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2,914,374

## BLEACHING OF KERATINOUS FIBROUS MATERIAL

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This invention relates to the treatment of pigmented keratinous fibrous materials such as wool, karakul, alpaca, cashmere, vicuna, cow hair, goat hair and the like, or mixtures of the same, so as to bleach such materials to a light color without impairing their desirable properties.

If powerful bleaching baths of the prior art are used in such strength as is required to obtain the degree of bleaching obtained by our process, serious weakening of the fibers occurs and the material acquires a gelatinous feel when wet and a harsh feel when dry. For example, alpaca and cashmere so treated by prior art methods to obtain a light color suffer loss of desirable soft hand, a valuable property of the luxury fibers alpaca and cashmere. Even when keratin fibers are treated by the process described in our United States Patent No. 2,508,713 prior to bleaching with the powerful peroxide baths which would be necessary to obtain the degree of bleaching obtained by the process of this invention, damaged fibers of unsatisfactory quality are obtained. On the other hand, if lower concentrations of peroxide are used (such as are used in the process of this invention) with keratin fibers stabilized by the process of our United States Patent 2,508,713, insufficient bleaching results, i.e., inadequate lightening of color, is obtained.

It is an object of the invention to provide a process for the bleaching of keratinous materials, especially dark pigmented wool and hair fibers, which process will give a degree of natural-color removal hitherto unavailable to the art without serious deleterious effect on the quality of the material being treated.

The process of the present invention produces well bleached materials without impairing the tensile properties or the desirable handle of the treated animal fiber.

The process is easily controlled, giving reproducible results, and is flexible, so that by adjustment of conditions the ordinary dark pigmented keratinous materials of commerce may be bleached white.

The process of the present invention is faster and more economical than prior processes. Because of the high stability imparted to the keratinous material in our process, higher temperatures of the bleaching baths can be utilized without any deleterious effects, resulting in more rapid treatment or lower consumption of hydrogen peroxide, or both.

In accordance with the invention the keratinous fibrous material is first treated with an aqueous solution, at a temperature of 150° to 212° F., containing free formaldehyde and a ferrous salt, and thereafter is treated with a solution at 120° to 195° F. containing hydrogen peroxide, and preferably also containing a peroxide stabilizing agent such as a condensed phosphate, a silicate, or an oxalate, the pH of said latter solution being adjusted within the range 7.0 to 9.0. For convenience, our treatment with the first solution (containing inter alia, formaldehyde and a ferrous salt) at elevated temperatures is hereinafter called the "stabilizing-catalyzing" step; the treatment with the second solution (containing inter alia,

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hydrogen peroxide) is hereinafter called the "bleaching" step.

Desirably we also include in the stabilizing-catalyzing bath a reducing agent for keratin, as its presence provides a more stable bath, keeps the iron salt in a reduced state, provides better chemical stabilization of the keratin and leads to a lighter color in the final bleached product.

Preferably we also include in the stabilizing-catalyzing bath a sequestering agent for iron, as this, we have found, prevents precipitation of iron on the keratinous material, permits the use of a stabilizing-catalyzing bath of a higher pH and improves the bleaching effect.

Treatment of keratinous material prior to bleaching with iron salts alone will enhance the bleaching effect, but because of difficulty in securing penetration of the iron salt and consequent uneven distribution, inadequate color removal and spotty results are obtained due to localization of the iron on the fiber. Moreover, such uneven distribution of the iron results in the formation of damaged spots after bleaching at the points where excessive iron is deposited. In the process of our invention, treatment of the keratinous material at elevated temperatures with free formaldehyde concurrently with the treatment with the iron salt results in protection of the keratin against the chemical oxidizing treatment during the subsequent bleaching step. Simultaneous treatment of the keratinous material at elevated temperatures with a ferrous salt, free formaldehyde, and a reducing agent in the presence of a sequestering agent, better protects the keratin against the subsequent chemical oxidizing treatment, results in level distribution of the iron, and brings about unusually thorough penetration of iron into the keratinous material so that the iron reaches the site of pigment particles in the fiber. Because the iron penetrates the fibers to the site of the pigment particles, a very high degree of color removal is obtained even on heavily naturally-pigmented fibers.

