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(56) Documents cited
GB A 2181146 GB 1604472 US 4189468
GB A 2177916 GB 1494915

(58) Field of search
A5B
Selected US specifications from IPC sub-class A61K

(54) Use of polyaminoamides to protect hair against light

(57) A composition comprising at least one polyaminoamide in a cosmetic medium is used for the preservation of mechanical properties of hair against deterioration by exposure to light. The composition can be formulated as an aerosol, cream, gel, emulsion, shampoo etc.

GB 2 191 399 A

SPECIFICATION

Use of polyaminoamides for protecting hair against light, and a process for protecting hair employing such polyaminoamides

The present invention relates to the use of a polyaminoamide as an agent for protecting hair keratin against atmospheric attack and in particular light, and to a process for protecting hair against atmospheric attack, and in particular against light.

It has been known for a long time that light attacks the keratin in hair and in the skin. Many publications disclose that natural light destroys certain amino acids in hair and that, by modifying the hair fibre, it consequently decreases the fibre's mechanical properties; a decrease in the mechanical properties is understood to mean chiefly that there is a decrease in the plateau at 15% elongation and in the breaking load.

The plateau at 15% elongation is the weight which must be applied to a wet hair of a given length in order to elongate it by 15%. The higher the weight, the more elastic and the stronger is the hair.

The breaking load is the weight which must be applied to a wet hair, of a given length, in order to break it.

In order to combat the attack on hair keratin due to light, it has already been proposed to employ substances capable of filtering out luminous radiation. In particular, filtering agents such as benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone, or dibenzoylmethane derivatives, for example 4-tert-butyl-4'-methoxydibenzoylmethane have been suggested.

However, these filtering substances have not been found effective in preserving the mechanical properties of hair, namely its elasticity and its wet strength, against the harmful effects of light.

On the contrary, it has become apparent that their presence in certain cosmetic compositions could even accentuate the deterioration in mechanical properties, particularly the decrease in the plateau at 15% elongation and in the breaking load.

We have now surprisingly found that certain polyaminoamide polymers are capable of preserving the mechanical properties of hair against damage by light. It is possible to demonstrate this property by exposure to natural light (sunny environment) and to artificial light (xenon lamp of an accelerated aging apparatus of the Suntest Hanau type).

The present invention thus relates to the use of certain polyaminoamides as agents for protecting the mechanical properties of hair, in particular the plateau at 15% elongation and the breaking load, against the degradation caused by atmospheric attacks, especially by light.

The present invention provides the use of a composition comprising at least one polyaminoamide as hereinafter defined in a cosmetically acceptable medium, in the preservation of mechanical properties of hair against deterioration by exposure to light:

1. A polyaminoamide (A) prepared by polycondensation of an acidic compound which is: (a) an organic dicarboxylic acid; (b) an aliphatic mono- or dicarboxylic acid containing a double bond; (c) an ester of an abovementioned acid, preferably as ester with an alkanol containing 1 to 6 carbon atoms; or (d) a mixture of the abovementioned compounds,

with a polyamine which is a mono- or bis-secondary bis-primary polyalkylenepolyamine, it being possible for up to 40 mol % of the polyamine to be replaced by a bis-primary amine, preferably ethylenediamine, or by a bis-secondary amine, preferably piperazine, and it being possible for up to 20 mol % to be replaced by hexamethylene-diamine;

a polyaminoamide (A) as defined above crosslinked with a crosslinking agent (B) which is an epihalohydrin, diepoxide, dianhydride, unsaturated anhydride or bis-unsaturated derivative in a proportion of from 0.025 to 0.35 mole of crosslinking agent per secondary amine group of the polyaminoamide (A); or

a polyaminoamide (A) crosslinked with a crosslinking agent (B) as defined above alkylated with an epoxide such as glycidol, ethylene oxide, propylene oxide, trimethylepoxypropylammonium chloride or with an unsaturated derivative such as acrylamide.

The crosslinked, optionally alkylated, polyaminoamide (A) should preferably be completely soluble in water at a concentration of 10% without forming a gel; the viscosity of a solution of the polymer at a concentration of 10% in water at 25°C is generally higher than 0.003 Pa s. It generally does not have reactive group, has no alkylating properties and is chemically stable.

These polymers and their preparation are described in greater detail in, for example, French Patent No. 2,252,840.

