Abstract:
A method of mitigating hair damage comprising the step of applying to the hair a composition comprising a group III metal salt.

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HAIR TREATMENT COMPOSITIONS

The present invention relates to hair treatment compositions which can be used to repair dry, damaged hair.

Damage to the hair typically manifests itself in cuticle and protein loss from the hair fibre, hair fibre dryness, hair fibre brittleness and breakage and frayed or split ends.

US 4 960 588 discloses metal salts having a valency of at least II in hair styling compositions to improve set retention.

The present inventors have found that hair treated with compositions comprising certain metal salts can strengthen and repair damaged hair. Furthermore the compositions of the invention mitigate hair damage.

The present invention relates to a method of mitigating hair damage comprising the step of applying to the hair a composition comprising a group III metal salt.

Metal Salts

Compositions of the invention comprise a group III metal salt.

It is particularly preferred if the metal salt is aluminium, particularly preferred is aluminium chloride.

The level of metal salt in the total composition is preferably from 0.005 to 10 wt%, more preferably from 0.01 to 5 wt%, most preferably from 0.05 to 1 wt%.
The pH of the formulations of the invention are in the range from pH 3 to pH 6, more preferably used at pH 3-5.

Hair treatment compositions according to the invention may suitably take the form of shampoos, conditioners, sprays, mousses, gels, waxes or lotions.

In one preferred embodiment the composition is formulated as a rinse off product. In the context of this invention rinse off products are applied to the hair left for a maximum time of 60 minutes then rinsed off.

A preferred method of treatment comprises the following sequential steps

i) application of a composition comprising a group III salt, preferably aluminium, for a maximum time period of 30 minutes, more preferably 20 minutes, most preferably 15 minutes;

ii) rinsing the hair.

In an alternative embodiment the composition can be applied to the hair as a leave in composition, in that the product is applied to the hair and any subsequent rinsing is not part of the treatment process. Leave on products are normally left on the hair for longer than 60 minutes, preferably longer than 2 hours.

Shampoo compositions of the invention are generally aqueous, i.e. they have water or an aqueous solution or a lyotrophic liquid crystalline phase as their major component.

Suitably, the shampoo composition will comprise from 50 to 98%, preferably from 60 to 90% water by weight based on the total weight of the composition.
Shampoo compositions according to the invention will generally comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphasuccinates, alkyl ether sulphasuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, and alkyl ether carboxylic acids and salts thereof, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts.

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphasuccinate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium lauryl ether sulphasuccinate, ammonium lauryl sulphate, ammonium lauryl ether sulphate, sodium dodecyl benzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate, lauryl ether carboxylic acid and sodium N-lauryl sarcosinate.

Preferred anionic cleansing surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate (n)EO, (where n is from 1 to 3), sodium lauryl ether sulphasuccinate(n)EO, (where n is from 1 to 3), ammonium lauryl sulphate, ammonium lauryl ether sulphate(n)EO, (where n is from 1 to 3), sodium cocoyl isethionate and lauryl ether carboxylic acid (n) EO (where n is from 10 to 20).

Mixtures of any of the foregoing anionic cleansing surfactants may also be suitable.

The total amount of anionic cleansing surfactant in shampoo compositions of the invention generally ranges from 0.5 to 45%, preferably from 1.5 to 35%, more
preferably from 5 to 20% by total weight anionic cleansing surfactant based on the total weight of the composition.

The composition can include co-surfactants, to help impart aesthetic, physical or cleansing properties to the composition.

An example of a co-surfactant is a nonionic surfactant, which can be included in an amount ranging from 0.5 to 8%, preferably from 2 to 5% by weight based on the total weight of the composition.

For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic (Cs - Cis) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

Other representative nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs).

A preferred example of a co-surfactant is an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0.5 to about 8%, preferably from 1 to 4% by weight based on the total weight of the composition.

Examples of amphoteric or zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycines, alkyl carboxyglycinates, alkyl amphotacetates, alkyl amphopropionates,
alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine, lauryl betaine, cocamidopropyl betaine and sodium cocoamphoacetate.

A particularly preferred amphoteric or zwitterionic surfactant is cocamidopropyl betaine.

Mixtures of any of the foregoing amphoteric or zwitterionic surfactants may also be suitable. Preferred mixtures are those of cocamidopropyl betaine with further amphoteric or zwitterionic surfactants as described above. A preferred further amphoteric or zwitterionic surfactant is sodium cocoamphoacetate.

The total amount of surfactant (including any co-surfactant, and/or any emulsifier) in a shampoo composition of the invention is generally from 1 to 50%, preferably from 2 to 40%, more preferably from 10 to 25% by total weight surfactant based on the total weight of the composition.