As the ferrous salt, ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) is preferred. Ferrous ammonium sulfate may also be used.

Although a wide variety of reducing agents may be used, preferred ones are the sulfoxylate formaldehyde compounds, the hydrosulfites and the sulfites, bisulfites and metabisulfites. The alkali metal salts of these compounds are soluble and are preferred, although the zinc salts of commerce may be used. Other reducing agents which may be used are mercaptans, such as thioglycolic acid, and compounds like sodium thiosulfate and hydroxylamine salts, such as the hydrochloride. Many of the reducing agents, such as sodium hydrosulfite, can react with formaldehyde and when used in the stabilizing-catalyzing step the amounts of the reducing agents are such that even after reaction, an excess of formaldehyde is always present.

As the sequestering agent, any of the following classes of compounds may be used: (a) organic substituted carboxylic acids such as citric, salicylic, tartaric, succinic, gluconic, lactic, malonic, and ethylene-diaminetetraacetic. Either the free acids or the alkali metal salts may be used. (b) Substituted pyridine derivatives such as o-phenanthroline and  $\alpha, \alpha'$ -dipyridyl. Preferred materials are citric acids and salicylic acid and their sodium salts.

Because of the interdependent reactions which occur in the stabilizing-catalyzing step, it is important that the quantities of materials present be kept within certain limits. The amount of formaldehyde used should be in the range of 1.4% to 18.6% (calculated as HCHO), based on the weight of the keratinous material. The amount of the ferrous sulfate should be between 0.6% and 10%. Other iron salts if used are included in equivalent amount.

The amount of reducing agent when used should be in the range of 0.1% to 2.7%. In the preferred stabilizing-catalyzing solution, which includes both reducing agent

and a sequestering agent, the sequestering agent is present in an amount between 0.1% and 1.5%.

All percentages given herein are based on the amount of keratinous material being treated.

Prior to the stabilizing-catalyzing step it is with some stocks advantageous to scour the material in an alkaline bath. For example, the bleaching of alpaca is greatly improved by a preliminary alkaline treatment. Baths containing 1.0% to 3.0% sodium carbonate at 125° F. for 30 minutes, or 2.0% to 5.0% ammonium hydroxide (aqueous, 28%) for 15 minutes at the boil may be used. In either case, 0.7% to 3.0% of a non-ionic wetting agent, such as Triton X-100 [polyoxyethylene (about 10 ethoxy groups) ether of tertiary octyl phenol] or Igepal CA [polyoxyethylene (about 10 ethoxy groups) ether of nonyl phenol] is used in addition to the sodium carbonate or ammonium hydroxide. If this scouring step is omitted, it is preferred to include in the stabilizing-catalyzing solution a small amount of a non-ionic wetting agent, usually less than 1% on the weight of the stock. Alternatively, the stock may be rinsed briefly with a solution of a non-ionic detergent prior to being added to the stabilizing-catalyzing bath.

The temperature of the solution during the stabilizing-catalyzing step may be in the range 150° to 212° F.; a particularly useful range is 180° to 195° F.

The pH of the stabilizing-catalyzing bath should be in the range 2.8 to 9.5.

When the pH of the stabilizing-catalyzing bath is in the range of about 2.8 to about 4.0, it is generally not necessary to include a sequestering agent in the bath. As the pH of the bath is increased above 4.0 it is preferred to have a sequestering agent for iron present.

Dependent on whether the keratinous material is acidic or alkaline in nature, the pH of the bath may change on the addition of the stock. The greatest portion of the change in pH takes place during the first 15 to 20 minutes of treatment. In such cases, adjustment of the pH may be made by addition of either alkali or acid to bring the bath to the desired pH within the stated range.

Because of the high temperatures used in the stabilizing-catalyzing step, the treatment can be accomplished in a short time, 10 to 90 minutes, although a time period up to 150 minutes may be used.

The liquor to stock ratio may be varied, as required for the conventional mill equipment used, over the range 10 to 1 to 40 to 1 or more.