II. a water-soluble crosslinked polyaminoamide obtained by crosslinking a polyaminoamide (A) as defined above with a crosslinking agent which is:

II.1 a simple difunctional compound which is:

(1) a bishalohydrin, (2) a bisazetidinium, (3) a bishaloacyldiamine or (4) an alkyl bishalide;

II.2 an oligomer obtained by a reaction of a compound (a) which is (1) a bishalohydrin, (2) a bisazetidinium, (3) a bishaloacyldiamine, (4) an alkyl bishalide, (5) an epihalohydrin, (6) a diepoxide or (7) a bis-unsaturated derivatives,

with a compound (b) which is difunctional compound which is able to react with the compound (a);

II.3 a product of quaternization of a compound as defined in II.1 or an oligomer as defined in II.2 which contains one or more tertiary amine groups capable of being completely or partially alkylated with an alkylating agent (c) which is methyl or ethyl chloride, bromide, iodide, sulphate, meslyate or tosylate, benzyl chloride or bromide, ethylene oxide, propylene oxide or glycidol;

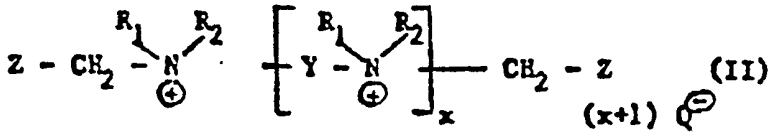
the crosslinking being carried out with 0.025 to 0.35 molecules, in particular 0.025 to 0.2 molecules and more particularly 0.025 to 0.1 molecules, of crosslinking agent per amine group of the polyaminoamide.

These crosslinking agents and these polymers, as well as the process for preparing them, are described in, for example, French Patent Application No. 2,368,508.

III. a water-soluble polyaminoamide derivative resulting from the condensation of a polyalkylenepolyamine containing two primary amino groups, at least one secondary amino group and at least one alkylene group containing 2 to 4 carbon atoms with a dicarboxylic acid of formula:

$$HOOC-C_mH_{2m}-COOH$$

in which m denotes an integer of from 4 to 8, or with a functional derivative thereof, in a molar ratio of from 0.8:1 to 1.2:1, followed by an alkylation in aqueous solution with a difunctional alkylating agent of formula:

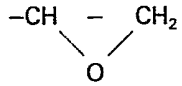


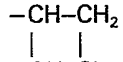
(II)

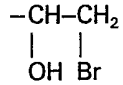
in which:

x denoes an integer of from 0 to 7,

z denotes one of the following groups







R_1 and R_2 each independently denote a C_1–C_4 alkyl group or a C_1–C_4 hydroxyalkyl group, Y denotes an alkylene group containing 2 to 6 carbon atoms, a 2-hydroxy-1,3-propylene group or a group of formula:

$-CH_2-CH_2-NH-CO-NH-CH_2-CH_2-$or
$-CH_2-CH_2-CH_2-NH-CO-NH-CH_2-CH_2-CH_2-$,

and $Q^{\ominus}$ denoes a halogen, sulphate or methosulphate anion,

the quantity of difunctional alkylating agent being chosen so that the alkylation product still remains in solution.

Examples of polyaminoamides of this type are adipic acid-dialkylaminohydroxyalkyl-dialkylenetriamine polymers in which each alkyl radical independently contains 1 to 4 carbon atoms, and is preferably methyl, ethyl or propyl, which are described, for example, in French Patent 1,583,363.

Compounds which permit particularly advantageous results to be obtained are the adipic acid-dimethylaminohydroxypropyl-diethylenetriamine polymers sold by Sandoz under the trade names "Cartaretine F, F_4 or F_8" (Trade Mark).

IV. a water-soluble polymer obtained by a reaction of a polyalkylenepolyamine containing two primary amine groups and at least one secondary amine group with a dicarboxylic acid which is

diglycolic acid or a saturated aliphatic dicarboxylic acid containing 3 to 8 carbon atoms, the molar ratio of the polyalkylenepolyamine to the dicarboxylic acid being from 0.8:1 to 1.4:1; the resultant polyamide being reacted with epichlorohydrin in a molar ratio of epichlorohydrin to the secondary amine group of the polyamide of from 0.5:1 to 1.8:1, which polymers are described, for example, in US Patents 3,227,615 and 2,961,347.