Cationic polymers are preferred ingredients composition of the invention for enhancing conditioning performance.

Suitable cationic polymers may be homopolymers which are cationically substituted or may be formed from two or more types of monomers. The weight average (\(M_w\)) molecular weight of the polymers will generally be between 100 000 and 2 million daltons.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides,
alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyi and dialkyi substituted monomers preferably have C1-C7 alkyi groups, more preferably C1-3 alkyi groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

Amine substituted vinyl monomers and amines can be polymerised in the amine form and then converted to ammonium by quaternization.

The cationic polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic polymers include, for example:

- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;

- mineral acid salts of amino-alkyl esters of homo-and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, (as described in U.S. Patent 4,009,256);

- cationic polyacrylamides (as described in WO95/22311).
Other cationic polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives.

Cationic polysaccharide polymers suitable for use in compositions of the invention include monomers of the formula:

\[ A-O-[R-N^+ (R_1^2)(R_3^3)]X, \]

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof. \( R_1, R_2 \) and \( R_3 \) independently represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in \( R_1, R_2 \) and \( R_3 \)) is preferably about 20 or less, and \( X \) is an anionic counterion.

Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from the Amerchol Corporation, for instance under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimethylammonium
chloride (commercially available from Rhodia in their JAGUAR trademark series). Examples of such materials are JAGUAR C13S, JAGUAR C14, JAGUAR C15, and JAGUAR C17.

Mixtures of any of the above cationic polymers may be used.

Cationic polymer will generally be present in a shampoo composition of the invention at levels of from 0.01 to 5%, preferably from 0.05 to 1%, more preferably from 0.08 to 0.5% by total weight of cationic polymer based on the total weight of the composition.

Preferably a composition of the invention further comprises a suspending agent. Suitable suspending agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives, since these impart pearlescence to the composition. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493.

Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used; they are available commercially as Carbopol 910, Carbopol 934, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trademark) materials are available from Goodrich.
Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

Mixture of any of the above suspending agents may be used. Preferred is a mixture of cross-linked polymer of acrylic acid and crystalline long chain acyl derivative.

Suspender will generally be present in a shampoo composition of the invention at levels of from 0.1 to 10%, preferably from 0.5 to 6%, more preferably from 0.9 to 4% by total weight of suspender agent based on the total weight of the composition.

Conditioner compositions will typically comprise one or more cationic conditioning surfactants which are cosmetically acceptable and suitable for topical application to the hair.

Preferably, the cationic conditioning surfactants have the formula $N^+(R^1)(R^2)(R^3)(R^4)$, wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently (C1 to C30) alkyl or benzyl.

More preferably, one or two of $R^1$, $R^2$, $R^3$ and $R^4$ are independently (C6 to C30) alkyl and the other $R^1$, $R^2$, $R^3$ and $R^4$ group or groups are (C1-C6) alkyl or benzyl groups. Optionally, the alkyl groups may comprise one or more ester (-OCO- or -COO-) and/or ether (-O-) linkages within the alkyl chain. Alkyl groups may optionally be substituted with one or more hydroxyl groups. Alkyl groups may be straight chain or branched and, for alkyl groups having 3 or more carbon atoms, cyclic. The
alkyl groups may be saturated or may contain one or more carbon-carbon double bonds (e.g., oleyl). Alkyl groups are optionally ethoxylated on the alkyl chain with one or more ethyleneoxy groups.

Suitable cationic conditioning surfactants for use in conditioner compositions according to the invention include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride, cetylpyridinium chloride, tetramethylammonium chloride, tetraethylammonium chloride, octyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecyl(dimethylammonium chloride, dioctadecyl(dimethylammonium chloride, tallowtrimethylammonium chloride, dihydrogenated tallow dimethyl ammonium chloride (e.g., Arquad 2HT/75 from Akzo Nobel), cocotrimethylammonium chloride, PEG-2-oleammonium chloride and the corresponding hydroxides thereof. Further suitable cationic surfactants include those materials having the CTFA designations Quaternium-5, Quaternium-31 and Quaternium-18. Mixtures of any of the foregoing materials may also be suitable. A particularly useful cationic surfactant for use in conditioners according to the invention is cetyltrimethylammonium chloride, available commercially, for example as GENAMIN CTAC, ex Hoechst Celanese. Another particularly useful cationic surfactant for use in conditioners according to the invention is behenyltrimethylammonium chloride, available commercially, for example as GENAMIN KDMP, ex Clariant.