After the stabilizing-catalyzing step, the bath is preferably dropped and the stock briefly rinsed. The material is now ready for the bleaching step. Although the material is usually bleached immediately after the rinsing, it may be set aside, and even dried at this point, and then bleached as described hereinafter at a later time. In fact, if convenient for mill practice, the stock may be treated by the catalyzing-stabilizing step on one day, set aside overnight, and bleached the next day if so desired.

The bleaching step comprises treatment with a solution containing hydrogen peroxide. We prefer to include in the bleaching bath a peroxide-stabilizing and iron-removing agent. Typical peroxide-stabilizing and iron-removing agents are: (a) alkali metal, condensed phosphates such as tetrasodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate and sodium tetrakisphosphate; (b) alkali metal silicates such as sodium metasilicate or water glass; (c) oxalic acid or alkali metal oxalates such as sodium oxalate. Mixtures of the above agents may also be used. Preferred agents are tetrasodium pyrophosphate, either alone, or in admixture with oxalic acid.

In the practice of the present invention it is exceedingly important that the initial pH of the bleaching bath, after the addition of the stock, be within the range of 7.0 to 9.0. If the pH of the bath is below 7.0 not only inferior bleaching of the keratinous material is obtained but also

inferior quality of the material is noted. On the other hand, if the pH of the bath is above 9.0 excessive decomposition of the peroxide as indicated by liberation of oxygen gas, results in inferior bleaching effects. Even better results are obtained if the pH is maintained within the range 7.5 to 8.5.

In order to bring the initial pH of the bleaching solution within the desired range, the solution is adjusted with alkaline materials such as sodium carbonate or ammonium hydroxide when the pH is below pH 7, or with an acid such as sulfuric acid when the pH is above pH 9. While the stock is being treated in the bleaching solution, a decrease in the pH of the solution results and it is advantageous to add alkaline materials to adjust the pH within the preferred range of 7.5 to 8.5. If the initial pH is about 8.0 it may be maintained at about this value with periodic additions of sodium carbonate or ammonium hydroxide during the course of the treatment. Alternatively, the initial pH may be in the range 7.0 to 7.5, and it can be adjusted upward within the range with periodic additions of these same alkaline materials during the course of the treatment.

All pH values in this specification are for measurements made on solutions cooled to 25° C., using a glass electrode.

The amount of hydrogen peroxide in the bleaching solution (calculated as 100% H<sub>2</sub>O<sub>2</sub>) may vary from 6% to 40% based on the amount of stock being treated. The peroxide in the bath may be provided by addition of any suitable peroxide, such as the peroxides of hydrogen, the alkali metals, the alkaline earth metals, perborates of alkali metals and persulfates or percarbonates of the alkali metals.

The amount of tetrasodium pyrophosphate may vary, for example from 5% to 40%, and the amount of oxalic acid may vary from 2.5% to 15% based on the weight of the fiber treated. The amount of sodium carbonate required to maintain the pH within the stated range may vary, for example, from 5% to 40% based on the weight of material being treated.

Because of the interdependent reactions occurring in this step, the relative amounts of materials within the ranges cited are adjusted to give an optimal bleaching effect as illustrated by the examples which follow herein.

The temperature of the bleaching bath may vary from 120° F. to 195° F., these high temperatures being possible because of the previous stabilization of the keratinous material.

The time of treatment in the bleaching step may vary from about 0.5 to about 5 hours dependent on the temperature of the bleaching solution; the higher the temperature, the shorter the time, and on the amount of color removal obtained with the particular material being used.

