FORM 1 625139

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

I\We,

UNILEVER PLC

of UNILEVER HOUSE
BLACKFRIARS
LONDON EC4
ENGLAND

hereby apply for the grant of a standard patent for an invention entitled:

HAIR SETTING COMPOSITION.

which is described in the accompanying complete specification

Details of basic application(s):

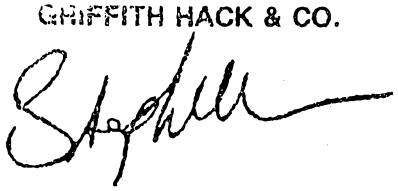
Number of basic application	Name of Convention country in which basic application was filed	Date of basic application
8918079.8	GB	08 AUG 89

My/our address for service is care of GRIFFITH HACK & CO., Patent Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria, Australia.

DATED this 03rd day of August 1990

UNILEVER PLC

GRIFFITH HACK & CO.



TO: The Commissioner of Patents.

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AUSTRALIA

B

PATENTS ACT 1952

APPLICATION BY ASSIGNEE OF INVENTOR

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

NAME OF APPLICANT

In support of an application made by:

UNILEVER PLC

TITLE

for a patent for an invention entitled:

HAIR SETTING COMPOSITION

FULL NAME AND ADDRESS OF SIGNATORY

I, Dilshad RAJAN

of Unilever House, Blackfriars,

London EC4, England.

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this declaration on its behalf.

FULL NAME AND ADDRESS OF INVENTOR(S)

2. The name and address of each actual inventor of the invention is as follows:

Peter GALLAGHER 1 Mission Cottage (off Moss Lane), Burscough, Lancashire, England; Thomas McGEE 74 Stanley Road, Hoylake, Wirral, Merseyside L47 LH2, England; and Ezat KHOSHDEL The Nook, Church Lane, Neston, Wirral, Merseyside L64 9US, England (respectively)

SEE NOTES OVER

3. The facts upon which the applicant is entitled to make this application are as follows:

The applicant would be entitled to have assigned to it a patent granted to any of the actual inventors in respect of the said invention

DELETE PARAGRAPHS 3 AND 4 FOR NON-CONVENTION APPLICATION

4. The basic application(s) as defined by Section 141 of the Act was (were) made as follows:

Country Great Britain on 8August 1989

in the name(s) UNILEVER PLC

and in on

in the name(s)

PLACE AND DATE OF SIGNING

5. The basic application(s) referred to in the preceding paragraph was (were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

Declared at London, England

this 20th day of July 1990

Signed

Position Authorised Signatory

GRIFFITH HACK & CO

PATENT AND TRADE MARK ATTORNEYS

MELBOURNE · SYDNEY · PERTH

(12) PATENT ABRIDGMENT (11) Document No. AU-B-60157/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 625139

(54) Title
HAIR SETTING COMPOSITION

International Patent Classification(s)
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(21) Application No. : **60157/90** (22) Application Date : **03.08.90**

(30) Priority Data

(31) Number	(32) Date	(33) Country
8918079	**08.08.89**	**GB UNITED KINGDOM**

(43) Publication Date : **14.02.91**

(44) Publication Date of Accepted Application : **02.07.92**

(71) Applicant(s)
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(56) Prior Art Documents
AU 57069/90 A61K 007/01
US 4780310

(57) Claim

1. A hair setting composition comprising a derivative of polyaminoglucose glycan polymer complex which is soluble in non-hydrogen bonded solvents, an organic or aqueous organic solvent, and at least 20% by weight of a non hydrogen-bonded cosolvent, where said derivative is dissolved in a mixture of the solvent and the cosolvent.

AUSTRALIA 625139

PATENTS ACT 1952

Form 10

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
Lodged:

Complete Specification-Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant:
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Address of Applicant: UNILEVER HOUSE
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Address for Service: GRIFFITH HACK & CO.,
601 St. Kilda Road,
Melbourne, Victoria 3004,
Australia.

Complete Specification for the invention entitled:
HAIR SETTING COMPOSITION.

The following statement is a full description of this invention including the best method of performing it known to me:-

HAIR SETTING COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a hair setting composition, particularly to a hair setting composition containing a derivative of polyaminoglucose glycan polymer complex (PAGGPC) in solution in a mixture of alcoholic or aqueous/alcoholic solvent and non hydrogen-bonded cosolvent.

