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COMPOSITION AND METHOD OF COLD WAVING

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This invention relates to a novel composition and method for use in the cold permanent waving of hair.

The term "cold permanent waving" is used in the art and herein to mean the production of an enduring wave or curl in hair without the application of elevated temperature to the hair, as distinguished from "hot permanent waving" in which the hair is heated to elevated temperature of around 200° F. or higher.

Both hot and cold permanent waving involve winding the hair tress into curl form, softening or plasticizing the hair before or after winding, and subsequently, while the curl is mechanically maintained, hardening or setting the hair in curled form. The hot and cold processes differ basically, however, in that in the hot process, heat is the primary active agent both in plasticizing and resetting the hair, whereas in the cold process the plasticizing of the hair is effected by a chemical solution, generally called a "hair waving" solution, and the hardening or resetting of the hair is normally produced by the action of a later applied, different chemical solution, generally called a "neutralizer." Chemical waving solutions are usually applied in hot permanent waving but they are adjuvants, since a substantial permanent wave can be produced with heat and moisture alone.

This invention concerns only cold permanent waving and further, it concerns a hair waving or hair plasticizing composition and method for use in such waving, neutralizing not being involved except to the extent that any of the usual neutralization compositions or methods may be employed therewith.

According to present understanding in the art, the softening or plasticizing of hair necessary to permanent waving is produced essentially by breaking certain bonds or linkages in the keratin structure of the hair, primarily the disulfide linkages. In cold waving, this is accomplished by the use of chemical reducing agents, alkaline mercaptan solutions such as aqueous ammonium thioglycolate solution being the reducing agent presently used commercially for most cold permanent waving.

Alkaline mercaptan cold waving solutions heretofore in commercial use have had relatively high free alkali concentrations and high hydroxyl ion concentrations as reflected by pH readings in the range of pH 9 to 10. Unless the free alkali concentration is kept high and of the order stated, it is found that the softening action of the solution is too light or too slow for practical cold waving usage.

These alkali mercaptan solutions, while efficient for cold waving, have had certain shortcomings which have proved troublesome, mainly due to their high concentration of free alkali. For one thing, this high free alkali concentration makes the solutions irritating to the skin, making advisable certain troublesome precautions in handling the solution, such as the wearing of protective gloves on the hands or frequent rinsing of the hands during use of the solution, and care not to apply excessive amounts of the solution to the scalp (which often shows

noticeable flushing even when normal amounts are applied thereto during the waving). Also at high alkali and mercaptan concentrations the action on the hair may be undesirably severe in some cases. Many of these difficulties are troublesome enough in the beauty shops but are much more so in home waving where the solutions are usually handled by non-professionals.

In addition, these alkalinities have in the past been normally obtained by the employment of ammonium hydroxide because it has always been a desirable mild base for waving preparations. The high ammonia content of solutions adjusted to a pH above 9.0 with ammonium hydroxide has led to a strong and undesirable odor in the lotion.

These deficiencies of the mercaptan cold waving solutions have long been apparent and the art has been active in seeking to solve the problem. Attempts have been made to produce a satisfactory mercaptan solution with lower free alkali concentrations and at a lower pH by using larger amounts of mercaptan than are ordinarily employed (about 4% to 8% mercaptan concentration being the range used commercially for ammonium thioglycolate solutions, the type of mercaptan solution generally used). However, it was found that such compositions were not sufficiently effective and furthermore, involved other difficulties such as malodor, decomposition, possible toxicity, and expense. The solutions in commercial use have continued to employ only alkali-mercaptan combinations as the waving agent (plus the usual neutral additives such as perfume, wetting agent, creaming agent). The search for other and more satisfactory waving compositions has been extensive, but so far has supplied nothing acceptable for commercial use.

One object of our invention is to overcome or substantially reduce these difficulties with present mercaptan waving solutions by providing a novel alkaline mercaptan solution which is at least as effective a cold waving agent as prior solutions, but which has a substantially lower pH.

Another object is to provide such a solution which possesses less undesirable odor than prior solutions.

Another object is to provide a solution which has less tendency to cause yellowing when used with gray hair than prior solutions.

Another object is to provide such a solution which is less irritating to the skin and which has substantially less toxicity than prior solutions.

A further object is to provide such a solution which is less destructive (substantially non-destructive) to the hair than prior solutions.

Another object is to provide a new and improved method of hair waving employing such solution.

Other and further objects will be apparent from the description which follows:

We have discovered that these objects are attained by employing in aqueous ammoniacal mercaptan solutions, such as aqueous ammonium thioglycolate solutions, ammonium carbonate or a mixture of ammonium carbonate and ammonium bicarbonate. The addition of these salts to the lotion does not require any change in the concentration of the ammonium thioglycolate which may remain at the usual concentration of 0.4 M. to 0.8 M. The ammonium carbonate or mixture of ammonium carbonate with ammonium bicarbonate may be employed in concentrations from 0.1 M up to saturation, preferably from 0.1 to 0.9 M. A desirable range is from 0.25 M up to saturation, while best results are obtained in the range of concentration from 0.25 to 0.6 M. The pH of such solutions will lie in the range from 7.7 to 9.0, optimum results generally being obtained at pH 8.6 to 8.7.

