comprising
5 an antiperspirant active.

17. A composition according to claim 11 which is an antiperspirant composition comprising a particulate antiperspirant active in suspension in said water-
10 immiscible carrier liquid.

18. A composition according to any one of claims 4 to 10 which is an antiperspirant composition comprising an antiperspirant active dissolved in said disperse phase.
15

19. A composition according to any one of claims 16 to 18 wherein the antiperspirant active comprises an aluminium and/or zirconium halohydrate, an activated aluminium and/or zirconium halohydrate, or an aluminium and/or
20 zirconium complex or an activated aluminium and/or zirconium complex.

20. A composition according to claim 19 which is a halohydrate or complex in which aluminium and zirconium
25 are both present.

21. A composition according to any one of claims 16 to 20 wherein the proportion of antiperspirant active is from 5

156
159

to 40% by weight of the composition.

22. A composition according to any one of the preceding claims in which a firm gel such that a penetrometer needle
5 with a cone angle of 9 degrees 20 minutes, drops into the gel for no more than 30 mm when allowed to drop under a total weight of 50 grams for 5 seconds.

23. A composition according to any one of the preceding
10 claims which is translucent or transparent.

24. A composition according to claim 24 which has at least 1%, and preferably at least 3%, light transmittance at 580 nm through a 1 cm thickness of the composition at
15 22°C.

25. An antiperspirant product comprising a dispensing container having at least one aperture for delivery of the contents of the container, means for urging the contents
20 of the container to the said aperture or apertures, and a composition according to any one of the preceding claims accommodated within the container.

26. A product according to claim 25 wherein the
25 composition is in the form of a stick and the container has an open end at which an end portion of the stick of composition is exposed for use.

27. A process for the production of a composition according to any one of claims 1 to 20 comprising, not necessarily in any order, the steps of

- incorporating a structurant into a water-immiscible liquid carrier
 - optionally mixing the liquid carrier with a disperse solid or liquid phase,
 - heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,
- followed by cooling or permitting the mixture to cool to a temperature at which it is thickened or solidified.

28. A process according to claim 27 which includes a step of pouring the mixture at elevated temperature into a dispensing container and allowing it to cool therein so as to produce a product according to claim 25 or claim 26.

29. A method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition according to any one of claims 16 to 20.

Unilever
00.026.09,
188
155

TRADUCCION OFICIAL No. 105

**TRADUCCION OFICIAL DE UN DOCUMENTO PRESENTADO EN INGLES.
LEGALIZACION TRASPASO INVENCIÓN "COMPOSICIONES COSMETICAS" A
UNILEVER N.V.**

J 3463(C) /CO

TRASPASO INVENCIÓN

YO/NOSOTROS, el suscrito, por el presente traspaso a:

UNILEVER N.V.
Una compañía holandesa de
Weena 455
3013 AL Rotterdam
Holanda

todos mis/nuestros derechos para solicitar y obtener una patente en:

COLOMBIA

de una invención hecha por mí/nosotros, titulada:

COMPOSICIONES COSMETICAS

Fechado: (en blanco)

Firmado: **Kevin Ronald FRANKLIN**
c/o Unilever Research Port Sunlight, Quarry Road East, Bebington,
Wirral, Merseyside, CH63 3JW, Reino Unido

Firmado: **M. G. Walker**
Notario Público
24/3/00

Sello del Notario Público de Heswall, Michael Glenn Walker


ANITA SALASMANCA DE ADNEU
TRADUCTORA OFICIAL
RES. MINISTERIO 3711

189
156

Firmado: **Andrew HOPKINSON**

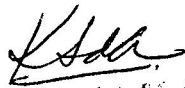
c/o Unilever Research Port Sunlight, Quarry Road East, Bebington,
Wirral, Merseyside, CH63 3JW, Reino Unido

Firmado: **M. G. Walker**

Notario Público

24/3/00

Sello del Notario Público de Heswall, Michael Glenn Walker


ANITA SALAMANCA DE ARNEU
TRADUCTORA OFICIAL
SES. MINJUSTICIA 3288

160
157

REINO UNIDO DE GRAN BRETAÑA E IRLANDA DEL NORTE

No. D 613511

Fecha: marzo 28, 2000

Este documento lleva la firma/sello de

Michael G Walker

Quien actúa en su condición de **Notario Público**

Firmado por: **J. M.A. Mason**

Principal Secretario de Estado de su Majestad para
Asuntos Extranjeros y del Commonwealth

Hay sello en altorrelieve y plano de la Foreign and Commonwealth Office de
Londres.


JANIS LALAMANDER DE MASON
TRADUCTORA OF
BES. MINISTROS 223

161
158

**CONSULADO GENERAL DE COLOMBIA
LONDRES**

AUTENTICACIÓN No. 0546-03

CERTIFICA el cargo y funciones de **J.M.A. MASON** y la autenticidad de su sello y firma. Expedida marzo 29, 2000, en Londres

Firmado: **ANA GEORGINA CHARRY**
Primer Cónsul

Hay sello del Consulado General de Colombia en Londres

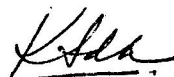
**MINISTERIO DE RELACIONES EXTERIORES
SANTA FE DE BOGOTA**

N° 065342

CERTIFICA la firma y el cargo del funcionario consular **ANA GEORGINA CHARRY**, el día mayo 22, 2000.

(Firma Ilegible)

JEFE DE LEGALIZACIONES
Santafé de Bogotá, D.C.


ANA SALAMANCA DE ABREU
TRADUCTORA DEL
RES. MINISTERIO DE JUSTICIA

for & sec Unilever 00-076091
J3463 (C) / CO
162
189

ASSIGNMENT OF INVENTION

I/We, the undersigned, do hereby assign to:

UNILEVER N.V.
a Dutch company of
Weena 455
3013 AL Rotterdam
Netherlands

my/our entire right to apply for and to obtain a patent in:

COLOMBIA

on an invention made by me/us, entitled:

COSMETIC COMPOSITIONS

Dated the day of

Kevin Ronald Franklin

Kevin Ronald FRANKLIN

c/o Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside, CH63 3JW,
United Kingdom

W. G. Walker Notary Public 24/3/00

Andrew Hopkinson

Andrew HOPKINSON

c/o Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside, CH63 3JW,
United Kingdom

W. G. Walker Notary Public 24/3/00

Notarise/Apostile/Legalise

65

66

NO SE ASUME
RESPONSABILIDAD DEL
GOBIERNO
MAY 22 P 08
D613511
JEF DE LEGALIZACIONES
SAFIDE DE BOGOTA

UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

28 March, 2000

This document bears
the signature / seal of

Michael G Walker

Acting in the capacity of

Notary Public

Signed by: J. M. A. Mason



[Signature]
For Her Majesty's Principal Secretary of State
For Foreign and Commonwealth Affairs