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(54) COSMETIC COMPOSITION BASED ON CROSSLINKED QUATERNISED POLYMERS

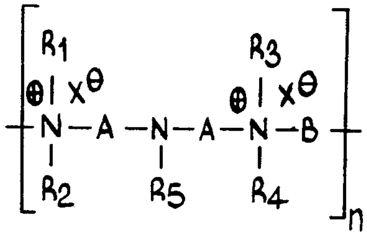
(71) We, L'OREAL, a French Body Corporate of 14, Rue Royale, 75008 Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the use, as cosmetic agents, of crosslinked amine polymers possessing quaternised ammonium groups.

Certain polymers possessing quaternised nitrogen atoms in the macro-chain are known and their use as pesticides, as flocculating agents, as surface-active agents or as ion exchangers has already been proposed.

It has now been found that, surprisingly, certain crosslinked amine polymers possessing quaternised ammonium groups exhibit valuable cosmetic properties when they are introduced into compositions applied to the hair or to the skin.

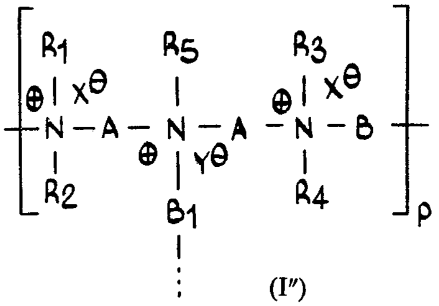
This invention provides a composition suitable for use in cosmetics, which comprises at least one cosmetically acceptable vehicle i.e. a vehicle suitable for application to the hair and/or the skin, and at least one crosslinked polymer (of the formula I) possessing recurring units of the formulae:



$$\left[-\underset{R_2}{\overset{R_1\,X^{\ominus}}{\overset{\oplus}{N}}}-A-\underset{R_5}{N}-A-\underset{R_4}{\overset{R_3\,X^{\ominus}}{\overset{\oplus}{N}}}-B-\right]_n$$

(I′)

and



$$\left[-\underset{R_2}{\overset{R_1\,X^{\ominus}}{\overset{\oplus}{N}}}-A-\underset{\underset{\vdots}{B_1}}{\overset{R_5}{\overset{\oplus}{N}}}Y^{\ominus}-A-\underset{R_4}{\overset{R_3\,X^{\ominus}}{\overset{\oplus}{N}}}-B-\right]_p$$

(I″)

in which:

A is a polymethylene group having 2 or 3 carbon atoms,

B_1 and B, which may be identical or different, represent a polymethylene group having 3 to 10 carbon atoms, a (ortho-, meta- or para-) xylylidenyl group $—CH_2—C_6H_4—CH_2—$, a $—(CH_2)_x—O—(CH_2)_x—$ group, where x is a number equal to 2 or 3, or a $—CH_2—CHOH—CH_2—$ group,

R_1 and R_3, which may be identical or different, represent an aliphatic radical having 1 to 12 carbon atoms,

R_2 and R_4, which may be identical or different, represent an aliphatic radical having 1 to 20 carbon atoms,

R_5 is a hydrogen atom or an aliphatic, alicyclic, aryl or araliphatic radical containing at most 20 carbon atoms,

$X^{\ominus}$ represents a halide, especially chloride or bromide, anion,

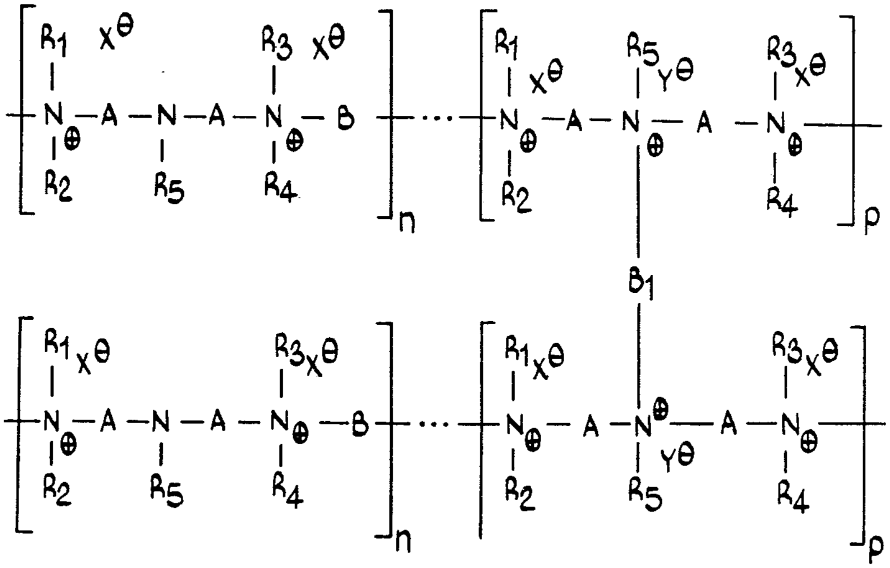
$Y^{\ominus}$ is a halide, especially chloride or bromide, anion and

n and p are integers, the polymers being crosslinked via the radicals B_1.

The polymers consisting of both units I′ and units I″ are here referred to as polymers of the formula I.

It will be seen that in the formula I″ the group B_1 is shown with a free valency, which indicates that the I″ units are bonded by a crosslinking bond to similar units of another macromolecular chain.

In other words, the polymers of the formula I have a structure of the following type:



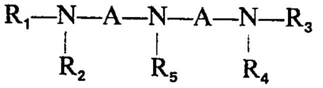
In the polymers of the formula I:

R_1 and R_3 in particular represent an alkyl radical having 1 to 12 carbon atoms, R_2 and R_4 in particular represent an alkyl radical having 1 to 20 carbon atoms, if R_5 represents an aliphatic radical, this is in particular an alkyl or cycloalkyl-alkyl radical having at most 20 carbon atoms, and preferably 1 to 16 carbon atoms, if R_5 represents an alicyclic radical, this is in particular a cycloalkyl radical with 5 or 6 chain members, and if R_5 represents an araliphatic radical, this is in particular an aralkyl radical such as a phenylalkyl radical, of which the alkyl group preferably contains from 1 to 3 carbon atoms, and in particular the benzyl radical.