Inasmuch as the ammonium carbonate of commerce, even reagent grade ammonium carbonate, normally is impure and contains substantial quantities of ammonium

bicarbonate, it has been found convenient to form the ammonium carbonate in situ in the solution by first adding ammonium bicarbonate in the desired amount (ammonium bicarbonate of high purity is commercially available), then adding sufficient ammonium hydroxide to convert part or all of the ammonium bicarbonate to ammonium carbonate.

We have found that the waving lotions of the present invention possess the following highly desirable and surprising properties;

1. The pH range at which the solution is effective for commercial cold waving is substantially lowered without impairment of the waving properties of the solution and indeed, in many cases, with improvement of the waving properties.

2. Even at substantially lower pH values, this solution, in many cases, substantially increases the speed of the waving process.

3. The solution of the present invention has less tendency to over-wave degraded or damaged hair.

4. The condition of the hair after waving with the present solution has improved combing properties, appearance, and feel.

5. The new solution is less irritating to the skin and the irritating odor of free ammonia is substantially reduced.

6. The new solution has substantially less tendency to cause yellowing of gray hair.

It is preferred to employ the ammonium carbonate, or mixture of ammonium carbonate and ammonium bicarbonate, in amounts less than the maximum which is soluble in the solution, the preferred range of concentration, as pointed out above, being from 0.25 to 0.6 M. The lower ranges of concentration are preferred because these amounts provide a more stable solution, and the lower salt content provides better control of the swelling action of the solution on the hair. Furthermore, although the initial ammonia odor of the solution (prior to application of the solution to the hair) is less, regardless of the amount of carbonate or bicarbonate present, than that of alkaline lotions containing no carbonate at all, it has been found, surprisingly enough, that the odor is less after the solution has been applied to the hair, if the carbonate or bicarbonate content is low than is the case when the carbonate or bicarbonate content is high, despite the fact that the pH of the preparation may be the same in both cases. This advantage is particularly important when the solution is employed in a process which makes use of aerial oxidation of the hair instead of chemical oxidation or neutralization. Since aerial oxidation normally requires a much longer time than does oxidation or neutralization with a conventional neutralizing agent, the user of the lotion is exposed to the odor for a much longer period of time.

The marked advantages of the solution of the present invention are illustrated by the following comparisons:

A typical home cold waving lotion in present commercial use is an aqueous solution of 0.5 M ammonium thioglycolate containing free ammonia so that it has a pH usually above 9, together with small quantities of a wetting agent, an opacifier, and a perfume.

For comparison with such a regular lotion containing 0.5 M ammonium thioglycolate and 0.5 M free ammonia, pH approximately 9.4, a lotion was prepared according to the present invention containing 0.5 M thioglycolic acid and 0.8 M ammonium bicarbonate, the solution being brought to a pH of 8.6 to 8.7 by the addition of ammonia or ammonium hydroxide, the addition of ammonium hydroxide serving to convert a portion of the ammonium bicarbonate to ammonium carbonate. The lotion also included the same wetting agent, opacifier, and perfume, as mentioned above in the same amounts.

The two solutions were then extensively compared by the so-called "split head" technique in which a wave is given to one side of a head of hair with one lotion and simultaneously, to the other side of the same head of hair with the other lotion. The waving procedure employed with both lotions was the same, being that used with the regular lotion in commercial practice, including treatment with a conventional neutralizing solution, aqueous potassium bromate solution, after processing for up to 90 minutes with the waving lotion. These comparative tests continued on a large number of different heads showed consistently that:

In many cases, particularly on normal or resistant hair, the optimum wave of desired character was obtained in 20 to 30 minutes less time with the carbonate lotion; the optimum wave produced on the carbonate lotion side was at least equal to and, in many cases, superior to the optimum wave produced on the regular lotion side in the development of curl strength, uniformity of wave, and wave permanence, for all types of hair;

there was less change in the physical properties of the hair throughout the waving process with the carbonate lotion, and in general, the hair was in better condition after waving with the carbonate lotion than it was after waving with the regular lotion, having a more lustrous appearance, better combing properties, better resilience, and better feel;

the carbonate lotion had substantially less tendency to over-wave degraded or damaged hair and less tendency to cause yellowing of gray hair;

there was less skin irritation on the carbonate lotion side, which was apparent from the fact that there was less flushing of the scalp on that side and less smarting, whereas in some cases, smarting occurred on the regular lotion side.