Polymers which are of particular interest are those sold by Hercules Incorporated under the trade name "Hercosett 57" (Trade Mark) or by Hercules Incorporated under the trade name "PD 170" (Trade Mark) (copolymer of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin) and "Delesette 101" (Trade Mark) (adipic acid-epoxypropyl-diethylenetriamine copolymer).

The polyaminoamide is preferably present in the composition in an amount of form 0.1 to 8% by weight, more preferably from 0.2 to 3.5% by weight, relative to the total weight of the composition.

The polyaminoamides I to IV may be employed to protect, for example, natural or sensitized hair. "Sensitized hair" means hair which has undergone a permanent-waving, dyeing or bleaching treatment.

The cosmetic compositions may, for example, be in the form of aqueous or aqueous-alcoholic solution or dispersion (the alcohol being in most cases a lower (for example C_1–C_6 or C_1–C_4) alkanol such as ethanol or isopropanol), which are, for example, thickened or unthickened, oily compositions, creams, gels, aerosol foams or sprays and may comprise adjuvants usually employed in hair compositions adapted for the intended application.

The application of the composition may, or may not, be followed by a rinse. The composition may, for example, be in the form of a shampoo, after-shampoo, a product for rinsing for applying before or after a shampoo, before or after dyeing or bleaching, before or after permanent-waving or hair-straightening, unrinsed composition such as a lotion, gel, cream, spray or foam for hair setting, for blow-drying, or a restructuring composition.

When the application of the cosmetic composition is not followed by a rinsing, the polyamiof hair against eight, is preferably pleasant in a proportionnoamide, as the active agent preserving the mechanical properties of from 0.1 to 5% by weight, more preferably 0.2 to 2% by weight, based on the total weight of the composition.

When the application of the cosmetic composition is followed by a rinsing, the polyaminoamide is preferably present in a proportion of from 0.1 to 8% by weight, more preferably 0.5 to 3.5% by weight, based on the total weight of the composition.

The cosmetic compositions generally have a pH of from 2 to 11, preferably from 3 to 9. The cosmetic compositions may also comprise cosmetic agents which are well-known in the art, provided that they do not themselves substantially alter the mechanical properties of the hair keratin.

The adjuvants or cosmetic agents which may be present in the cosmetic compositions employed according to the invention are, for example, cationic, anionic, amphoteric or nonionic surface agents or their mixtures, thickeners, polymers other than polyaminoamides as defined in paragraphs I to IV above, softeners, preservatives, foam-stabilizers, electrolytes, oils, pH regulating agents, waxes, anti-grease agents, sequestering agents, perfumes, colourants, synergists or organic solvents.

The cationic, anionic, nonionic or amphoteric surface-active agent or a mixture thereof is generally present in a proportion of from 0.1 to 70% by weight, preferably 0.5 to 50% by weight, based on the total weight of the composition.

When the cosmetic composition is in the form of a shampoo, the cosmetically acceptable medium is, for example, an aqueous or oily medium and the composition additionally comprises at least one anionic, cationic, nonionic or amphoteric surface-active agent or a mixture thereof. The shampoo may also, for example, conain various adjuvants such as a colourant, preservative, thickener, foam-stabilizer, synergist, softener, electrolyte, sequenstrant, one or more cosmetic resins, perfume, natural essence, oil or any other adjuvant usually employed in shampoos. The concentration of surface-active agent in the shampoo is generally from 2 to 50% by weight relative to the total weight of the composition. Their pH is generally (6˜ from 3 to 9.

When the application of the composition is not rinsed, for example, when the composition is in the form of a lotion, cream, gel, foam or spray for blow-drying, for hair setting, or for dressing or treating the hair, the cosmetically acceptable medium may, for example be aqueous-alcoholic and the composition may, for example, comprise at least one cationic, anionic, nonionic or amphoteric polymer or mixture thereof, generally in an amount of from 0.1 to 10%, preferably from 0.1 to 3%, by weight relative to the total weight of the composition and, if desired, a foam-suppressor. The polyaminoamide in this case may, for example, be present in an amount of from 0.1 to 5% by weight relative to the total weight of the composition.

When the hair compositions are rinsed lotions (also called a "rinse"), they may be applied before or after dyeing or bleaching, before or after permanent-waving, before or after shampooing or between two stages of shampooing, and are then rinsed off after a period of being left in

place.

These compositions may, for example, be aqueous or aqueous-alcoholic solutions which optionally contain surfactants. They may also be, for example, emulsions or gels or pressurized in aerosols in the form of sprays or foams.