Preferably, $R_1 = R_3 = CH_3$, in particular with $R_2 = R_4$.

The terminal groups of the polymers of the formula I are of the —B_1—Y or —B—X type.

To prepare the polymers of the formula I with $B_1 = B$, a triamine of the formula II:



$$\underset{\substack{|\\R_2}}{R_1\text{—}N}\text{—A—}\underset{\substack{|\\R_5}}{N}\text{—A—}\underset{\substack{|\\R_4}}{N\text{—}R_3} \qquad \text{(II)}$$

can be subjected to a polycondensation reaction with an excess of a dihalide of the formula III:

$$X\text{—}B\text{—}X \qquad \text{(III)}$$

in which:

R_1, R_2, R_3, R_4, R_5, A, B and X are defined as above.

The compound III is used in excess, that is to say that per mol of triamine II employed, the dihalide III is used in the reaction in an amount greater than 1 mol.

To prepare the polymers of the formula I with B_1 different from B, a triamine of the formula II can be subjected to a polycondensation reaction, as above, with a substantially equimolecular amount of a dihalide of the formula III, and the polymer consisting of units of the formula I′, obtained as an intermediate, then subjected to the action of a compound of the formula Y—B_1—Y, B_1 and Y being defined as above.

The treatment with the compound Y—B_1—Y can be carried out either by adding this compound to the reaction mixture or after having isolated the intermediate polymer I' and having redissolved it in an appropriate solvent.

In the two processes described above, the reaction is carried out, for example, in a solvent or in a mixture of solvents which favour the quaternisation reactions, such as water, dimethylformamide, acetonitrile, lower alcohols, especially lower alkanols such as methanol.

The reaction temperature is suitably from 10 to 150°C and preferably from 20 to 100°C.

The reaction time depends on the nature of the solvent, the starting reactants and the desired degree of polymerisation.

The resulting polycondensate can be isolated, if desired, at the end of the reaction, either by filtration or by concentrating the reaction mixture.

It is possible to regulate the mean chain length by adding, at the start of, or during, the reaction, a small amount e.g. 1 to 15 mol % relative to the reactant II, of a monofunctional reactant such as a tertiary amine.

In this case, at least a part of the terminal groups of the resulting polymer I are derived from tertiary amine group used.

The invention includes the cosmetic use of the polymers of the formula I which possess such terminal groups.

In the two abovementioned processes of preparation of the polymers of the formula I, the final product can be isolated at the end of the reaction either by filtration or by concentrating the reaction mixture and, if appropriate, crystallising the material by adding a suitable anhydrous organic liquid.

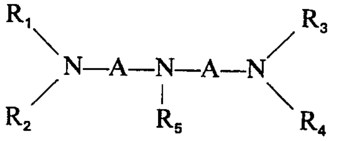
To prepare the polymers of the formula I (with B_1 different from B), the reactant $Y—B_1—Y$ can be used in any amount up to a maximum of 3 mols per mol of triamine starting material. Preferably, from 0.1 to 3 mols of $Y—B_1—Y$ are used per mol of triamine. The polymers of the formula I can be isolated under conditions which allow the excess of the reactant $Y—B_1—Y$ to be removed.

It is in this way possible to obtain a whole range of polymers I having varying degrees of crosslinking and containing a statistical distribution of units of the formulae I' and I''. Although in theory a large excess of dihalide might react with all the reactive tertiary nitrogen atoms of the triamine, in practice this does not happen so that the polymer will still possess some recurring units of formula (I').

The triamine starting materials can be obtained in accordance with the methods of working described in the literature.

For example the N_1, N_1, N_2, N_3, N_3-pentamethylated dialkylenetriamines can be prepared by methylating the corresponding dialkylenetriamines with the aid of formaldehyde and formic acid.

Using the same method, the triamines of the formula



in which:

$A = (CH_2)_2$,

$R_1 = R_2 = R_3 = R_4 = CH_3$

and R_5 is different from H and from CH_3, can be obtained from triamines in which $R_1 = R_2 = R_3 = R_4 = H$, themselves obtained in accordance with British Specification No. 913,471.

Again using this method, the triamines of the above formula in which:

$R_1 = R_3 = CH_3$,

$R_3 = R_4 = R_5 \neq CH_3$

can be obtained from the triamines in which $R_1 = R_3 = H$, themselves obtained according to a technique similar to that described by F. B. ZIENTY, Journal of The American Chemical Society, *68*, page 1388, 1945.

The triamines in which:

$$R_1 = R_2 = R_3 = R_4 = R_5 \neq CH_3$$

can be prepared by a method described in U.S. Patent No. 3,324,182.

Finally, the triamines in which:

$$R_1 = R_3$$

$$R_2 = R_4$$

$$R_5 \neq CH_3$$

can be prepared by the method of S. M. KUPCHAN, G. BONDESSON and A. P. DAVIES, Journal of Medicinal Chemistry, *15* (1), page 65, 1972.

The polymers of the formula I are generally soluble in at least one of the following three solvents: water, ethanol or a water-ethanol mixture.

By evaporating their solution it is possible to obtain films which in particular exhibit good affinity to the hair.

As indicated above, the polymers of the formula I exhibit valuable cosmetic properties.

The cosmetic compositions of the invention comprise polymers of the formula I either by way of the principal active ingredient or by way of an additive.

These cosmetic compositions can in particular be presented in the form of aqueous, alcoholic or aqueous-alcoholic solutions (the alcohol being in particular a lower alkanol such as ethanol or isopropanol), or in the form of creams, gels or emulsions, or in the form of sprays, for example in aerosol containers which also contain a propellant such as nitrogen, nitrous oxide or chlorofluorinated hydrocarbons of the "Freon" (Registered Trade Mark) type.