The following examples will serve to illustrate the invention but are not to be regarded as limiting the invention in any way:

#### Example I

A 250 lbs. lot of dark Aleppo carpet wool was bleached in a Riggs and Lombard stainless steel dye kettle. The volume of the kettle and expansion tank was approximately 1900 litres. The wool was immersed in the kettle in a stabilizing-catalyzing solution comprising:

3.5 lbs. ferrous sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O)  
1.1 lbs. citric acid  
0.35 lb. sodium sulfoxylate formaldehyde  
11.1 litres formaldehyde solution (40% CH<sub>2</sub>O)  
0.9 lb. Triton X-100

Treatment with this solution was carried out at 180° F. for 1½ hours, during which time the pH was adjusted to pH 5.5-6.0 with acetic acid. The stock was rinsed twice at 110° F. for 3 minutes and then treated in a bleaching solution comprising:

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16.8 lbs. oxalic acid (technical)  
47 lbs. tetrasodium pyrophosphate (anhydrous)  
29.4 lbs. sodium carbonate (soda ash)  
16.6 gallons of 120 volume H<sub>2</sub>O<sub>2</sub>

After about 1 hour 2 lbs. of soda ash were added to maintain the pH at about 8.2. The initial temperature of the bleaching solution was 130° F. and final temperature 140° F. Bleaching was carried out for 3.5 hours. The stock was then rinsed.

This dark Aleppo wool was found to have been bleached to a cream color. The alkali-solubility value was found to be unchanged and the breaking strength only slightly reduced, as shown in the following table:

	Alkali Solubility (Percent)	Dry Breaking Strength (lbs./in. <sup>2</sup> )
Aleppo (Untreated).....	12	21,800
Aleppo (Bleached).....	12	18,200

(Alkali solubility is a measure of damage to the fibre, high alkali solubility indicating extensive damage.)

#### Example II

The procedure of Example I was repeated with a 250 lbs. lot of dark grey-brown Iranian carpet wool. This wool was bleached to a light grey-white; the alkali solubility was slightly improved and the tensile only slightly reduced, as shown in the following table.

	Alkali Solubility (Percent)	Dry Breaking Strength (lbs./in. <sup>2</sup> )
Iranian (Untreated).....	21	19,800
Iranian (Bleached).....	18	17,100

#### Example III

A grey-brown karakul was treated at 15 to 1 bath ratio in the following manner.

Stabilizing-catalyzing solution:

1.1% ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O)  
1.1% sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O)  
.3% sodium sulfoxylate formaldehyde

(NaHSO<sub>2</sub>·HCHO·2H<sub>2</sub>O)

4.2% formaldehyde  
.45% Triton X-100  
1.4% sodium carbonate

Treatment with this solution was carried out at 185° F. for 1.5 hours. The pH was initially 9.5 and decreased to 8.0 during the course of the stabilizing-catalyzing step.

The stock was rinsed briefly and then bleached for 70 minutes at a temperature of 195° F. in the following bleaching solution:

1.5% tetrasodium pyrophosphate (anhydrous)  
.6% oxalic acid (technical)  
1.1% sodium carbonate  
9% hydrogen peroxide

The initial pH of the bleaching solution was 8.3 and the final pH 7.7.

The bleached stock was white in color.

#### Example IV

Another sample of the karakul stock of Example III was treated as in Example III except that time of treatment in the stabilizing-catalyzing bath was 10 minutes rather than 90 minutes.

A light tan, satisfactory bleached product was obtained.

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#### Example V

A brown alpaca was given a preliminary scour at 125° F. for 30 minutes in an aqueous solution (bath ratios throughout the example are 20:1) comprising:

5 3% sodium carbonate  
.6% Triton X-100

The stock was rinsed and then treated for 90 minutes at 185° F. in a stabilizing-catalyzing solution comprising:

10 3% ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O)  
.6% citric acid  
.2% sodium sulfoxylate formaldehyde  
5.5% formaldehyde

15 The initial pH was 3.3 and the final pH 5.9.

The stock was then rinsed and bleached for 2.5 hours at 135° F. in a bleaching solution comprising:

20 20% sodium tripolyphosphate  
24% hydrogen peroxide

20 Sulfuric acid was added to decrease the initial pH to 8.7. During the course of the bleaching, the pH dropped and sodium carbonate was added. The final pH was 7.2.

#### Example VI

25 A commercially scoured grey Awassi carpet wool was treated in the following manner:

Stabilizing-catalyzing solution:

30 1.2% ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O)  
.36% salicylic acid  
.24% sodium sulfoxylate formaldehyde  
3.4% formaldehyde  
.36% Triton X-100

35 Treatment with this solution was effected for 90 minutes. The initial pH before the stock was added was 3.5. After the alkaline stock was added the pH of the treating bath increased to pH 7.6 in about 20 minutes. It remained at this value throughout the treatment.