In these rinsed compositions, the surface-active agent is preferably present in an amount of from 0.1 to 10%, more preferably from 0.5 to 7%, by weight relative to the total weight of the composition. The composition may also comprise at least one nonionic, cationic, anionic or amphoteric polymer.

When the hair compositions are in the form of gels, to be rinsed or not, they may contain a thickener in the presence or absence of solvents.

The thickener may, for example, be sodium alginate, gum arabic or xanthane gum or a cellulose derivative such as methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose or a carboxylic polymer such as the "Carbopols". Thickening of the composition, for example in the form of a lotion, may also be produced by using a mixture of polyethylene glycol and polyethylene glycol stearate or distearate or by using a mixture of phosphoric esters and amides. The concentration of thickener may vary, for example, from 0.1 to 30%, preferably from 0.2 to 15%, by weight relative to the total weight of the composition.

The pH of the rinsed lotion is generally from 2 to 10 and is preferably from 3 to 8.

When the hair compositions are restructuring lotions, they contain products which strengthen the keratin chain of hair. This class of products includes the methylolated derivatives such as those described in French Patents 1,527,085 and 1,519,979.

Cosmetic compositions to be applied to sensitized hair advantageously contain an electrolyte.

The presence of the electrolyte in the composition reduces or eliminates the tendency, exhibited by sensitized hair, to fix the polymers permanently. The electrolytes employed are generally water-soluble alkali metal or alkaline-earth metal salts of inorganic or organic acids, preferably sodium, potassium, ammonium or calcium chloride or acetate. The quantity of electrolyte used is preferably from 0.01 to 5% by weight, advantageously from 0.4 to 3% by weight, based on the total weight of the composition.

The present invention also provides a process for protecting hair keratin against atmospheric attacks, and in particular against light, wherein a composition comprising at least one polyaminoamide as defined above, in a cosmetically acceptable medium, is applied to the hair.

The Examples which follow further illustrate the invention.

Examples 1 to 3 illustrate the use of polyaminoamides as agents for protecting the mechanical propeties of hair against the degradation due to light.

Examples 4 to 8 illustrate cosmetic compositions which protect hair against atmospheric attacks and especially against light.

EXAMPLE 1

Hanks of bleached hair were exposed to natural light for 130 hours. The hair was then immersed in softened water at 20°C overnight and then the load and the elongation at break were measured on a Lhomargy DY 11 tensometer, together with the plateau at 15% elongation, both for exposed and for control, that is to say unexposed, hair, the tensile measurements being made in water at 20°C.

In this way it was possible to record a loss of 8% in this plateau at 15% elongation and a loss of 11% in the breaking load in the case of hair which had been subjected to an extended exposure to natural light, when compared with the unexposed hair controls.

Hanks of bleached hair were then treated with an aqueous solution containing 3% by weight of polyaminoamide prepared according to Example Ia of French Patent 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide.

After being rinsed, rough-dried and dried, the hair was immersed in softened water at 20°C overnight and then the parameters described above were measured under the same conditions, and a loss of only 4% was observed in the breaking load and in the plateau at 15% elongation, compared with the unexposed hank controls.

The protective effect of the polyamide on the hair fibre, against light, has therefore been demonstrated by measuring the decrease in the deterioration of the mechanical properties of the fibre subjected to an extended exposure to natural light.

EXAMPLE 2

Using the same tensometer, the parameters described in Example 1 were measured in the case of hanks of bleached hair which had been subjected to a "sun test" lasting for 5×24h, with the aid of a "Suntest Hanau" apparatus. This apparatus consists of a xenon lamp and a system of filters producing a radiation which, to a very large extent, corresponds to solar radiation. The energetic radiation is approximately 585 W/m^2 in the region of wavelengths

between 300 and 830 nm (total radiation).

When compared with bleached hank controls, the hanks which have been subjected to a "sun test" show a loss of 11% in the plateau at 15% elongation and 10% in the breaking load. On the other hand, bleached hanks treated with an aqueous solution containing 3% of polyaminoamide prepared according to Example Ia of Patent 2,252,840, and then rinsed, rough-dried and dried, show only a loss of 3% in the plateau at 15% elongation and 6% in the breaking load.