Adjuvants are generally present in the cosmetic compositions of the invention, such adjuvants being, for example, perfumes, dyestuffs, preservatives, sequestering agents and thickeners.

It should be noted that the cosmetic compositions according to the invention include both ready-to-use compositions and concentrates which require dilution before use. Accordingly, the cosmetic compositions of the invention are not limited to a particular range of concentration of the polymer of the formula I.

In general, in the cosmetic compositions of the invention, the concentration of polymers of the formula I is from 0.01 to 10% by weight, especially from 0.5 to 10% and preferably from 0.5 to 5% by weight.

The polymers of the formula I in particular exhibit valuable cosmetic properties when they are applied to the hair.

Thus, when they are applied to the head of hair, either by themselves or together with other active substances, in the course of a treatment such as a shampoo, dyeing treatment or wave-set, they significantly improve the properties of the hair.

For example, they favour the treatment and facilitate the combing-out of the wet hair. Even at a high concentration, they generally do not impart a sticky touch to the wet hair.

Contrary to the usual cationic agents, they do not make the dry hair heavy and thus facilitate loose hair styles. They impart springy properties, and a glossy appearance, to the dry hair.

They contribute efficiently to eliminating the shortcomings of hair which has been sensitised by treatments such as bleaching treatments, permanent waving or dyeing treatments. In fact, it is known that sensitised hair is frequently dry, dull and rough and difficult to comb cut and to style.

In particular, they are of great value when used as pre-treatment agents, especially before an anionic and/or non-ionic shampoo or before an oxidation dyeing treatment which is itself followed by an anionic and/or non-ionic shampoo. The hair is then particularly easy to comb out and is very soft to the touch.

They can also be used as pre-treatment agents in other hair treatment operations, for example permanent waving treatments.

The cosmetic compositions according to the invention are in particular cosmetic compositions for hair.

These cosmetic compositions for hair can be presented in the forms mentioned above.

The adjuvants generally present in such compositions are those mentioned above or, for example, resins usually employed in cosmetic compositions for hair.

Thus the compositions for hair, according to the invention, contain the polymer either as an additive or as the main active ingredient, in, for example, wavesetting lotions, treatment lotions, hair-styling creams or gels, or by way of an additive in, for example, shampoo compositions, wavesetting compositions, permanent waving compositions, dyeing compositions, restructuring lotions, antiseborrhoeic treatment lotions or hair lacquers.

The hair compositions, according to this invention, thus in particular comprise:

a) treatment compositions, characterised in that they contain, by way of active ingredients, at least one polymer of the formula I in aqueous or aqueous-alcoholic solution.

The content of polymer of the formula I can vary from 0.01 to 10% by weight and preferably from 0.1 to 5% by weight.

The pH of these lotions is approximately neutral, for example from 6 to 8. It is possible, if necessary, to bring the pH to the desired value by adding either an acid such as citric acid or a base, especially an alkanolamine such as monoethanolamine or triethanolamine.

In order to treat the hair with such a lotion, the said lotion may be applied to the wet hair and is allowed to act, for say 3 to 15 minutes, after which the hair is rinsed.

Thereafter, a conventional waveset may be carried out, if desired;

b) shampoos, characterised in that they contain at least one polymer of the formula I and a cationic, nonionic or anionic detergent.

The cationic detergents are in particular long-chain quaternary ammonium compounds, esters of fatty acids and aminoalcohols or polyether-amines.

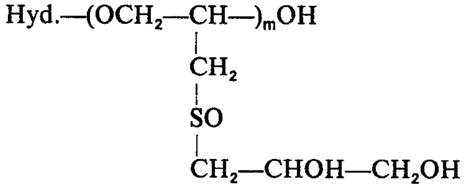
The non-ionic detergents, which can be used as a mixture with the anionic detergents, are in particular:

alcohols, diols, alkylphenols, thiols or amides with C_{12} to C_{18} linear chains, which are oxyethyleneated, oxypropyleneated, glycerolated or glycidolated;

alcohols, thiols or alkylphenols with C_2 to C_{10} chains, which are oxyethyleneated and/or oxypropyleneated;

polycondensates of ethylene oxide and propylene oxide;

compounds of the formula



$$\text{Hyd.—}(\text{OCH}_2\text{—}\underset{\substack{|\\ \text{CH}_2\\ |\\ \text{SO}\\ |\\ \text{CH}_2\text{—CHOH—CH}_2\text{OH}}}{\text{CH}}\text{—})_m\text{OH}$$

where m is an integer and Hyd. represents a hydrocarbon radical.

The anionic detergents are in particular:

the alkali metal salts, magnesium salts, ammonium salts, amine salts or aminoalcohol (especially ethanolamine or isopropanolamine) salts of the following compounds: fatty acids such as oleic acid, ricinoleic acid, copra oil acids or hydrogenated copra oil acids: alkyl-sulphuric acids, wherein the alkyl radical has a C_{12} to C_{18} linear chain; sulphated and ethoxylated alkylamides with C_{12} to C_{18} linear chains; sulphonated alpha-olefines with C_{12} to C_{18} linear chains; polyglycol ether-carboxylic acids of the formula $\text{Alk—}(\text{OCH}_2\text{—CH}_2)_m\text{—OCH}_2\ \text{CO}_2\ \text{H}$, Alk being a C_{12} to C_{18} linear chain and m an integer;

the condensation products of fatty acids with sarcosine and its derivatives, the isethionates, the polypeptides, the alkylsulphosuccinates or their derivatives, taurine and methyltaurine;

the sulphosuccinates of ethoxylated C_{12}—C_{18} alcohols, or the corresponding C_{12}—C_{18} amide derivatives; and

the alkylbenzenesulphonates. alkylaryl-polyethersulphates and sulphated monoglycerides.

All these anionic detergents, as well as numerous others not mentioned, are well known and are described in the literature.