Another example of a class of suitable cationic conditioning surfactants for use in the invention, either alone or in admixture with one or more other cationic conditioning surfactants, is a combination of (i) and (ii) below:

(i) an amidoamine corresponding to the general formula (I):

\[
R^1 \text{CONH(CH}_2\text{)}_m\text{N} \quad (R^2) \quad R^3
\]
in which $R^1$ is a hydrocarbyl chain having 10 or more carbon atoms,
$R^2$ and $R^3$ are independently selected from hydrocarbyl chains of from 1 to
10 carbon atoms, and

$$m$$ is an integer from 1 to about 10; and

(ii) an acid.

As used herein, the term hydrocarbyl chain means an alkyl or alkenyl chain.

Preferred amidoamine compounds are those corresponding to formula (I) in which

$R^1$ is a hydrocarbyl residue having from about 11 to about 24 carbon atoms,
$R^2$ and $R^3$ are each independently hydrocarbyl residues, preferably alkyl groups,

having from 1 to about 4 carbon atoms, and

$$m$$ is an integer from 1 to about 4.

Preferably, $R^2$ and $R^3$ are methyl or ethyl groups.

Preferably, $m$ is 2 or 3, i.e. an ethylene or propylene group.

Preferred amidoamines useful herein include stearamido-propyldimethylamine,
stearamidopropyldiethylamine, stearamidoethyldiethylamine,
stearamidoethyldimethylamine, palmitamidopropyldimethylamine,

palmitamidopropyldiethylamine, palmitamidoethyldiethylamine,
palmitamidoethyldimethylamine, behenamidopropylidimethylamine,
behenamidopropyldiethylamine, behenamidoethylidimethylamine,
behenamidoethyldimethylamine, arachidamidopropyldimethylamine,
arachidamidopropyldiethylamine, arachid-amidoethyldiethylamine,
arachidamidoethyldimethylamine, and mixtures thereof.
Particularly preferred amidoamines useful herein are stearamidopropyl dimethylamine, stearamidoethyl diethylamine, and mixtures thereof.

Commercially available amidoamines useful herein include:
stearamidopropyl dimethylamine with tradenames LEXAMINE S-1 3 available from Inolex (Philadelphia Pennsylvania, USA) and AMIDOAMINE MSP available from Nikko (Tokyo, Japan), stearamidoethyl diethylamine with a tradename AMIDOAMINE S available from Nikko, behenamidopropyl dimethylamine with a tradename INCROMINE BB available from Croda (North Humberside, England), and various amidoamines with tradenames SCHERCODINE series available from Scher (Clifton New Jersey, USA).

Acid (ii) may be any organic or mineral acid which is capable of protonating the amidoamine in the hair treatment composition. Suitable acids useful herein include hydrochloric acid, acetic acid, tartaric acid, fumaric acid, lactic acid, malic acid, succinic acid, and mixtures thereof. Preferably, the acid is selected from the group consisting of acetic acid, tartaric acid, hydrochloric acid, fumaric acid, and mixtures thereof.

The primary role of the acid is to protonate the amidoamine in the hair treatment composition thus forming a tertiary amine salt (TAS) in situ in the hair treatment composition. The TAS in effect is a non-permanent quaternary ammonium or pseudo-quaternary ammonium cationic surfactant.

Suitably, the acid is included in a sufficient amount to protonate all the amidoamine present, i.e. at a level which is at least equimolar to the amount of amidoamine present in the composition.
In compositions of the invention, the level of cationic conditioning surfactant will generally range from 0.01 to 10%, more preferably 0.05 to 7.5%, most preferably 0.1 to 5% by total weight of cationic conditioning surfactant based on the total weight of the composition.

Compositions of the invention may also incorporate a fatty alcohol. The combined use of fatty alcohols and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a lamellar phase, in which the cationic surfactant is dispersed.

Representative fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 22. Fatty alcohols are typically compounds containing straight chain alkyl groups. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

The level of fatty alcohol if present in compositions of the invention will generally range from 0.01 to 10%, preferably from 0.1 to 8%, more preferably from 0.2 to 7%, most preferably from 0.3 to 6% by weight of the composition. The weight ratio of cationic surfactant to fatty alcohol is suitably from 1:1 to 1:10, preferably from 1:1.5 to 1:8, optimally from 1:2 to 1:5. If the weight ratio of cationic surfactant to fatty alcohol is too high, this can lead to eye irritancy from the composition. If it is too low, it can make the hair feel squeaky for some consumers.

Compositions of the invention may suitably take the form of a hair oil, for pre-wash or post-wash use. Typically, hair oils will predominantly comprise water-insoluble oily conditioning materials, such as triglycerides, mineral oil and mixtures thereof.