EXAMPLE 3

In an identical manner to Example 1, bleached hanks treated with an aqueous solution containing 3% of the polyaminoamide prepared according to French Patent No. 2,252,840 by alkylation of the compound prepared in Example Ia with the aid of trimethylepoxypropylammonium chloride, and then rinsed, rough-dried and dried, show only a loss of 4% in this plateau at 15% elongation and 3% in the breaking load.

EXAMPLE 4

A shampoo with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorhydrin per 100 secondary amine groups of the polyaminoamide		2.5 g AS (active substance)
Sodium alkyl (C_{12}–C_{14}) ether sulphate, oxyethylenated with 2.2 moles of ethylene oxide		7 g AS
Cocamidopropylbetaine sold at a concentration of 30% of AS by Goldschmidt under the trade name "Tego-Betaïn"		5 g AS
HCl	q.s. pH : 8.1	
Perfume, preservative	q.s.	
Water	q.s.	100 g

EXAMPLE 5

A shampoo with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		3.5 g AS
Laureth-5 carboxylic acid sold in a concentration of 90% AS by Chem-Y under the trade name "Akypo RLM 45"		12 g AS
Copra fatty acids diethanolamide sold by Henkel under the trade name "Comperlan KD"		2 g
HCl	q.s. pH : 7	
Perfume, preservative	q.s.	
Water	q.s.	100 g

EXAMPLE 6

The blow-drying lotion with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		0.5 g AS
Quaternary polyvinylpyrrolidone copolymer with a MW of 100,000, marketed by General Aniline under the trade name "Gafquat 734" at 50% AS		0.5 g AS
Ethyl alcohol	q.s.	10°
Perfume, preservative	q.s.	
Lactic acid	q.s. pH : 7.5	
Water	q.s.	100 g

EXAMPLE 7

The hair setting lotion with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		1.5 g AS
Polyvinylpyrrolidone		1 g
Perfume, preservative	q.s.	
Lactic acid	q.s. pH : 7.5	
Water	q.s.	100 g

EXAMPLE 8

The blow-drying lotion with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		0.5 g AS
Hydroxyethyl cellulose sold by Hercules under the trade name "Natrosol 250 HHR"		0.8 g
Lactic acid	q.s. pH : 7.5	
Perfume, preservative, colourant	q.s.	
Water	q.s.	100 g

EXAMPLE 9

A foaming oil which is applied to hair for a few minutes and which is rinsed off, with the following composition, is prepared:

Cartaretine F4 from Sandoz (adipic acid-dimethylamino-hydroxypropyl-diethylenetriamine polymer)		3 g AS
Mixture of a monoisopropanolamine salt of lauryl ether sulphate, of nonionic, and of diethanolamides of copra fatty acids sold by Henkel under the trade name "Texapon WW 99"		35 g
Liquid paraffin		30 g
Perfume, preservative	q.s.	
Rapeseed oil	q.s.	100 g

EXAMPLE 10

between 300 and 830 nm (total radiation).

When compared with bleached hank controls, the hanks which have been subjected to a "sun test" show a loss of 11% in the plateau at 15% elongation and 10% in the breaking load. On the other hand, bleached hanks treated with an aqueous solution containing 3% of polyaminoamide prepared according to Example Ia of Patent 2,252,840, and then rinsed, rough-dried and dried, show only a loss of 3% in the plateau at 15% elongation and 6% in the breaking load.

EXAMPLE 3

In an identical manner to Example 1, bleached hanks treated with an aqueous solution containing 3% of the polyaminoamide prepared according to French Patent No. 2,252,840 by alkylation of the compound prepared in Example Ia with the aid of trimethylepoxypropylammonium chloride, and then rinsed, rough-dried and dried, show only a loss of 4% in this plateau at 15% elongation and 3% in the breaking load.

EXAMPLE 4

A shampoo with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorhydrin per 100 secondary amine groups of the polyaminoamide		2.5 g AS (active substance)
Sodium alkyl (C_{12}–C_{14}) ether sulphate, oxyethylenated with 2.2 moles of ethylene oxide		7 g AS
Cocamidopropylbetaine sold at a concentration of 30% of AS by Goldschmidt under the trade name "Tego-Betaïn"		5 g AS
HCl	q.s. pH : 8.1	
Perfume, preservative	q.s.	
Water	q.s.	100 g

EXAMPLE 5

A shampoo with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		3.5 g AS
Laureth-5 carboxylic acid sold in a concentration of 90% AS by Chem-Y under the trade name "Akypo RLM 45"		12 g AS
Copra fatty acids diethanolamide sold by Henkel under the trade name "Comperlan KD"		2 g
HCl	q.s. pH : 7	
Perfume, preservative	q.s.	
Water	q.s.	100 g