These compositions in the form of shampoos can also contain various adjuvants such as, for example, perfumes, dyestuffs, preservatives, thickeners, foam stabilizers, softeners or one or more cosmetic resins.

In these shampoos, the detergent concentration is generally from 5 to 30% by weight and the concentration of polymer of the formula I from 0.01 to 3%, and preferably from 0.3 to 2%.

c) Wavesetting lotions, especially for sensitised hair, characterised in that they contain at least one polymer of the formula I in aqueous, alcoholic or aqueous-alcoholic solution.

They can furthermore contain another cosmetic resin. The cosmetic resins which can be used in such lotions are very varied. They are in particular homopolymers or copolymers of vinyl compounds or crotonyl compounds, such as polyvinylpyrrolidone, copolymers of vinylpyrrolidone and vinyl acetate and copolymers of crotonic acid and vinyl acetate.

The concentration of the polymers of the formula I in these wavesetting lotions generally varies from 0.1 to 5% and preferably from 0.2 to 3%, and the concentration of the other cosmetic resin varies substantially within the same proportions.

The pH of these wavesetting lotions generally varies from 3 to 9 and preferably from 4.5 to 7.5. The pH can be altered, if desired, for example by adding an alkanolamine such as monoethanolamine or triethanolamine;

d) hair dyeing compositions, characterised in that they contain at least one polymer of the formula I, a dyestuff and a vehicle.

The vehicle is preferably chosen so as to constitute a cream.

The concentration of the polymers of the formula I in these dyeing compositions is suitably from 0.1 to 10% by weight, especially from 0.5 to 10% and preferably from 0.5 to 6% by weight.

Of course, in these hair dyeing compositions, the principal active ingredient is the dyestuff (direct dyestuff) or its precursors, and not the polymer of the formula I.

It is known that oxidation dyeing operations employ so-called "oxidation dyestuffs", which are aromatic compounds of the diamine, aminophenol or phenol type. These aromatic compounds are converted to dyeing compounds by condensation in the presence of an oxidising agent, generally hydrogen peroxide. The ortho- or p-diamines or ortho- or p-monoaminophenols or -diaminophenols on oxidation yield compounds giving strong colours. The m-diamines, m-aminophenols and polyphenols only give weak shades. For this reason, the para-derivatives are referred to as "bases" and the meta-derivatives (and the polyphenols) are referred to as "modifiers".

The "bases" principally used are especially p-phenylenediamine, p-toluylenediamine, chloro-para-phenylenediamine, p-aminodiphenylamine, o-phenylenediamine, o-toluylenediamine, 2,5-diaminoanisole, o-aminophenol and p-aminophenol.

The "modifiers" principally used are especially m-phenylenediamine, m-toluylenediamine, 2,4-diaminoanisole, m-aminophenol, pyrocatechol, resorcinol, hydroquinone, alphanaphthol and 1,5-dihydroxynaphthalene.

The oxidation dyeing compositions principally contain a mixture of bases and of modifiers, with a vehicle which permits presentation in the form of a cream or of a gellable liquid. They can furthermore contain direct dyestuffs.

In the case of an oxidiation dyeing, the dyeing composition can be packaged in two parts, the second part being an oxidising agent such as hydrogen peroxide. The two parts are mixed at the time of use.

Examples of such compositions and of their use are given below;

e) hair lacquers, characterised in that they contain an alcoholic or aqueous-alcoholic solution of a usual cosmetic resin for lacquers, and at least one polymer of the formula I, this solution being placed in an aerosol container and mixed with a propellant.

For example, an aerosol lacquer according to the invention can be obtained by adding the usual cosmetic resin and the polymer of the formula I to the mixture of an anhydrous aliphatic alcohol, such as ethanol or isopropanol, and of a liquefied propellant or of a mixture of liquefied propellants such a halogenated hydrocarbons of the trichlorofluoromethane or dichlorodifluoromethane type.

In these hair lacquer compositions, the concentration of the cosmetic resin generally varies from 0.5 to 3% by weight and the concentration of the polymer of the formula I generally varies from 0.1 to 3% by weight.

Of course it is possible to add adjuvants such as dyestuffs, plasticisers or any other usual adjuvant to these hair lacquers according to the invention;

f) restructuring treatment lotions, characterised in that they contain at least one agent which possesses hair restructuring properties, and at least one polymer of the formula I.

The restructuring agents which can be used in such lotions are, for example, the methylolated derivatives described in French Patents No. 1,519,979, 1,519,980, 1,519,981, 1,519,982 and 1,527,085.

In these lotions, the concentration of the restructuring agent also generally varies from 0.1 to 10% by weight and the concentration of the polymer of the formula I generally varies from 0.1 to 5% by weight.

g) Pretreatment compositions presented in particular in the form of aqueous or aqueous-alcoholic solutions, if desired in an aerosol container, or in the form of creams or gels, these pretreatment compositions being intended to be applied to the hair before a shampoo, especially before an anionic and/or non-ionic shampoo, or before an oxidation dyeing treatment followed by an anionic and/or non-ionic shampoo, or before a permanent waving treatment.

In these pretreatment compositions, the polymer I constitutes the actual active ingredient, and its concentration generally varies from 0.1 to 10% and in particular from 0.2 to 5% by weight. The pH of these compositions generally varies from 3 to 9 and especially from 6 to 8.

These pretreatment compositions can contain various adjuvants (for example resins) usually employed in cosmetic compositions for the hair and pH modifiers (for example amino-alcohols such as monoethanolamine), as has been indicated for the compositions of paragraph (a) above.

The polymers of the formula I also exhibit valuable cosmetic properties when they are applied to the skin.

In particular they favour the hydration of the skin and thus avoid its drying out. They furthermore impart to the skin an appreciable softness to the touch.

The cosmetic compositions according to the invention can be cosmetic compositions for the skin.

They generally comprise at least one adjuvant usually employed in cosmetic compositions for the skin.

The cosmetic compositions for the skin, according to the invention are presented, for example, in the form of creams, gels, emulsions or aqueous, alcoholic or aqueous-alcoholic solutions.