Compositions of the invention may also take the form of a hair lotion, typically for use in between washes. Lotions are aqueous emulsions comprising water-insoluble oily
conditioning materials. Suitable surfactants can also be included in lotions to improve their stability to phase separation.

Hair treatment compositions according to the invention, particularly water-based shampoos and hair conditioners, will preferably also contain one or more silicone conditioning agents.

Particularly preferred silicone conditioning agents are silicone emulsions such as those formed from silicones such as polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone, polydimethylsiloxanes having hydroxyl end groups which have the CTFA designation dimethiconol, and amino-functional polydimethylsiloxanes which have the CTFA designation amodimethicone.

The emulsion droplets may typically have a Sauter mean droplet diameter ($D_{32}$) in the composition of the invention ranging from 0.01 to 20 micrometer, more preferably from 0.2 to 10 micrometer.

A suitable method for measuring the Sauter mean droplet diameter ($D_{32}$) is by laser light scattering using an instrument such as a Malvern Mastersizer.

Suitable silicone emulsions for use in compositions of the invention are available from suppliers of silicones such as Dow Corning and GE Silicones. The use of such pre-formed silicone emulsions is preferred for ease of processing and control of silicone particle size. Such pre-formed silicone emulsions will typically additionally comprise a suitable emulsifier such as an anionic or nonionic emulsifier, or mixture thereof, and may be prepared by a chemical emulsification process such as emulsion polymerisation, or by mechanical emulsification using a high shear mixer. Pre-formed silicone emulsions having a Sauter mean droplet
diameter \( (D_{32}) \) of less than 0.15 micrometers are generally termed microemulsions.

Examples of suitable pre-formed silicone emulsions include emulsions DC2-1766, DC2-1784, DC-1785, DC-1786, DC-1788 and microemulsions DC2-1865 and DC2-1870, all available from Dow Corning. These are all emulsions/microemulsions of dimethiconol. Also suitable are amodimethicone emulsions such as DC2-8177 and DC939 (from Dow Corning) and SME253 (from GE Silicones).

Also suitable are silicone emulsions in which certain types of surface active block copolymers of a high molecular weight have been blended with the silicone emulsion droplets, as described for example in WO03/094874. In such materials, the silicone emulsion droplets are preferably formed from polydiorganosiloxanes such as those described above. One preferred form of the surface active block copolymer is according to the following formula:

\[
\text{HO(CH}_2\text{CH}_2\text{O})_x(\text{CH}({\text{CH}_3}\text{CH}_2\text{O}))_y(\text{CH}_2\text{CH}_2\text{O})_x\text{H}
\]

wherein the mean value of \( x \) is 4 or more and the mean value of \( y \) is 25 or more.

Another preferred form of the surface active block copolymer is according to the following formula:

\[
(\text{HO(CH}_2\text{CH}_2\text{O})_a(\text{CH}({\text{CH}_3}\text{CH}_2\text{O}))_b)_2-\text{N-CH}_2\text{-CH}_2-\text{N}((\text{OCH}_2\text{CH}({\text{CH}_3}))_b(\text{OCH}_2\text{CH}_2)_a\text{OH})_2
\]

wherein the mean value of \( a \) is 2 or more and the mean value of \( b \) is 6 or more.

Mixtures of any of the above described silicone emulsions may also be used.
The above described silicone emulsions will generally be present in a composition of the invention at levels of from 0.05 to 10%, preferably 0.05 to 5%, more preferably from 0.5 to 2% by total weight of silicone based on the total weight of the composition.

A composition of the invention may contain other ingredients for enhancing performance and/or consumer acceptability. Such ingredients include fragrance, dyes and pigments, pH adjusting agents, pearlescers or opacifiers, viscosity modifiers, and preservatives or antimicrobials. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally these optional ingredients are included individually at a level of up to 5% by weight of the total composition.

Hair treatment compositions of the invention are primarily intended for topical application to the hair and/or scalp of a human subject, either in rinse-off or leave-on compositions, for the treatment of dry, damaged and/or unmanageable hair. Rinse-off compositions are preferred.

The invention will be further illustrated by the following, non-limiting Examples, in which all percentages quoted are by weight based on total weight unless otherwise stated.