EXAMPLE 6

The blow-drying lotion with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		0.5 g AS
Quaternary polyvinylpyrrolidone copolymer with a MW of 100,000, marketed by General Aniline under the trade name "Gafquat 734" at 50% AS		0.5 g AS
Ethyl alcohol	q.s.	10°
Perfume, preservative	q.s.	
Lactic acid	q.s. pH : 7.5	
Water	q.s.	100 g

EXAMPLE 7

The hair setting lotion with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		1.5 g AS
Polyvinylpyrrolidone		1 g
Perfume, preservative	q.s.	
Lactic acid	q.s. pH : 7.5	
Water	q.s.	100 g

EXAMPLE 8

The blow-drying lotion with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		0.5 g AS
Hydroxyethyl cellulose sold by Hercules under the trade name "Natrosol 250 HHR"		0.8 g
Lactic acid	q.s. pH : 7.5	
Perfume, preservative, colourant	q.s.	
Water	q.s.	100 g

EXAMPLE 9

A foaming oil which is applied to hair for a few minutes and which is rinsed off, with the following composition, is prepared:

Cartaretine F4 from Sandoz (adipic acid-dimethylamino-hydroxypropyl-diethylenetriamine polymer)		3 g AS
Mixture of a monoisopropanolamine salt of lauryl ether sulphate, of nonionic, and of diethanolamides of copra fatty acids sold by Henkel under the trade name "Texapon WW 99"		35 g
Liquid paraffin		30 g
Perfume, preservative	q.s.	
Rapeseed oil	q.s.	100 g

EXAMPLE 10

A rinsing gel with the following composition is prepared:

Xanthane gum sold by Kelco under the trade name "Keltrol T"		1 g
Sodium chloride		4 g
Cartaretine F4 from Sandoz		4 g AS
Sodium alkyl (C_{10} to C_{16}) ethoxy (30E) carboxylate sold by Marchon under the trade name "Empilan 2747–30"		1 g AS
HCl	q.s. pH : 4.8	
Perfume, preservative, q.s.		
Water	q.s.	100 g

EXAMPLE 11

A shampoo with the following composition is prepared:

Hercosett 57 from Hercules Inc. (copolymer of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin)		8 g
Nonionic surfactant obtained according to French Patent 2,091,516 by condensation of 3.5 moles of glycidol with a C_{11-14} α-diol		12 g
HCl	q.s. pH : 3	
Perfume, preservative, q.s.		
Water	q.s.	100 g

EXAMPLE 12

A rinsing emulsion with the following composition is prepared:

Hydroxyethyl cellulose sold by Hercules under the trade name "Natrosol 250 HHR"		1.2 g
Mixture of cetostearyl alcohol and of cetostearyl alcohol oxyethylenated with 33 moles of ethylene oxide, sold by Henkel under the trade name "Sinnowax AO"		2 g
Stearyl alcohol		1 g
Cetyl alcohol		1 g
"Delsette 101" from Hercules Inc. (adipic acid-epoxypropyldiethylenetriamine copolymer)		1 g
Triethanolamine	q.s. pH : 8	
Perfume, preservative, q.s.		
Water	q.s.	100 g

EXAMPLE 13

A rinsing foam with the following composition is prepared:

Polyaminoamide prepared according to Example Ia of French Patent No. 2,252,840: Polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of 11 moles of epichlorohydrin per 100 secondary amine groups of the polyaminoamide		3 g AS
Polyvinyl alcohol sold by Hoechst under the trade name "Mowiol 40/88"		1 g
Perfume, preservative, q.s.		
HCl	q.s. pH : 7	
Water	q.s.	100 g

The aerosol packaging is produced as follows:

above composition	90 g
"Freons 114/12" (43/57 by weight) sold by Du Pont de Nemours	10 g

CLAIMS

1. Use of a composition comprising at least one polyaminoamide as hereinafter defined in a cosmetically acceptable medium in the preservation of mechanical properties of hair against deterioration by exposure to light:

I. a polyaminoamide (A) prepared by polycondensation of an acidic compound which is: (a) an organic dicarboxylic acid; (b) an aliphatic mono- or dicarboxylic acid containing a double bond; (c) an ester of an abovementioned acid; or (d) a mixture of the abovementioned compounds,

with a polyamine which is a mono- or bis-secondary bis-primary polyalkylenepolyamine, it being possible for up to 40 mol % of the polyamine to be replaced by a bis-primary amine or by a bis-secondary amine and it being possible for up to 20 mol % to be replaced by hexamethylenediamine;

a polyaminoamide (A) as defined above crosslinked with a crosslinking agent (B) which is an epihalohydrin, diepoxide, dianhydride, unsaturated anhydride or bis-unsaturated derivative in a proportion of from 0.025 to 0.35 mole of crosslinking agent per secondary amine group of the polyaminoamide (A); or

a crosslinked polyaminoamide (A) as defined above alkylated with an epoxide or an unsaturated derivative;

II. a water-soluble crosslinked polyaminoamide obtained by crosslinking a polyaminoamide (A) as defined above with a crosslinking agent which is:

II.1 a simple difunctional compound which is: (1) a bishalohydrin, (2) a bisazetidinium, (3) a bishaloacyldiamine or (4) an alkyl bishalide;

II.2 an oligomer obtained by a reaction of a compound (a) which is: (1) a bishalohydrin, (2) a bisazetidinium, (3) a bishaloacyldiamine, (4) an alkyl bishalide, (5) an epihalohydrin, (6) a diepoxide or (7) a bis-unsaturated derivative

with a compound (b) which is a difunctional compound which is able to react with the compound (a);

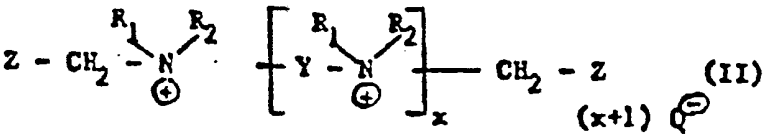
II.3 a product of quaternization of a compound as defined in II.1 or an oligomer as defined in II.2 which contains one or more tertiary amine groups capable of being completely or partially alkylated with an alkylating agent (c) which is methyl or ethyl chloride, bromide, iodide, sulphate, mesylate or tosylate, benzyl chloride or bromide, ethylene oxide, propylene oxide or glycidol;

the crosslinking being carried out with 0.025 to 0.35 molecules of crosslinking agent per amine group of the polyaminoamide.

III. a water soluble polyaminoamide derivative resulting from the condensation of a polyalkylenepolyamine containing two primary amino groups, at least one secondary amino group and at least one alkylene group containing 2 to 4 carbon atoms with a dicarboxylic acid of formula:

$$HOOC–C_mH_{2m}–COOH$$

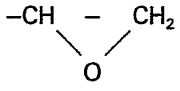
in which m denotes an integer of from 4 to 8, or with a functional derivative thereof, in a molar ratio of from 0.8:1 to 1.2:1, followed by an alkylation in aqueous solution with a difunctional alkylating agent of formula:

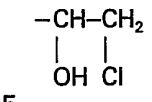


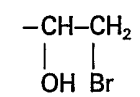
(II)

in which:

x denotes an integer of from 0 to 7.
Z denoes one of the following groups:







R_1 and R_2 each independently denote a C_1–C_4 alkyl group or a C_1–C_4 hydroxyalkyl group, Y denotes an alkylene group containing from 2 to 6 carbon atoms, a 2-hydroxy-1,3-propylene group or a group of formula:

$-CH_2-CH_2-NH-CO-NH-CH_2-CH_2-$ or
$-CH_2-CH_2-CH_2-NH-CO-NH-CH_2-CH_2-CH_2-$,

and $Q^{\ominus}$ denotes a halogen, sulphate or methosulphate anion,

the quantity of difunctional alkylating agent being chosen so that the alkylation product still remains in solution.

IV. A water-soluble polymer obtained by a reaction of a polyalkylenepolyamine containing two primary amine groups and at least one secondary amine group with a dicarboxylic acid which is diglycolic acid or a saturated aliphatic dicarboxylic acid containing 3 to 8 carbon atoms, the molar ratio of the polyalkylenepolyamine to the dicarboxylic acid being from 0.8:1 to 1.4:1; the resultant polyamide being reacted with epichlorohydrin in a molar ratio of epichlorohydrin to the secondary amine group of the polyamide of from 0.5:1 to 1.8:1.

2. Use according to claim 1, wherein the polyaminoamide is present in the composition in an amount of from 0.1 to 8% by weight relative to the total weight of the composition.