BACKGROUND OF THE INVENTION

Hair setting products are used to retain the hair in a particular style. These products may be in the form of gels, lotions, mousses or sprays and will normally contain film-forming materials as the setting agent.

Particulary effective setting agents are the water-soluble salts of PAGGPC referred to in our earlier patent application case J3115, filed in EPO as 90306499.6.

PAGGPC may be obtained by treating the mycelia of certain fungal species, such as Aspergillus niger, with strong alkali, as described in for example GB-A-2026516 (Muzzarelli) or US-A-4806474 (Miles). Aspergillus niger is a common waste product in industrial fermentation processes, for example in the production of citric acid.

Polyaminoglucose glycan polymer complex has not

been fully characterised, but NMR studies have shown that it is distinct in character from chitosan, and physical comparisons show that films formed by such a complex and by chitosan are different from each other. Polyaminoglucose glycan polymer complex is commercially available, for example as RIOSAN (Trademark) from Meyhall.

In hairspray and mousse preparations a very important criterion for the consumer is that the hairspray is not too wet. The main solvent in hairsprays is generally alcohol, or an aqueous/alcoholic mixture, which does not evaporate quickly enough to avoid imparting a wet feel to the hair. This may be avoided by the use of a more volatile, apolar cosolvent which results in a spray droplet from which most of the solvent evaporates before striking the hair fibre.

The water-soluble salts of PAGGPC referred to above are insoluble in non hydrogen-bonded solvents, and hair setting compositions containing these salts as setting agents are therefore limited in the amount of volatile cosolvent which may be used. Hairsprays of this type are therefore felt to be wet in use.

We have found that certain derivatives of PAGGPC may be incorporated into hairsprays. These derivatives must be soluble in the non hydrogen-bonded cosolvents, so that there is no need to restrict the amount of cosolvent used, and the resulting hair setting compositions are found not to give a wet feeling in use.

BRIEF SUMMARY OF THE INVENTION

Accordingly the invention provides a hair setting composition comprising a derivative of polyaminoglucose glycan polymer complex, an organic or aqueous/organic solvent, and a non hydrogen-bonded cosolvent, said derivative being soluble in a mixture of the solvent and the cosolvent.

DETAILED DESCRIPTION OF THE INVENTION

PAGGPC may be obtained by treating the mycelia of for example, Aspergillus niger with concentrated alkali to remove impurities and to partially deacetylate the polymer complex. PAGGPC is available for example as RIOSAN which is partially deacetylated.

Derivatives of PAGGPC

The derivatives of PAGGPC which are used as the film-forming material in the hair setting compositions of the invention preferably comprise the reaction products of PAGGPC with an electrophile.

The electrophile is suitably chosen from epoxide, C_{1-30} alkyl halide, polyethylene glycol halide, C_{1-30} acyl halide, acid anhydride, C_{1-30} alkyl ester, aryl ester, C_{1-30} aliphatic aldehyde, C_{2-32} epoxide, and C_{5-74} bis-epoxide.

Preferred example of epoxides which may be used as the electrophile include -

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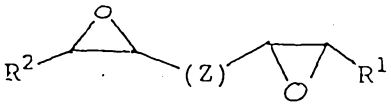
R where R is H, C_{1-20} saturated or unsaturated alkyl, C_{2-30} ethoxylated alkyl, saturated or unsaturated cycloalkyl, or



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where R^1, R^2 may be the same or different and are H, or C_{1-20} alkyl, Z is aryl, C_{1-30} saturated or unsaturated alkyl or C_{2-30} ethoxylated alkyl, or derivatives thereof.

Examples of suitable halides include 1-bromoethane, 1-bromohexane, 1-chlorododecane, chloropolyethylene glycol, ethanoyl chloride, propionyl chloride, benzoyl chloride and stearoyl chloride.

Suitable acid anhydrides include acetic, succinic, maleic, phthalic and citric anhydride, and suitable esters are ethyl ethanoate, ethyl benzoate and benzoyl benzoate.

The hair setting composition of the invention preferably comprises from 0.01 to 20% by weight of the derivative of PAGGPC and most preferably from 0.1 to 5% by weight.

