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PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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	Address:	14 RUE ROYALE, F-75008, PARIS, FRANCE
[54]	Invention Title:	COMPOSITIONS BASED ON DIHYDROXYACETONE AND THEIR COSMETIC USE
[72]	Name(s) of actual inventor(s):	ISABELLE HANSENNE, SERGE FORESTIER AND DELPHINE PETITDEMANGE

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BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
92 14105	FRANCE	FR	24TH NOVEMBER 1992

Basic Applicant(s): L'OREAL

Drawing number recommended to accompany the abstract .....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Registered Patent Attorney

DATED this 22nd ay of November 1993.

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P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **L'OREAL**, of 14 Rue Royale, F-75008, Paris, France, being the applicant in respect of Application No. 51855/93 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors, as the inventors were the employees of the applicant at the time of the invention.

The Person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

23 May 1997

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AU9351855

(12) PATENT ABRIDGMENT (11) Document No. AU-B-51855/93
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 680633

(54) Title
COMPOSITIONS BASED ON DIHYDROXYACETONE AND THEIR COSMETIC USE

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(56) Prior Art Documents
EP 503853
WO 92/17159
AU 41277/93

(57) Claim

1. Cosmetic composition for colouring the skin in the form of an oil-in-water emulsion or vesicular dispersion, characterized in that it contains at least dihydroxyacetone and at least one thickening agent, consisting of a partially or completely neutralized, crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid, in a cosmetically acceptable medium.

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: COMPOSITIONS BASED ON DIHYDROXYACETONE ND THEIR COSMETIC USE

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

Compositions based on dihydroxyacetone and their cosmetic use

The invention relates to new cosmetic compositions based on dihydroxyacetone or DHA and to the process for colouring the skin employing them.

Dihydroxyacetone or DHA has been known for many years in its application for colouring the skin.

Compositions containing DHA present, however, a number of problems, depending on the nature of the medium in which the DHA is formulated (see Bobin et al, Farmaco Ed Pr vol 38 part 11-1983 p.415-423). Thus, various factors are known to be able to influence the preservation of DHA in a cosmetic composition, and in particular the pH, the storage temperature, the reducing or oxidizing nature of the medium and the solvent.

The compositions based on DHA proposed hitherto were essentially thickened with cellulose derivatives such as, for example, hydroxypropylcellulose or hydroxyethylcellulose. These compositions possess, however, the drawback of creating problems of preservation over time. Thus, a fall in viscosity of these compositions and an undesirable yellowing have been noted after storage for two months at 45°C. Moreover, from a cosmetic standpoint, the compositions applied to the skin generally impart a sticky character.

The Applicant discovered that, by using DHA with a crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid in cosmetic compositions, it was possible to prepare compositions for colouring the skin that are particularly stable on storage. In particular, after storage under the abovementioned conditions, a fall in viscosity and yellowing of the composition are not observed. Furthermore, the use of these copolymers results in thickened compositions possessing good cosmetic properties inasmuch as the composition imparts softness to the skin without giving rise to a sensation of stickiness. Lastly, the composition according to the invention enables a coloration of the skin to

be obtained after application which is similar to a natural tan, is more intense and has better resistance to water.

The subject of the invention is hence a cosmetic composition based on dihydroxyacetone and a partially or completely neutralized, crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid.

Another subject of the invention consists of the process for colouring the skin employing such a composition.

Other subjects of the invention will become apparent on reading the description and the examples which follow.

The composition for colouring the skin according to the invention is essentially characterized in that it contains at least dihydroxyacetone and, as a thickening agent, at least one partially or completely neutralized, crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid in a cosmetically acceptable medium.

Dihydroxyacetone or DHA is present in the compositions according to the invention in sufficient proportions to impart to the skin, after application, a coloration similar to the coloration obtained following natural tanning. It is generally present in proportions of between 0.5 and 10% by weight relative to the total weight of the composition, and preferably between 1 and 7% by weight.

The partially or completely neutralized, crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid is, more especially, a copolymer crosslinked with a compound containing olefinic polyunsaturation, such as tetraallyloxyethane, allylsucrose, allylpentaerythritol or methylenebisacrylamide, partially or completely neutralized with a neutralizing agent such as sodium hydroxide, potassium hydroxide or a tertiary amine such as triethanolamine. These copolymers may be prepared by copolymerizing acrylamide and sodium 2-acrylamido-2-methylpropanesulphonate by a free-radical

method using initiating agents of the azobisisobutyronitrile type, followed by precipitation in an alcohol such as tert-butanol.