The concentration of the polymer of the formula I in these compositions for the skin generally varies from 0.1 to 10% by weight.

The adjuvants generally present in these cosmetic compositions are, for example, perfumes, dyestuffs, preservatives, thickeners, sequestering agents and emulsifiers.

These compositions for the skin in particular constitute creams or treatment lotions for the hands or the face, anti-sunburn creams, tinted creams, make-up remover milks, foam-bath liquids or deodorant compositions.

These compositions can be prepared in accordance with the usual methods.

For example, in order to obtain a cream, an aqueous phase containing the polymer of the formula I, and optionally other ingredients or adjuvants, in solution is emulsified with an oily phase.

The oily phase can consist of various products such as liquid paraffin, petroleum oil, sweet almond oil, avocado oil, olive oil, fatty acid esters such as glyceryl monostearate, ethyl or isopropyl palmitate and alkyl myristates such as propyl, butyl or cetyl myristate. It is furthermore possible to add fatty alcohols such as cetyl alcohol or waxes such as beeswax.

The polymers of the formula I can be present in the cosmetic compositions for the skin according to the invention, either by way of an additive or by way of the main active ingredient in creams or treatment lotions for the hands or the face or by way of an additive in compositions of e.g. anti-sunburn creams, tinted creams, make-up remover milks, foam-bath oils or liquids.

The invention also relates to a process of cosmetic treatment, characterised in that at least one polymer of the formula I is applied to the hair or to the skin by means of a cosmetic composition based on a polymer I as defined above.

In particular, the invention relates to a process for the treatment of hair which consists of applying at least one polymer of the formula I to the hair before an anionic and/or non-ionic shampoo or before an oxidation dyeing treatment followed by an anionic and/or non-ionic shampoo. The shampoo can itself contain polymers of the formula I or other cationic polymers.

The invention also provides the polymers of the formula I for which at least one of the substituents R_1, R_2, R_3, R_4 and R_5 is different from CH_3, that is to say contains at least two carbon atoms, as well as to the process for the preparation of these new products. This process is analogous to that described above for the polymers of the formula 1.

The Examples which follow illustrate the invention; Examples 1 to 10 illustrate the preparation of polymers used in the compositions of the present invention.

Example 1.

Polymer of the formula I with $B_1 = B = (CH_2)_4$, $R_1 = R_2 = R_3 = R_4 = R_5 = CH_3$, $A = (CH_2)_2$ and $X = Y = Br$.

A mixture of 17.30 g (0.1 mol) of pentamethyldiethylenetriamine and 32.4 g (0.15 mol) of 1,4-dibromobutane in 190 cm³ of methanol is heated under reflux for 100 hours. The mixture is concentrated under reduced pressure, the residue is taken up in ethyl ether and the precipitate obtained is filtered off. After drying in vacuo in the presence of phosphorus pentoxide, the product obtained contains 40.5% of Br^-; it is soluble in water.

Example 2.

Polymer of the formula I with $B = (CH_2)_6$, $B_1 = (CH_2)_{10}$, $R_1 = R_2 = R_3 = R_4 = R_5 = CH_3$, $A = (CH_2)_3$ and $X = Y = Br$.

A mixture of 20.13 g (0.1 mol) of pentamethyldipropylenetriamine and 24.4 g (0.1 mol) of 1,6-dibromohexane in 200 cm³ of methanol is heated under reflux for 100 hours. Thereafter 0.2 mol of 1,10-dibromodecane, that is to say 60 g, are added and heating is continued for 50 hours. The mixture is concentrated under reduced pressure, the residue is taken up in ethyl ether and the precipitate obtained is filtered off. It is dried under reduced pressure in the presence of phosphorus pentoxide. It is soluble in a mixture of water and ethanol.

Following a procedure analogous to that described in Example 1 (Examples 3 to 9) or in Example 2 (Examples 10 to 13), the following polymers of the formula I were prepared:

Example	R_1	R_2	R_3	R_4	A	R_5	B	B_1	Dihalide* / triamine	X	Y	Soluble in
3	CH_3	CH_3	CH_3	CH_3	$(CH_2)_2$	CH_3	$(CH_2)_4$	$(CH_2)_4$	1,1	Br	Br	Water
4	CH_3	CH_3	CH_3	CH_3	$(CH_2)_2$	CH_3	$(CH_2)_4$	$(CH_2)_4$	1,2	Br	Br	Water
5	CH_3	CH_3	CH_3	CH_3	$(CH_2)_2$	CH_3	$(CH_2)_4$	$(CH_2)_4$	1,3	Br	Br	Water
6	CH_3	CH_3	CH_3	CH_3	$(CH_2)_2$	CH_3	$(CH_2)_4$	$(CH_2)_4$	1,4	Br	Br	Water
7	CH_3	CH_3	CH_3	CH_3	$(CH_2)_3$	CH_3	$(CH_2)_6$	$(CH_2)_6$	1,5	Br	Br	Water
8	CH_3	CH_3	CH_3	CH_3	$(CH_2)_3$	CH_3	$(CH_2)_4$	$(CH_2)_4$	1,5	Br	Br	Water
9	CH_3	CH_3	CH_3	CH_3	$(CH_2)_3$	CH_3	$CH_2-CHOH-CH_2$	$CH_2-CHOH-CH_2$	1,5	Cl	Cl	Water
10	CH_3	CH_3	CH_3	CH_3	$(CH_2)_2$	CH_3	$(CH_2)_6$	$(CH_2)_2-O-(CH_2)_2$	1,5	Br	Cl	Water
11	CH_3	C_4H_9	CH_3	C_4H_9	$(CH_2)_3$	C_4H_9	$(CH_2)_4$	$(CH_2)_{10}$	1,5	Br	Br	Water-ethanol
12	CH_3	C_6H_{13}	CH_3	C_6H_{13}	$(CH_2)_3$	C_6H_{13}	$(CH_2)_2-O-(CH_2)_2$	$(CH_2)_6$	1,5	Cl	Br	Water-ethanol
13	C_4H_9	C_4H_9	C_4H_9	C_4H_9	$(CH_2)_3$	C_4H_9	$CH_2-CHOH-CH_2$	$(CH_2)_2-O-(CH_2)_2$	1,5	Cl	Br	Water

* Ratio of the number of mol's of dihalide ($X-B-X$ + optionally $Y-B_1-Y$) to the number of mol's of triamine of the formula II.