PAGGPC will normally contain free hydroxyl groups and some acetylated amine groups. Under suitable conditions the electrophile, from those outlined above, will add to the hydroxyl group or groups. However, reaction is often easier, and preferable, if the PAGGPC is deacetylated by treating with strong alkali. The electrophile, under suitable conditions, will then react with both the free amine and the hydroxyl groups, although the electrophile will preferentially attack the amine group(s).

It should be noted that for certain electrophiles eg. 1-bromododecane, only a low level of substitution is required to give a derivative of PAGGPC which is soluble in non hydrogen-bonded cosolvents. Higher levels of substitution give rise to derivatives which are not soluble

in non hydrogen-bonded cosolvents. Such derivatives would not be suitable for use in the composition of the invention since they would be insoluble in the mixture of organic or aqueous/organic solvent and non hydrogen-bonded cosolvent. The person skilled in the art will readily ascertain the required degree of substitution necessary for any given electrophile.

The use of derivatives having higher levels of substitution is the subject of our copending application J.3119 having the same date as this application.

Solvent

The hairspray composition of the invention also comprises an organic solvent or an aqueous organic solvent.

Suitable solvents for use in the compositions of the invention include ethanol, isopropanol, methylene chloride, methoxyethanol, 2-ethoxyethanol, and mixtures thereof with water. The composition may comprise more than one such solvent.

The composition will usually comprise from 5 to 90% by weight of solvent and when the composition is in the form of a hairspray in aerosol form, the solvent will preferably form from 20 to 80% by weight of the composition.

Non hydrogen-bonded cosolvent

The composition of the invention also comprises a

non hydrogen-bonded cosolvent. The cosolvent is of a type which quickly evaporates in use, leaving a spray droplet which feels dry. Chlorofluorocarbons, fluorocarbons, hydrocarbons and dimethyl ether and mixtures thereof are particularly suitable cosolvents. Especially suitable are trichlorofluoromethane, dichlorodifluoromethane, 1,2-dichlorotetrafluoroethane, chlorodifluoromethane, 1-chloro,1,1-difluoromethane, 1,1-difluoroethane, butane or propane. Further examples of non hydrogen-bonded solvents may be found in Table II at pages C-696 to C-698 of the Handbook of Chemistry and Physics, 1983-84, 64th Edition, Ed. Robert C Weast, CRC Press, parts A (nonpolar solvents) and B (moderately polar solvents).

The cosolvent is generally present in the composition in an amount of from 5 to 90% by weight, preferably 20 to 80% by weight.

The extent of the dry feeling experienced by the user will depend on the balance between the solvent and the cosolvent used in the composition. Other factors, such as cost, flammability and desired discharge rate must also be taken in to account.

Those skilled in the art will easily ascertain the appropriate balance of solvent and cosolvent for the derivative of PAGGPC. For example, when the solvent is ethanol and the cosolvent is a fluorocarbon, a mixture of ethanol and fluorocarbon in a ratio of 30:70 by weight will give an acceptable, safe spray.

When the cosolvent is hydrocarbon, the

flammability of the spray obtained when the product is in the form of a hairspray must also be taken into account. In general, the level of hydrocarbon in an ethanol/hydrocarbon system should be below 50% by weight of the ethanol/hydrocarbon mixture. The level of flammability may be reduced by using a water/ethanol mixture as solvent.

When dimethylether (DME) is used as cosolvent, it may suitably be used in amounts of up to 90% by weight of the solvent/DME mixture.

The ratio of solvent to cosolvent generally lies between 1:9 and 9:1 by weight.

Other ingredients

The composition of the invention may also include other ingredients such as perfume; alcohol denaturants, for example benzyl diethyl,2,6 -xylyl carbamoyl methyl ammonium benzoate and sucrose octacetate; conditioning agents such as lanolin derivative; alkyl quaternary ammonium compounds such as cetyl trimethyl ammonium bromide; volatile silicones; plasticisers, such as silicone oils or silicone glycol; drag reducing agents such as hydroxypropylcelluloses eg. the range available from Hercules Inc under their trade mark. Klucel or high molecular weight polymers such as PVP-K90 (polyvinyl pyrrolidone having a K value of 90); high molecular weight polymers, such as cationic cellulose resins; other film forming polymers such as polymers of vinyl pyrrolidone and/or vinyl acetate; pH modifiers such as sodium

hydroxide, 2 amino-2-methyl-1-propanol, triethanolamine, citric acid, or hydrochloric acid; ingredients to improve combing out such as polydimethyl siloxane-polyoxyalkylene copolymers; corrosion inhibitors, such as triethanolamine salt of alkyenyl amberacide anhydride or disodium dodecyl sulphosucconate; surfactants such as lauryl dimethyl amine oxide.