The copolymers of acrylamide and 2-acrylamido-2-methylpropanesulphonate which are more especially preferred according to the invention are those obtained by copolymerization of 70 to 55 mol% of acrylamide and 30 to 45 mol% of sodium 2-acrylamido-2-methylpropanesulphonate. The crosslinking agent is used in concentrations of 10^{-4} to 4×10^{-4} mol per mole of the mixture of monomers. A more especially preferred copolymer is the product marketed by the company SEPPIC under the name Sepigel 305, in the form of an oil-in-water emulsion containing from 35 to 40% by weight of this copolymer, from 15 to 25% by weight of a mixture of C_{12}-C_{13} isoparaffinic hydrocarbons, from 3 to 8% by weight of polyethylene glycol lauryl ether containing 7 mol of ethylene oxide and water.

The completely or partially neutralized, crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid is used in sufficient amounts to thicken the composition, which must be capable of being applied to the skin without running. This copolymer is preferably used in proportions of between 0.5 and 5% by weight of active substance relative to the total weight of the composition, and preferably between 0.75 and 3% by weight of active substance relative to the total weight of the composition.

The compositions according to the invention may take the form of a gel, gel-cream, oil-in-water emulsion or vesicular dispersion, or any other form generally used in cosmetics.

The medium used in these compositions generally contains water, a mixture of water and one or more organic solvents or a cosmetically acceptable organic solvent or mixture of solvents. This medium also contains, in a preferred embodiment, cosmetically acceptable silicones and/or fats.

The solvents are, in particular, chosen from C_1-C_4 lower alcohols such as ethyl alcohol, isopropyl alcohol;

saturated long-chain monohydric alcohols having 10 to 18 carbon atoms; polyols having 2 to 8 carbon atoms, such as glycerol, alkylene glycols such as ethylene glycol, propylene glycol, diethylene glycol; esters of mono- or dibasic acids preferably having 4 to 22 carbon atoms and of linear or branched saturated alcohols having from 1 to 22 carbon atoms. Among these, diisopropyl or di(2-ethylhexyl) adipate, di(2-ethylhexyl)maleate, the benzoates of C_{12}-C_{15} alcohols and isoarachidyl neopentanoate may be mentioned.

These solvents are generally used in the aqueous medium in proportions of between 0.5 and 75% by weight, and especially between 2 and 50% by weight, relative to the total weight of the overall composition.

Among fats, oils and waxes of mineral, animal, vegetable or synthetic origin may be mentioned, such as jojoba oil, castor oil, liquid paraffin; the synthetic oils are, in particular:

- either isoparaffins of viscosity below 0.5 Pa.s corresponding to the formula

$$H_3C-\left(\begin{matrix}CH_3\\ |\\ C\\ |\\ CH_3\end{matrix}-CH_2\right)_n-\begin{matrix}CH_3\\ |\\ CH\end{matrix}-CH_3$$

in which

n is between 2 and 16, and mixtures thereof with oils of identical structure in which n is greater than 18 and preferably between 18 and 40; such oils are sold by the company PRESPERSE INC. under the names PERMETHYL 99A, 101A, 102A, 104A, 106A,

or by the company ICI under the name ARLAMOL HD.

The ISOPARS sold by the company EXXON INC. may also be mentioned.

- or poly(α-olefin)s of the polydecene type, hydrogenated or otherwise; such products are sold by the company ETHYL CORPORATION under the name ETHYLFLO; polyisobutylenes, hydrogenated or otherwise, may also be mentioned.

The fats also comprise fatty acids; fatty alcohols such as lauryl, cetyl, myristyl, stearyl,

palmityl and oleyl alcohol as well as 2-octyldodecanol, fatty acid esters such as glycerol monostearate, polyethylene glycol monostearate, C_6-C_{18} fatty acid triglycerides such as caprylic/capric acid triglycerides.

The silicones which can be used in the compositions according to the invention are organopolysiloxanes such as organopolysiloxane oils, organic solutions of organosiloxane gums and/or resins.