**Hair Sample preparation**

European hair fibres were bleached with L'Oreal platine precision powder and Oxydant crème (1:1.5) for 30min, rinsed completely with running tap water and naturally dried overnight before the next application. The hair was washed with a surfactant base (SLES:CAPB 12:1:6). These hair fibres were treated with the Examples described below, the product left on the hair for 10 minutes, rinsed with water and naturally dried overnight. The fibres were cut into ~2mm length and used for DSC measurements.
**DSC conditions**

**DSC method:** For all DSC investigations the Mettler Toledo DSC1 analyser was used. A 6 mg of sample was weighted into a pressure resistant (20 bar), stainless steel, large volume pan (120 µl capacity) 50 µl of water was added and the pan was sealed. Samples were then mixed using a rotary mixer and left overnight to allow the water to equilibrate throughout the sample. Samples were run through a temperature programme of 100-180°C at a rate of 5°C/min in 30ml/min nitrogen atmosphere. The helix transition temperature was collected and analyzed with one-way ANOVA. Each sample analysis was carried out three times.

**DSC of Hair Fibre & DSC Results**

Using DSC one can observe any major transitions such as melting process or any other change in the crystal structure of hair fibre which would require additional energy and this will be manifested in the form of a peak on the DSC plot. The greater the degree of crystalinity or structural organisation in the sample, the higher the transition temperature that would be observed. Thus DSC is a powerful tool for observation of changes occurring in the structure of keratinous fibres.

The results of the DSC are given in table 1 below:
Table 1

<table>
<thead>
<tr>
<th>Example</th>
<th>Denaturation Temperature</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A water</td>
<td>138.40</td>
<td>1.39</td>
</tr>
<tr>
<td>Example 1</td>
<td>144.72</td>
<td>0.28</td>
</tr>
<tr>
<td>0.01 wt% Aluminium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 2</td>
<td>149.54</td>
<td>1.73</td>
</tr>
<tr>
<td>0.1 wt% Aluminium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 3</td>
<td>150.17</td>
<td>0.76</td>
</tr>
<tr>
<td>0.5 wt% Aluminium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 4</td>
<td>152.36</td>
<td>0.27</td>
</tr>
<tr>
<td>1 wt% Aluminium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 5</td>
<td>158.74</td>
<td>0.35</td>
</tr>
<tr>
<td>2 wt% Aluminium chloride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All the Examples above were aqueous.

The data given in table 2 show that the examples of the invention significantly increase the denaturation temperature of damaged hair, which means that aluminium salts and compositions containing them composition can strengthen and repair hair damaged by bleaching action.

The composition below is suitable for use with the method of the invention.
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Chemical name</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tegobetaine CK</td>
<td>Cocamidopropyl Betaine</td>
<td>1.6</td>
</tr>
<tr>
<td>Aluminium chloride hexahydrate</td>
<td>Aluminium chloride</td>
<td>1.0</td>
</tr>
<tr>
<td>Carbopol 940</td>
<td>Carbomer</td>
<td>0.4</td>
</tr>
<tr>
<td>Texapon N701</td>
<td>Sodium Laureth Sulphate</td>
<td>12.0</td>
</tr>
<tr>
<td>Mirasheen A220</td>
<td>Glycol Distearate</td>
<td>4.0</td>
</tr>
<tr>
<td>Jaguar C13S</td>
<td>Guar Hydroxypropyl Trimonium Chloride</td>
<td>0.2</td>
</tr>
<tr>
<td>Glydent</td>
<td>DMDM Hydantoin and 3-iodo-2propynylbuthyl carbamate</td>
<td>0.2</td>
</tr>
<tr>
<td>DC 1788</td>
<td>Dimethiconol/TEAS-DOBS</td>
<td>2.0</td>
</tr>
<tr>
<td>NaOH solution</td>
<td>Sodium Hydroxide</td>
<td>To pH 4</td>
</tr>
<tr>
<td>Water and minors</td>
<td>To 100 wt%</td>
<td></td>
</tr>
</tbody>
</table>
CLAIMS

1. A method of mitigating hair damage comprising the step of applying to the hair a composition comprising a group III metal salt.

2. A method according to claim 1 in which the metal salt is aluminium.

3. A method according to claim 2 in which the aluminium salt is aluminium chloride.

4. A method according to any preceding claim in which the level of metal salt in the total composition is from 0.05 to 1 wt%.

5. Method according to any preceding claim comprising the following sequential steps
   i) application of a composition comprising a group III metal salt for a maximum time period of 15 minutes;
   ii) rinsing the hair.

6. Use of a group III metal salt of to mitigate damage to hair.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/26 A61Q5/12 A61Q5/00

ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K
A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
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<td>EP 0 173 195 A2 (HENKEL KGAA [DE]) 5 March 1986 (1986-03-05) page 1, line 2 - line 5 page 2, line 13 - page 7, line 25; examples 1.1.1.3.2</td>
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* Further documents are listed in the continuation of Box C.

T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search
28 June 2012

Date of mailing of the international search report
06/07/2012

Name and mailing address of the ISA/
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Loloiu, Teodora

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