40 The stock was then rinsed and bleached for 3 hours at 135° F. in a bleaching solution comprising:

4.2% oxalic acid  
12% tetrasodium pyrophosphate  
9% sodium carbonate  
11% hydrogen peroxide

45 The initial pH was 8.25 and the final pH 8.0. The stock was then rinsed and dried.

The bleached wool was almost white in color.

#### Example VII

50 A brown cashmere was treated in an 11 to 1 bath ratio in the following manner:

Stabilizing-catalyzing solution:

55 1.6% ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O)  
.32% citric acid  
3.1% formaldehyde  
.32% Triton X-100

60 Treatment with this solution was effected at 185° F. for 90 minutes. The initial pH was 3.6 and the final pH 4.5.

The stock was rinsed and then bleached for 3 hours at 135° F. in a bleaching solution comprising:

65 4.4% oxalic acid  
11% tetrasodium pyrophosphate (anhydrous)  
8.3% sodium carbonate  
9.9% hydrogen peroxide

The initial pH was 8.3 and the final pH 8.0. The bleached cashmere was rinsed and dried.

70 The color of the bleached cashmere was a light yellow. In all of the above examples all quantities are based on the weight of the fiber.

Although the process of this invention may be used with many types of keratinous materials, the most striking results have been obtained with those pigmented

fibres which are not readily bleached by the methods of the prior art without serious deterioration of fibre quality. Keratinous materials particularly well bleached by the process of this invention are dark shades of alpaca, dark cashmere or light cashmere mixed with small amounts of dark material, karakul, dark carpet wools, camel hair, goat hair, cow hair and similar keratin materials.

The economic value of dark pigmented keratinous materials such as dark alpaca or karakul is much less than that of the material of desirable lighter shades since the lighter shades find wide use as such, and also they may be dyed to a great variety of commercially desirable shades. Moreover, the amounts of such dark materials produced in the world is much greater than that of the lighter shades, and the darker shades are much less expensive. For these reasons, the process of the present invention, which enables greater utilization of these natural dark pigmented materials with the production of light stocks of good quality, is of great economic advantage to the industry since the overall cost of bleached material made by the process of this invention is considerably less than that of the relatively scarce naturally occurring light material.

The present application is a continuation-in-part of our prior application Serial No. 352,059, filed April 29, 1953, now abandoned.

We claim:

1. The method of bleaching pigmented natural keratinous fibers which comprises treating said fibers for from 10 to 150 minutes with an aqueous solution at a temperature of 150° to 212° F. and a pH in the range 2.8-9.5, said aqueous solution comprising an inorganic, water-soluble ionizable ferrous salt in an amount equivalent to 0.6% to 10% ferrous sulfate, and 1.4% to 18.6% free formaldehyde, both on the weight of the said fibers, and thereafter treating said fibers for from about 0.5 to about 5 hours with an aqueous bleaching solution at a temperature of 120° F. to 195° F. and a pH in the range 7.0-9.0, said aqueous bleaching solution containing 6% to 40% hydrogen peroxide calculated as 100% H<sub>2</sub>O<sub>2</sub>, by weight on said fibers.

2. The method of bleaching pigmented natural keratinous fibers which comprises treating said fibers for from 10 to 150 minutes with an aqueous solution at a temperature of 150° to 212° F. and a pH in the range 2.8-9.5, said aqueous solution comprising an inorganic, water-soluble, ionizable ferrous salt in an amount equivalent to 0.6% to 10% ferrous sulfate, and 1.4% to 18.6% free formaldehyde, both on the weight of the said fibers, and thereafter treating said fibers for from about 0.5 to about 5 hours with an aqueous bleaching solution at a temperature of 120° F. to 195° F. and a pH in the range 7.0-9.0, said aqueous bleaching solution containing 6% to 40% hydrogen peroxide calculated as 100% H<sub>2</sub>O<sub>2</sub>, by weight on said fibers, and a peroxide-stabilizing and iron-removing agent selected from the class consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, sodium metasilicate, oxalic acid and alkali metal oxalates.