Among these silicones, there may be mentioned volatile silicones having a boiling point of between 60°C and 260°C, such as cyclic silicones having 3 to 7 silicon atoms, volatile linear silicones having from 2 to 9 silicon atoms and having a viscosity below or equal to 5×10^{-6} m^2/s at 25°C.

The non-volatile silicones consist mainly of polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, polyethersiloxane copolymers, modified or otherwise, silicone gums and resins and organo-modified polysiloxanes, as well as mixtures thereof.

Among polyalkylsiloxanes, there may be mentioned

- linear polydimethylsiloxanes of viscosity above 10^{-1} m^2/s, which can contain terminal trimethylsilyl, trihydroxysilyl or hydroxydimethylsilyl groups;
- polyalkylarylsiloxanes, such as polydimethylphenylsiloxanes, polymethyldiphenylsiloxanes, linear and/or branched, of viscosity from 10^{-5} to $5 \times 10^{-2} m^2/s$ at 25°C;
- poly(C_{10}-C_{30} alkyl)siloxanes containing terminal trimethylsilyl groups;
- the polyethersiloxane copolymers, modified or otherwise, are chosen, in particular, from copolymers of ethylene oxide and/or propylene oxide with a diorganosiloxane, such as dimethicone copolyols;
- the silicone gums are, inter alia, polydiorganosiloxanes of molecular mass between 200,000 and 1,000,000, used alone or mixed in a solvent chosen from volatile silicones, polydimethylsiloxane oils, polyphenylmethylsiloxane oils, isoparaffins, dodecane, tridecane, tetradecane or mixtures thereof;
- the organopolysiloxane resins which can be used

according to the invention are crosslinked siloxane systems containing $R_2SiO_{2/2}$, $RSiO_{3/2}$, $SiO_{4/2}$ units in which R represents a hydrocarbon group possessing from 1 to 6 carbon atoms or a phenyl group. The hydrocarbon group preferably denotes a C_1-C_4 alkyl radical;

- the organo-modified silicones are chosen, in particular, from the abovementioned silicones containing in their general structure one or more functional organic groups attached directly to the siloxane chain or attached via a hydrocarbon radical. There may be mentioned, in this connection, silicones containing perfluoro groups such as trifluoroalkyl groups; hydroxyl groups, for instance polyorganosiloxanes containing a hydroxyalkyl function; alkoxy groups; acyloxyalkyl groups.

Especially preferred polyorganosiloxanes are chosen from non-volatile silicones of the linear polyalkylsiloxane type containing terminal trimethylsilyl groups, such as

- the SILBIONE oils of the 70 047 and 47 series, such as the oil 47V 500 000 marketed by the company Rhône Poulenc;
- mixtures of organopolysiloxanes and cyclic silicone, such as the product Q2 1 401 of the company Dow Corning or SF 1214 SILICONE FLUID of the company General Electric;
- fluorosilicones of the polyalkylsiloxane type containing terminal trimethylsilyl groups and substituted on the chain with trifluoropropyl groups, such as the fluorosilicone sold by the company SHIN ETSU under the name X 22-821;
- volatile linear or cyclic silicones, and more especially decamethylcyclopentasiloxane.

The polyorganosiloxanes are generally used in the compositions in proportions of between 0.5 and 50% by weight, and preferably between 1 and 30% by weight, relative to the total weight of the composition.

According to a preferred embodiment of the invention, the composition contains fat-soluble and

water-soluble UV-B and/or UB-A sunscreen agents.

These sunscreen agents are chosen, in particular, from cinnamic derivatives such as, for example, 2-ethylhexyl p-methoxycinnamate; salicylic derivatives such as, for example, 2-ethylhexyl salicylate; camphor derivatives such as, for example, 4-methylbenzylidene-camphor, benzene-1,4-bis(3-methylidene-10-camphor-sulphonic acid); benzimidazole derivatives such as 2-phenylbenzimidazole-5-sulphonic acid; triazine derivatives such as 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)anilino]-1,3,5-triazine; benzophenone derivatives such as 2-hydroxy-4-methoxybenzophenone; dibenzoylmethane derivatives such as 4-tert-butyl-4'-methoxydibenzoylmethane; β,β-diphenylacrylate derivatives such as 2-ethylhexyl α-cyano-β,β-diphenyl-acrylate.