EXAMPLES OF COMPOSITIONS.

Example A.

Example A

DYEING SHAMPOO

Nonylphenol polyoxyethyleneated with 4 mols of ethylene oxide	25 g
Nonylphenol polyoxyethyleneated with 9 mols of ethylene oxide	23
compound of Example 5	4
96% strength ethyl alcohol	7
propylene glycol	14
ammonia, 22° Bé strength	10 ml
Dyestuffs:	
m-diaminoanisole sulphate	0.030 g
resorcinol	0.400
m-aminophenol base	0.150
p-aminophenol base	0.087
nitro-p-phenylenediamine	1.000
Trilon B* (Registered Trade Mark)	3.000
sodium bisulphite, d = 1.32	1.200
water, q.s.p.	100.000

50 g of this formula are mixed, in a bowl, with the same amount of hydrogen peroxide of 20 volumes strength and the gel obtained is applied to hair with a brush.

The gel is left for 30 minutes and the hair is then rinsed.

The hair combs out easily and is silky to the touch. It is set in waves and dried.

The hair is glossy, springy and bulky, and silky to the touch, and combs out easily.

On a brown background, a chestnut shade is obtained. *Trilon B: ethylenediaminetetraacetic acid.

Example B.

CREAM VEHICLE FOR A DYEING COMPOSITION (oxidation dyeing)

Cetyl/stearyl alcohol	22 g
oleyl diethanolamide	5
sodium cetyl/stearyl sulphate	4
compound of Example 1	3
ammonia, 22° Bé strength	12 ml

Example B. — Continued

Dyestuffs:

m-diaminoanisole sulphate	0.048 g
resorcinol	0.420
m-aminophenol base	0.150
nitro-p-phenylenediamine	0.085
p-toluylenediamine	0.004
Trilon B	1.000
sodium bisulphite, d = 1.32	1.200
water, q.s.p.	100.000

30 g of this formula are mixed with 45 g of hydrogen peroxide of 20 volumes strength and a smooth thick cream is obtained, which is pleasant to apply and which adheres well to the hair.

After waiting for 30 minutes, the hair is rinsed and dried.

On 100% white hair, a blond shade is obtained.

The hair is easy to comb out both wet and dry.

The hair has a glossy appearance and is pleasant and silky to the touch.

Example C.

STRUCTURE-BUILDING LOTION (applied with rinsing)

2 g of dimethylolethylenethiourea are mixed, before use, with 25 ml of a solution containing:

compound of Example 3	5 g
hydrochloric acid, q.s.	pH 2.5
water, q.s.p.	100 ml

The mixture is applied to washed and drained hair.

It is left on the hair for 10 minutes and the hair is then rinsed.

The hair is easy to comb out and is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair combs out easily and is glossy, springy and bulky.

Example D.

WAVE-SETTING LOTIONS FOR SENSITISED HAIR

1. An alcoholic solution is prepared with:

polyvinylpyrrolidone	1.5 g
compound of Example 9	2.5
ethyl alcohol, q.s.	100 ml

The solution is applied to the hair, and the hair is set in waves and dried.

The hair is strengthened and plasticised. It is glossy and bulky, and silky to the touch, and combs out easily.

2. Analogous results are obtained by replacing the polymer of Example 9 in the above formula by the polymer of Example 13.

3. A lotion of the following formula is prepared:

polymer of Example 8	1 g
60:40 vinylpyrrolidone/vinyl acetate	1.0 g
triethanolamine, q.s.	pH 6
water, q.s.p.	100 ml

The lotion is applied to bleached hair. The hair is set in waves and dried. Results analogous to those of the preceding example are obtained.

4. A lotion of the following formula is prepared:

polymer of Example 11	1.1 g
60:40 vinylpyrrolidone/vinyl acetate copolymer	1 g
ethyl alcohol, q.s. 50%	
triethanolamine, q.s.	pH 7
water, q.s.p.	100 ml

The lotion is applied to bleached hair. The hair is set in waves and dried. Results analogous to those of the preceding example are obtained.

5. A lotion of the following formula is prepared:

polymer of Example 7	1.3 g
90:10 vinyl acetate/crotonic acid copolymer	1.7 g
triethanolamine, q.s.	pH 7.5
water, q.s.p.	100 ml

The lotion is applied to bleached hair. The hair is set in waves and dried. Results analogous to those of the preceding example are obtained.

8. The following solution is prepared:

polymer of Example 2	1.5 g
90:10 vinyl acetate/crotonic acid copolymer	1.5 g
monoethanolamine, q.s.	pH 7
water, q.s.p.	100 ml

The solution is applied to bleached hair, which is set in waves and dried. Results analogous to those of the preceding example are obtained.

Example E.

TREATMENT LOTIONS (applied with rinsing)

1. 30 ml of the following solution are applied to wet and clean hair:

polymer of Example 4	4 g
monoethanolamine, q.s.	pH 7.5
water. q.s.p.	100 ml

The lotion is allowed to act for 5 minutes and the hair is then rinsed.

The hair is soft to the touch and combs out easily.

It is set in waves and dried. The dry hair combs out easily and is glossy, springy and bulky.

2. 25 ml of the following solution are applied to wet and clean hair:

polymer of Example 3	6 g
citric acid, q.s.	pH 6
water, q.s.p.	100 ml

The lotion is allowed to act for 5 minutes and the hair is then rinsed.

The hair is soft to the touch and combs out easily.

It is set in waves and dried. The dry hair combs easily and is glossy, springy and bulky.