Product form

The composition of the invention may be packed in aerosol cans or aerosol PVA packs, or may be in the form of mechanical pumps such as squeeze sprays or pump sprays.

In aerosol hairspray or mousse form, where the cosolvent does not act as a propellant in use, a propellant gas such as air, nitrogen or carbon dioxide may be added. The gas may be situated in the same compartment as the product to be dispensed or in a separate compartment.

The invention is further illustrated by the following Examples.

EXAMPLES

Preparation of PAGGPC derivatives

Preparation Example A

PAGGPC was N-propoxylated by heating deacetylated PAGGPC in a sealed tube (or an autoclave) with propylene oxide in an aqueous ethanol solvent for 12 hours at 100°C, to give N-hydroxypropyl PAGGPC (A).

Preparation Example B

The N-hydroxypropyl PAGGPC derivative obtained in Preparation Example A above was further functionalised by heating at between 60 and 80°C in an autoclave with 1-bromopropane in acetone in the presence of NaOH for 18 hours. O-propyl,N-hydroxypropyl PAGGPC (B) was obtained.

Preparation Example C

Crude, acetylated PAGGPC was heated in dimethyl formamide (DMF) at 100°C for 15 hours in the presence of 1-bromooctane to give O-octyl PAGGPC (C).

Preparation Example D

Deacetylated PAGGPC was heated in DMF with 1-bromohexane at 80°C for 15 hours to give N-hexyl PAGGPC (D).

Preparation Example E

Deacetylated PAGGPC was reacted with succinic anhydride in DMF which contained a small amount of

triethylamine, for 18 hours at 85°C, to give N-succinyl PAGGPC (E).

Preparation Example F

PAGGPC was reacted with stearoyl chloride in DMF in the presence of pyridine to give O-stearoyl PAGGPC (F).

In the following examples of hair setting compositions which illustrate the invention, all quantities are % by weight.

EXAMPLE	1	2	3
PAGGPC (A)	3.5	3.0	1.8
Water	17.5	10.0	-
DME	55.0	45.0	-
CFC 11/12[1] (65:35)	-	-	60.0
Perfume	0.13	0.13	0.13
Sucrose octacetate	0.03	0.06	0.06
Klucel HF	0.06	0.06	-
Silicone glycol	0.03	0.02	-
Ethanol to	100	100	100

1 - CFC 11/12 (65:35) is a mixture of
65% by weight trichlorofluoromethane and
35% by weight dichlorodifluoromethane.

EXAMPLE	4	5	6
PAGGPC (B)	2.0	1.5	3.0
DME	40	35	35
Water	20	20	20
Isopropanol	10	15	-
Sucrose octacetate	0.1	0.1	0.1
Perfume	0.2	0.2	0.2
Klucel HF	0.05	0.04	0.04
Silicone glycol	0.03	0.03	0.04
Ethanol to	100	100	100

EXAMPLE	7	8	9
PAGGPC (C)	3.0	3.0	2.0
CFC F114 [2]	50	-	-
Hydrocarbon (CAP 30)	-	45	30
Methylene chloride	-	2	5
Water	-	-	10
Compressed air	-	-	0.5
Isopropanol	10	15	10
Sucrose octaacetate	0.1	0.1	0.1
Perfume	0.2	0.2	0.2
PVP-K90	0.04	0.05	0.04
Ethanol to	100	100	100

2 - CFC F114 is 1,2-dichlorotetrafluoroethane

EXAMPLE		10	11	12
PAGGPC (D)		1.5	1.0	3.0
DME		40	40	45
Water		15	15	20
Isopropanol		20	20	20
Sucrose octacetate		0.1	0.1	0.1
Perfume		0.2	0.2	0.2
Klucel HF		0.06	0.03	0.03
Silicone glycol		0.05	0.02	0.02
Ethanol	to	100	100	100

EXAMPLE		13	14	15
PAGGPC (E)		1.5	1.5	3.0
CFC F114		35	40	40
Methylene chloride		4	4	2
Nitrogen		0.5	-	0.1
Carbon dioxide		-	4.5	-
Isopropanol		15	5	-
Perfume		0.2	0.2	0.2
PVP-K90		0.04	0.05	0.05
Ethanol	to	100	100	100