These sunscreen agents are used in proportions of between 0.01 and 15% by weight relative to the total weight of the composition.

The pH of the compositions according to the invention is generally between 4 and 10, and preferably between 5 and 7.5.

In the case of an emulsion, it is possible to use emulsifiers that are well known in cosmetics, and in particular cetyl alcohol or oleyl alcohol oxyethylenated with 5 to 30 mol of ethylene oxide, sorbitan oleate oxyethylenated with 10 to 40 mol of ethylene oxide, mixtures of glycerol monostearate and polyethylene glycol stearate containing 50 to 100 mol of ethylene oxide.

The compositions may also take the form of vesicular dispersions of ionic or nonionic amphiphilic lipids prepared according to known processes. The lipids may, for example, be swollen in an aqueous solution to form spherules dispersed in the aqueous medium, as described in the paper by BANGHAM, STANDISH and WATKINS, J.mol. Biol., 13, 238 (1965) or in Patents FR-2,315,991 and 2,416,008; a description of the various methods of preparation will be found in "Les liposomes en biologie cellulaire et pharmacologie" [Liposomes in cell biology

and pharmacology], Edition INSERM, John Libbery - Eurotext, 1987, pages 6 to 18.

The compositions according to the invention may also contain any other adjuvant customarily used in cosmetic compositions for the skin, and more especially surfactants, preferably nonionic surfactants, hydrating agents, demulcents, vitamins, antioxidants, opacifiers, colorants, perfumes and/or preservatives.

The solvents, fats or adjuvants used in compositions according to the invention should not contain either a primary or secondary amino group or an oxidizing group capable of interfering with the DHA.

These compositions may also contain or be used jointly with substances capable of modifying the shade or imparting additional coloration to the skin in combination with dihydroxyacetone. Hydroxyindols may, in particular, be used for this purpose.

The process for colouring the skin which is another subject of the invention is essentially characterized in that a composition as defined above is applied to the skin in sufficient amounts to impart to the skin a coloration similar to a natural tan.

The examples which follow are intended to illustrate the invention, no limitation being implied thereby.

Example 1: Self-tanning gel

DHA	5 g
Mixture of dimethiconol (13%), octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane (87%), sold under the name DC Q2 1401 by the company Dow Corning	5 g
Decamethylcyclopentasiloxane (Dow Corning DC 245 Fluid)	5 g
Oil-in-water emulsion of crosslinked copolymer of acrylamide and sodium 2-acrylamido-2-methylpropanesulphonate, sold under the name SEPIGEL 305 by the company SEPPIC	2 g AS
Preservative	Qs
Perfume	Qs
Water	Qs 100 g

Example 2: Self-tanning gel-cream

DHA	3 g
Jojoba oil	10 g
Benzene-1,4-bis(3-methylidene-10-camphorsulphonic acid)	1 g AS
Triethanolamine	0.6 g
Oil-in-water emulsion of crosslinked copolymer of acrylamide and sodium 2-acrylamido-2-methylpropanesulphonate, sold under the name SEPIGEL 305 by the company SEPPIC	2.5 g AS
Preservative	Qs
Perfume	Qs
Water	Qs 100 g

Example 3: Self-tanning emulsion

Oxyethylenated cetyl alcohol containing 10 mol of ethylene oxide, sold under the name Brij 56 by the company ICI	5 g
Cetyl alcohol	2 g
Liquid paraffin	10 g
2-Ethylhexyl para-methoxycinnamate sold under the name Parsol MCX	3 g
Decamethylcyclopentasiloxane sold under the name DC 245 Fluid by the company Dow Corning	5 g
DHA	5 g
Oil-in-water emulsion of crosslinked copolymer of acrylamide and sodium 2-acrylamido-2-methylpropanesulphonate, sold under the name SEPIGEL 305 by the company SEPPIC	1 g AS
Preservative	Qs
Perfume	Qs
Water	Qs 100 g