3. The method of claim 2 wherein the temperature of said first-mentioned aqueous solution is in the range 180°-195° F.

4. The method of claim 3 wherein said ferrous salt comprises ferrous sulfate in an amount between 0.6% and 10% of the weight of said fibers, and wherein said peroxide-stabilizing and iron-removing agent comprises tetrasodium pyrophosphate in an amount between 5% and 40% of the weight of said fibers.

5. The method of bleaching pigmented natural keratinous fibers which comprises treating said fibers for from 10 to 150 minutes with an aqueous solution at a temperature of 150° to 212° F. and a pH in the range 2.8-9.5, said aqueous solution comprising a chemical reducing agent for keratin, an inorganic, water-soluble ionizable ferrous salt in an amount equivalent to 0.6% to 10%

ferrous sulfate, and 1.4% to 18.6% free formaldehyde, all on the weight of said fibers, and thereafter treating said fibers for from about 0.5 to about 5 hours with an aqueous bleaching solution at a temperature of 120° F. to 195° F. and a pH in the range 7.0-9.0, said aqueous bleaching solution containing 6% to 40% hydrogen peroxide calculated as 100% H<sub>2</sub>O<sub>2</sub>, by weight on said fibers, and a peroxide-stabilizing and iron-removing agent selected from the class consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, sodium metasilicate, oxalic acid and alkali metal oxalates.

6. The method of claim 5 wherein the temperature of said first-mentioned aqueous solution is in the range 180°-195° F.

7. The method of claim 6 wherein said ferrous salt comprises ferrous sulfate in an amount between 0.6% and 10%, wherein said reducing agent comprises sodium sulfoxylate formaldehyde in an amount between 0.1% and 2.7% and wherein said peroxide-stabilizing and iron removing agent comprises tetrasodium pyrophosphate in an amount between 5% and 40%, all on the weight of said fibers.

8. The method of bleaching pigmented natural keratinous fibers which comprises treating said fibers for from 10 to 150 minutes with an aqueous solution at a temperature of 150° to 212° F. and a pH in the range 2.8-9.5, said aqueous solution comprising a chemical reducing agent for keratin, an iron sequestering agent, an inorganic, water-soluble, ionizable ferrous salt in an amount equivalent to 0.6% to 10% ferrous sulfate, and 1.4% to 18.6% free formaldehyde, all on the weight of said fibers, and thereafter treating said fibers for from about 0.5 to about 5 hours with an aqueous bleaching solution at a temperature of 120° to 195° F. and a pH in the range 7.0-9.0, said aqueous bleaching solution containing 6% to 40% hydrogen peroxide calculated as 100% H<sub>2</sub>O<sub>2</sub>, by weight on said fibers, and a peroxide-stabilizing and iron-removing agent selected from the class consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, sodium metasilicate, oxalic acid and alkali metal oxalates.

9. The method of claim 8 wherein the temperature of said first-mentioned solution is in the range 180°-195° F., wherein said sequestering agent comprises citric acid in an amount between 0.1% and 1.5%, wherein said reducing agent comprises sodium sulfoxylate formaldehyde in an amount between 0.1% and 2.7%, and wherein said peroxide-stabilizing and iron-removing agent comprises tetrasodium pyrophosphate in an amount between 5% and 40%, all on the weight of said fibers.

10. A process for preparing pigmented natural keratinous fibers for bleaching with hydrogen-peroxide which comprises treating said fibers for 10 to 150 minutes with an aqueous solution at a temperature of 150° to 212° F. and a pH in the range 2.8-9.5, said aqueous solution containing an inorganic, water-soluble ionizable ferrous salt in an amount equivalent to 0.6% to 10% ferrous sulfate, and 1.4% to 18.6% free formaldehyde, both on the weight of said fibers.

11. The process of claim 10 wherein said aqueous solution contains a chemical reducing agent for keratin.

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