EXAMPLE	16	17	18	19
PAGGPC (F)	4.0	3.5	2.5	1.0
CFC 142 B [3]	60	-	-	40
Hydrocarbon (CAP 30)	-	40	5	-
Methylene chloride	5	5	5	-
Carbon dioxide	-	-	1	1
Isopropanol	10	15	15	10
Sucrose octacetate	0.1	0.1	0.1	0.1
Perfume	0.3	0.3	0.3	0.3
Klucel HF	0.03	0.04	0.04	0.05
Ethanol to	100	100	100	100

3 - CFC 142 B is 1-chloro,1,1-difluoromethane.

Example 20

The following is an example of a mousse according to the invention:

	% w/w
PAGGPC (B)	2.0
Ethanol	15
DME	7
Empigen OB [4]	0.03
Silicone glycol	0.05
Perfume	q.s.
Arquad 16/50 [5]	0.08
Water	to 100

4 - Empigen OB is lauryl dimethylamine oxide

5 - Arquad 16/50 is a mixture of trimethylammonium chloride and isopropyl alcohol

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A hair setting composition comprising a derivative of polyaminoglucose glycan polymer complex which is soluble in non-hydrogen bonded solvents, an organic or aqueous organic solvent, and at least 20% by weight of a non hydrogen-bonded cosolvent, where said derivative is dissolved in a mixture of the solvent and the cosolvent.

2. A hair setting composition as claimed in Claim 1 wherein the derivative of polyaminoglucose glycan polymer complex comprises the reaction product of the polymer with an electrophile.

3. A hair setting composition as claimed in Claim 2 wherein the polyaminoglucose glycan polymer complex is bonded through nitrogen or oxygen to residues of the electrophile which are aliphatic or aromatic groups containing one to thirty two carbon atoms.

4. A hair setting composition as claimed in Claims 2 or 3 wherein the electrophile is chosen from C_{2-32} epoxide, C_{5-74} bisepoxide, C_{1-30} alkyl halide, polyethylene glycol halide, C_{1-30} acyl halide, acid anhydride, C_{1-30} alkyl esters, aryl esters or C_{1-30} aliphatic aldehyde.

5. A hair setting composition as claimed in any one of Claims 1 to 4 wherein the epoxide is chosen from

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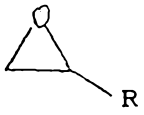

where R is H, C_{1-20} saturated or unsaturated alkyl, C_{2-30} ethoxylated alkyl, saturated or unsaturated C_{3-10} cycloalkyl, or

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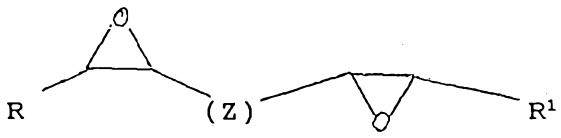

where R, R^1 may be the same or different and are H, or C_{1-20} alkyl, and Z is aryl, C_{1-30} saturated or unsaturated alkyl or C_{2-30} ethoxylated alkyl, or derivatives thereof.

6. A hair setting composition as claimed in any one of Claims 1 to 4 wherein the acid anhydride is chosen from acetic, succincic, maleic, phthalic or citric anhydride.

7. A hair setting composition as claimed in any preceding claim wherein the derivative of polyaminoglucose glycan polymer complex is present in an amount of from 0.01 to 20% by weight.

8. A hair setting composition as claimed in Claim 7

wherein the derivative of polyaminoglucose glycan polymer complex is present is an amount of from 0.1 to 5% by weight.

9. A hair setting composition as claimed in any preceding claim wherein the solvent is chosen from ethanol, isopropanol, methylene chloride, methoxyethanol and 2-ethoxyethanol, mixtures thereof, and mixtures thereof with water.

10. A hair setting composition as claimed in any preceding claim wherein the non hydrogen-bonded cosolvent is chosen from chlorofluorocarbons, fluorocarbons, hydrocarbons and dimethylether.

DATED THIS 3RD DAY OF AUGUST 1990
UNILEVER PLC
By its Patent Attorneys:
GRIFFITH HACK & CO.
Fellows Institute of Patent
Attorneys of Australia