Example 4: Self-tanning emulsion

Dihydroxyacetone	3.5 g
O/W emulsion of crosslinked copolymer of acrylamide and sodium 2-acrylamido-2-methylpropanesulphonate, sold by the company SEPPIC under the name SEPIGEL 305	1.6 g AS
Mixture of dimethiconol (13%), octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane (87%), sold under the name Q2-1407 by the company Dow Corning	10 g
Liquid paraffin	10 g
Mixture of glycerol stearate and polyethylene glycol stearate containing 100 mol of ethylene oxide, sold under the name ARLACEL 165 by the company ICI	2 g
Preservative, perfume	qs
Water	qs 100 g

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

CLAIMS

1. Cosmetic composition for colouring the skin, in the form of an oil-in-water emulsion or vesicular dispersion, characterized in that it contains at least dihydroxyacetone and at least one thickening agent, consisting of a partially or completely neutralized, crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid, in a cosmetically acceptable medium.

2. Composition according to Claim 1, characterized in that dihydroxyacetone is used in proportions of between 0.5 and 10% by weight relative to the total weight of the composition, and preferably between 1 and 7% by weight.

3. Composition according to Claim 1 or 2, characterized in that the crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid is a copolymer crosslinked with a compound containing olefinic polyunsaturation, partially or completely neutralized with a neutralizing agent chosen from sodium hydroxide, potassium hydroxide and a tertiary amine.

4. Composition according to any one of Claims 1 to 3, characterized in that the copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonate is obtained by copolymerization of 70 to 55 mol% of acrylamide and 30 to 45 mol% of sodium 2-acrylamido-2-methylpropanesulphonate, and is crosslinked with a compound containing olefinic polyunsaturation in the proportion of 10^{-4} to 4×10^{-4} mol per mole of the mixture of monomers.

5. Composition according to any one of Claims 1 to 4, characterized in that the crosslinked copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid is in an O/W emulsion containing 35 to 40% by weight of copolymer, from 15 to 25% of the weight of a mixture of C_{12}-C_{13} isoparaffinic hydrocarbons, from 3 to 8% by weight of polyethylene glycol lauryl ether containing 7 mol of ethylene oxide and water.

6. Composition according to any one of Claims 1 to 5, characterized in that the partially or completely neutralized copolymer of acrylamide and 2-acrylamido-2-methylpropanesulphonic acid is present in proportions

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of between 0.5 and 5% of active substance relative to the total weight of the composition, and preferably from 0.75 to 3% by weight of active substance relative to the total weight of the composition.

7. Composition according to any one of Claims 1 to 6, characterized in that it also contains fat-soluble and/or water soluble UV-B and UV-A sunscreen agents.

8. Composition according to Claim 7, characterized in that the sunscreen agents are chosen from cinnamic derivatives, salicylates, benzylidenecamphor derivatives, benzimidazole derivatives, triazine derivatives, benzophenone derivatives, dibenzoylmethane derivatives and β,β-diphenylacrylate derivatives.

9. Composition according to any one of Claims 1 to 8, characterized in that it takes the form of a gel, gel-cream, oil-in-water emulsion or vesicular dispersion.

~~10.~~ 9. Composition according to any one of Claims 1 to 8, characterized in that the cosmetically acceptable medium comprises water, a mixture of water and one or more organic solvents or a cosmetically acceptable organic solvent or mixture of solvents.

~~11.~~ 10. Composition according to any one of Claims 1 to 9, characterized in that the composition contains fats chosen from oils and waxes of mineral, animal, vegetable or synthetic origin, fatty acids, fatty alcohols, C_6-C_{18} fatty acid triglycerides and esters of mono- or dibasic acids.

~~12.~~ 11. Composition according to any one of Claims 1 to 10, characterized in that it also contains an organopolysiloxane.

~~13.~~ 12. Composition according to Claim 10, characterized in that the organopolysiloxane is a volatile silicone having a boiling point of between 60 and 260°C, or alternatively a non-volatile silicone chosen from polyalkylsiloxanes, polyarylsiloxanes, polyarylalkylsiloxanes, polyethersiloxane copolymers, modified or otherwise, silicone gums and resins and organo-modified polysiloxanes, as well as mixtures thereof.

~~14.~~ 13. Process for colouring the skin in order to impart

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thereto a tan similar to a natural tan, characterized in that at least one composition as defined in any one of Claims 1 to 12 is applied to the skin.

DATED this 22nd day of November 1993.

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