3. Use according to claim 2 wherein the polyaminoamide is present in an amount of from 0.2 to 3.5% by weight.

4. Use according to any one of claims 1 to 3 wherein the polyaminoamide is a polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of about 11 molecules of epichlorohydrin per 100 secondary amine groups of the polyamide.

5. Use according to any one of claims 1 to 3 wherein the polyamide is a polycondensate of adipic acid with diethylenetriamine, crosslinked with epichlorohydrin in a proportion of about 11 molecules of epichlorohydrin per 100 secondary amine groups of the polyaminoamide and alkylated with trimethylepoxypropylammonium chloride.

6. Use according to any one of claims 1 to 3 wherein the polyaminoamide is a dialkylaminohydroxyalkyl-dialkylenetriamine polymer in which each alkyl moeity independently contains from 1 to 4 carbon atoms.

7. Use according to claim 6 wherein the polyaminoamide is a dimethylaminohydroxypropyl-diethylenetriamine polymer.

8. Use according to anyone of claims 1 to 3 wherein the polyaminoamide is a copolymer of adipic acid and diethylenetriamine, crosslinked with epichlorohydrin or an adipic acid-epoxypropyl-diethylenetriamine copolymer.

9. Use according to any one of claims 1 to 8 wherein the composition is in the form of an aqueous or aqueous-alcoholic solution or dispersion, oily composition, cream, gel, aerosol foam or spray.

10. Use according to any one of claims 1 to 9 wherein the composition additionally comprises at least one surface-active agent, the chosen, polymer other than a polyaminoamide, softener, preservative, foam-stabilizer, electrolyte, organic solvent, silicone derivative, oil, wax, antigrease agent, pH control agent colourant, perfume or sequestering agent.

11. Use according to any one of claims 1 to 10 wherein the composition is in the form of a shampoo wherein the cosmetically acceptable medium is an aqueous or oily medium, which additionally comprises at least one anionic, cationic, nonionic or amphoteric surface-active agent or a mixture thereof in an amount of from 2 to 50% by weight relative to the total weight of the composition.

12. Use according to any one of claims 1 to 10 wherein the composition is in the form of a lotion, gel, cream, spray or foam, which are not rinsed, wherein the cosmetically acceptable medium is aqueous or aqueous-alcoholic, wherein the polyaminoamide is present in an amount of from 0.1 to 5% by weight relative to the total weight of the composition, which additionally comprises a cationic, anionic, nonionic or amphoteric polymer or mixture thereof in an amount of from 0.1 to 10% by weight relative to the total weight of the composition.

13. Use according to any one of claims 1 to 10 wherein the composition is in the form of an emulsion, gel, foam or spray for rinsing wherein the cosmetically acceptable medium is

aqueous or aqueous-alcoholic, wherein the polyaminoamide is present in an amount of from 0.1 to 8% by weight relative to the total weight of the composition, and which may additionally comprise a surfactant, if desired, in an amount of from 0.1 to 10% by weight relative to the total weight of the composition, or a nonionic, cationic, anionic or amphoteric polymer.

14. Use according to any one of claims 1 to 13 wherein the composition is in the form of a gel which additionally comprises a thickener in an amount of from 0.1 to 30% by weight relative to the total weight of the composition and, optionally, a solvent.

15. Use according to claim 1 substantially as hereinbefore described in any one of the Examples.

16. A process for protecting hair keratin against the effect of light, wherein a composition comprising at least one polyaminoamide as defined in any one of claims 1 to 8, in a cosmetically acceptable medium, is applied to the hair.

17. A process according to claim 16 wherein the composition is in the form of a shampoo, after-shampoo, rinsing product, unrinsed product for hair setting, or for blow-drying, or restructuring composition.

18. A process for protecting hair according to claim 16 or 17 wherein the composition is in the form of a thickened or unthickened aqueous or aqueous-alcoholic solution or dispersion, oily composition, cream, gel, aerosol foam or spray, which additionally comprises at least one of a surface-active agent, thickener, polymer other than a polyaminoamide, softener, preservative, foam-stabilizer, electrolyte, organic solvent, oil, wax, antigrease agent, pH control agent, perfume, colourant, sequestrant or synergist.

19. A process according to claim 16 substantially as hereinbefore defined in any one of the Examples.

20. A composition as defined in any one of claims 1 to 15.

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