Example F.
SHAMPOOS

1. The following solution is prepared:

C_{11}—C_{14} α-diol condensed with 3 to 4 molecules of glycidol	17 g
polymer of Example 2	3 g
lactic acid, q.s.p.	pH 3.5
water, q.s.p.	100 cm^3

When applied to the head, this solution, which has a limpid appearance, produces a copious and rather soft foam and assists combing out of the wet hair. After drying, the hair is springy, light and glossy.

2. The following solution is prepared:

lauryl ether polyglycerolated with 4 molecules of glycerol	15 g
polymer of Example 5	2 g
tertiary stearylamine polyoxyethyleneated with 5 mols of ethylene oxide	1.5 g
lactic acid, q.s.p.	pH 4.5
water, q.s.p.	100 cm^3

When applied to the head, this solution, which has a limpid appearance, produces a copious and soft foam which is easily removed on rinsing. The hair combs out very easily and after drying is bulky and springy whilst remaining soft and docile when styled.

3. The following solution is prepared:

C_{11}—C_{14} α-diol condensed with 3 to 4 molecules of glycidol	17 g
polymer of Example 9	3 g
lactic acid, q.s.p.	pH 3.5
water. q.s.p.	100 cm^3

When applied to the head, this solution, which has a limpid appearance, produces a copious and rather soft foam and permits an improvement of the combing out of the wet hair. After drying, the hair is soft and glossy and has a light appearance.

Example G.
STRUCTURE-BUILDING LOTION (applied with rinsing)

1. 2 g of N,N′-di-(hydroxymethyl)-ethylenethiourea are mixed, before use, with 25 cm^3 of a solution containing:

compound of Example 3	5 g
hydrochloric acid, q.s.	pH 2.5
water, q.s.p.	100 cm^3

The mixture is applied to washed and drained hair. It is left on the hair for 10 minutes and the hair is then rinsed.

Combing out is easy and the hair is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair combs out easily and is glossy, springy and bulky.

2. 2 g of N,N'-di-(hydroxymethyl)-ethylenethiourea are mixed, before use, with 25 cm³ of a solution containing:

compound of Example 4	3 g
hydrochloric acid, q.s.	pH 2.5
water, q.s.p.	100 cm³

The mixture is applied to washed and drained hair.

It is left on the hair for 10 minutes and the hair is then rinsed.

Combing out is easy and the hair is soft to the touch.

Example H.

PRE-SHAMPOOING COMPOSITIONS

1. 10 g of the following solution are applied to dirty and dry hair:

compound of Example 1	2 g
monoethanolamine q.s.p.	pH 7
water, q.s.p.	100 cm³

After waiting for two minutes, a conventional anionic shampoo is carried out in two stages.

The wet hair is easy to comb out and the hair is soft.

After setting in waves and drying, the hair combs out easily and is soft to the touch, glossy and springy.

This same solution can be packaged as an aerosol.

2. 15 g of the following solution are applied to dirty and dry hair:

compound of Example 2	1 g
compound of Example 5	1 g
monoethanolamine q.s.p.	pH 7
water, q.s.p.	100 cm³

After waiting for two minutes, a conventional anionic shampoo is carried out in two stages.

The wet hair is easy to comb out and the hair is soft.

After setting in waves and drying, the hair combs out easily and is soft to the touch, glossy and springy.

This same solution can be packaged as an aerosol with nitrogen or nitrous oxide or freons as propellants.

Example I.

TREATMENT LOTION FOR USE BEFORE DYEING

20 cm³ of the following solution are applied to dry and dirty hair:

compound of Example 3	3 g
monoethanolamine q.s.p.	pH 8
water, q.s.p.	100 g

After waiting for 5 minutes, a conventional ammoniacal oxidation dyeing composition is applied and left for 30 minutes.

After rinsing, and using an anionic shampoo, the hair combs out very easily.

After setting in waves and drying, the hair is silky, glossy, springy and easy to style.

Example J.
ANIONIC SHAMPOO

triethanolamine lauryl-sulphate	10 g
compound of Example 6	1 g
triethanolamine, q.s.p.	pH 8
water, q.s.p.	100 g

Example K.
PRE-SHAMPOOING COMPOSITION IN THE FORM OF AN AEROSOL FOAM

The following formula is prepared as in an aerosol:

Na cetyl/stearyl-sulphate	1.3 g
nonylphenol ethoxylated with 4 mols of ethylene oxide	2.5 g
nonylphenol ethoxylated with 9 moles of ethylene oxide	1.5 g
compound of Example 3	3.0 g
water	81.7 g
mixture of Freon 114 and Freon 12 (70:30)	10.0 g

degree of filling: 60%

The foam is applied to dirty and dry hair whilst rubbing to ensure good distribution of the product.

Thereafter, a conventional anionic shampoo is applied.

After 2 to 3 minutes, the hair is rinsed. It is soft to the touch and combs out easily.

After setting in waves and drying, the hair combs out easily.

Example L.
HAND TREATMENT CREAM

1. The following cream is prepared:

vaseline oil	10 g
cetyl alcohol	6 g
self-emulsifiable glyceryl monostearate	4 g
triethanolamine	2 g
methyl p-hydroxybenzoate	0.1 g
polymer of Example 1	2 g
water, q.s.p.	100 g

This cream is applied to the hands whilst rubbing to cause the cream to penetrate.

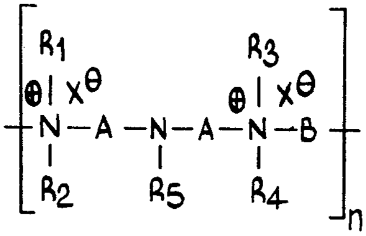
The hands are soft and pleasant to the touch.

2. Analogous results are obtained by replacing the polymer of Example 1 in the above formula for a cream by the polymer of Example 13.

British Specification No. 702695 (published in January 1954) discloses the dyeing of textile fibres, and, in particular, cellulosic fibres, with a direct dye in combination with a quaternary ammonium compound obtained by reacting an aliphatic tertiary polyamine with an aliphatic dihalide, and a water soluble copper compound. Insofar as any of the quaternary ammonium compounds are crosslinked polymers possessing recurring units of formulae (I′) and (I″), no claim is made herein to compositions containing such compounds, a direct dye and a water-soluble copper compound.

WHAT WE CLAIM IS:—

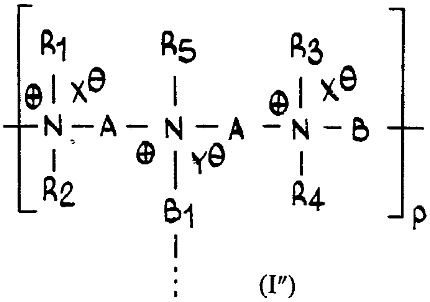
1. A composition suitable for use in cosmetics which comprises a cosmetically acceptable vehicle and at least one crosslinked polymer possessing recurring units of the formulae:



$$\left[-\underset{R_2}{\overset{R_1}{\overset{\oplus | X^\ominus}{N}}} - A - \underset{R_5}{N} - A - \underset{R_4}{\overset{R_3}{\overset{\oplus | X^\ominus}{N}}} - B - \right]_n$$

(I′)

and



$$\left[-\underset{R_2}{\overset{R_1}{\overset{\oplus | X^\ominus}{N}}} - A - \underset{\underset{\vdots}{B_1}}{\overset{R_5}{\underset{\oplus | Y^\ominus}{N}}} - A - \underset{R_4}{\overset{R_3}{\overset{\oplus | X^\ominus}{N}}} - B - \right]_p$$

(I″)

in which

A is a polymethylene group haing 2 or 3 carbon atoms,

each of B_1 and B, which may be identical or different, is a polymethylene group having 3 to 10 carbon atoms, a *ortho-*, *meta-* or *para-* xylylidenyl group —CH_2—C_6H_4—CH_2—, a —$(CH_2)_x$—O—$(CH_2)_x$— group, where x is 2 or 3, or a —CH_2—CHOH—CH_2— group,

each of R_1 and R_3, which may be identical or different, is an aliphatic radical having 1 to 12 carbon atoms,

each of R_2 and R_4, which may be identical or different, is an aliphatic radical having 1 to 20 carbon atoms,

R_5 is a hydrogen atom or an aliphatic, alicyclic, aryl or araliphatic radical containing at most 20 carbon atoms,

$X^\ominus$ is a halide anion,

$Y^\ominus$ is a halide anion, and

n and p are independent integers, the polymer being crosslinked via the radicals B_1.

2. A composition according to claim 1 in which X and/or Y is a chloride or bromide anion.

3. A composition according to claim 1 or 2, which contains 0.5 to 10% by weight of polymer.

4. A composition according to any one of claims 1 to 3 which contains a hair dye.

5. A composition according to claim 4 which contains an oxidation dye.

6. A composition according to any one of claims 1 to 3 is in the form of a shampoo and contains a cationic, non-ionic or anionic detergent.

7. A composition according to any one of claims 1 to 3 which is in the form of a wave-setting or hair lacquer and contains, additionally, a resin conventionally used in wave-setting lotions or hair lacquers.

8. A composition according to any one of claims 1 to 3 which is in the form of a hair restructuring agent and contains a methylolated hair restructuring compound.

9. A composition according to any one of the preceding claims which is in the form of an aerosol.

10. A composition according to any one of the preceding claims which contains at least one of a perfume, preservative, sequestering agent or thickener.

11. A composition according to any one of the preceding claims in which A is $(CH_2)_2$ or $(CH_2)_3$.

12. A composition according to any one of the preceding claims in which B_1 and/or B is $(CH_2)_4$, $(CH_2)_6$, $(CH_2)_{10}$, —$(CH_2)_2$—O—$(CH_2)_2$— or —CH_2—CHOH—CH_2—.

13. A composition according to any one of the preceding claims in which R_1 and/or R_3 is a methyl or butyl.

14. A composition according to any one of the preceding claims in which R_2 and/or R_4 and/or R_5 is a methyl, butyl or hexyl.

15. A polymer of formula I as defined in claim 1 in which at least one of the substituents R_1, R_2, R_3, R_4 and R_5 is not methyl.

16. A polymer according to claim 15 which has one or more of the features of claims 11 to 14.

17. A polymer according to claim 15 specifically identified herein.

18. Process for the preparation of a polymer as claimed in claim 15 with $B_1 = B$, which comprises polycondensing a triamine of the formula $R_1R_2N—A—N(R_5)—A—NR_3R_4$ with an excess of a dihalide of the formula X—B—X.

19. Process for the preparation of a polymer as claimed in claim 15 with B_1 different from B, which comprises polycondensing a triamine of the formula $R_1R_2N—A—N(R_5)—A—NR_3R_4$ with a substantially equimolar amount of a dihalide X—B—X and reacting the resulting polymer with a compound of the formula $Y—B_1—Y$.

20. Process according to claim 18 or 19 substantially as hereinbefore described.

21. A polymer as defined in claim 15 whenever prepared by a process as claimed in any one of claims 18 to 20.

22. A composition according to any one of claims 1 to 14 in which the polymer is as claimed in claim 21.

23. A composition according to any one of claims 1 to 14 in which the polymer is as claimed in any one of claims 15 to 17 and 22.

24. A composition according to claim 1 substantially as hereinbefore described.

25. A composition according to claim 1 substantially as described in any one of Examples A to L or part thereof.

26. A process for treating the skin or hair which comprises applying thereto a composition as claimed in any one of claims 1 to 14 and 22 to 25.

27. A process according to claim 26 in which the composition is applied to the hair prior to an anionic and/or non-ionic shampooing or prior to an oxidation dyeing followed by an anionic and/or non-ionic shampooing.

28. A process according to claim 26 substantially as hereinbefore described.

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