In the following table, there are presented several different lotions which are typical of those within the scope of the present invention, all of which give substantially the same advantages as described above when employed in the same procedure;

	A	B	C	D	E	F	G	H	I	J
Ammonium thioglycolate, molarity	0.5	0.6	0.7	0.7	0.6	0.65	0.65	0.60	0.6	0.7
Ammonium bicarbonate, molarity	0.8	0.6	0.6	0.2	0.4	0.70	0.10	0.15	0.8	0.7
Ammonium carbonate, molarity	------	------	------	------	------	------	0.25	0.30	------	------
Ammonium hydroxide, molarity	0.5	0.5	0.5	0.2	0.3	0.55	------	------	0.50	0.07
Total ammonia, molarity	1.8	1.7	1.8	1.1	1.3	1.9	1.25	1.35	1.9	1.47
pH	8.7	8.8	8.7	8.4	8.6	8.7	8.5	8.6	8.6	7.8

The advantages of the waving lotion of the present invention may be obtained when the lotion is employed in a variety of different waving procedures. The lotion may be applied to dry or slightly moist (damp) hair in an amount sufficient to wet the hair thoroughly. By lightly combing the hair, the waving lotion can be distributed more evently throughout the hair tresses. A tress of hair is then wound smoothly around a conventional curling rod following which it is resaturated with a waving lotion. The tress, while wound around the

curler, is allowed to process for forty to sixty minutes at room temperature, then rinsed with water. After towel blotting, excess waving lotion is neutralized and the disulfide linkages of the hair keratin restored by pouring through the hair repeatedly an aqueous solution of sodium perborate or any other suitable neutralizing agent.

If desired, the processing time may be reduced to 25 to 30 minutes, in which case the solution of neutralizing agent may be dispensed with. In this procedure, the hair, following the rinsing step, may be covered by a towel or turban and then allowed to stand in the wound condition for approximately six hours. At the end of six hours, the hair will be substantially dry and the disulfide linkages will have been restored by aerial oxidation. The curling rods may then be removed and the hair may be rinsed and brushed as desired.

As a further modification of the procedure, the processing time may be reduced still further to a period of about 15 to 20 minutes, following which it is rinsed and allowed to stand preferably while covered with a towel or turban for about 30 to 35 minutes while still wound on the curling rods. A solution of a conventional neutralizing agent, such as a 1% sodium perborate solution, is then poured through the hair following which the hair is rinsed and set in any suitable style.

With any of the foregoing procedures, the advantages of the waving solution of the present invention are obtained, the advantages being particularly noticeable in the procedure where aerial oxidation is employed.

It should be noted that aqueous ammonium thioglycolate solution alone, at a pH of 8.6 to 8.7, containing neither carbonate nor bicarbonate, will not produce a satisfactory cold permanent wave by the conventional chemical neutralization process used in the above comparative tests, the waves obtained with such a solution being far looser and less enduring than the commercially acceptable waves obtained in the above comparative tests, even with much longer processing time. It is well known, of course, that aqueous solutions of ammonium carbonate alone, or of mixtures of ammonium carbonate with ammonium bicarbonate, are not themselves effective in the cold waving of hair. Accordingly, that the advantages we have found should accrue from the combination of ammonium carbonate or the mixture of ammonium carbonate and ammonium bicarbonate when used with a mercaptan waving agent, is most surprising and not predictable from the known properties of the ingredients.

The mercaptan, with which the ammonium carbonate or mixture of ammonium carbonate and ammonium bicarbonate may be combined in aqueous ammoniacal solutions, need not be thioglycolic acid, but may alternatively be any of the water soluble mercaptans such as mercaptocarboxylic acids, hydroxy mercaptans, amino mercaptans, and the like, and their water-soluble derivatives such as amides, the advantages of the present invention being obtained regardless of the specific mercaptan employed. Thioglycolic acid is the preferred mercaptan because of its availability and low cost. It will be understood that the thioglycolic acid is present in the form of its ammonium salt and the finished lotion is alkaline. If desired, the thioglycolic acid may be dissolved in the solution in the desired concentration followed by addition of an equivalent amount of ammonia or ammonium hydroxide to provide ammonium thioglycolate. The desired quantity of ammonium bicarbonate is then added followed by the addition of further ammonium hydroxide to give the desired proportion of ammonium carbonate and ammonium bicarbonate. It should be noted that if pure ammonium bicarbonate in the amount of 0.8 M is added to an aqueous solution of 0.6 M ammonium thioglycolate, the pH of the finished solution will be about 7.5. Such a solution is ineffective for the purposes of the present invention and requires the addition of sufficient ammonia or ammonium hydroxide to bring the pH up to at least 7.7 (with the concomitant conversion of a portion of the ammonium bicarbonate to ammonium carbonate) in order to provide a satisfactory waving lotion within the scope of the present invention.

If pure ammonium carbonate is available, it may be added directly to the solution of ammonium thioglycolate with or without the addition of ammonium bicarbonate. It will be noted that when 0.8 M pure ammonium carbonate is employed in solution with 0.6 M ammonium thioglycolate, the pH of the resulting solution is about 9.0 or slightly less. When low molar concentrations of ammonium carbonate or bicarbonate are employed, it may sometimes be found that an excess of ammonia, over and above that required to convert the ammonium bicarbonate to ammonium carbonate, may be used to achieve a solution having a pH value within the preferred range. This excess of ammonia, while generally unnecessary, does not prevent the attainment of the advantages of the present invention. These advantages are obtained when the ammonium carbonate, or a mixture of ammonium carbonate and ammonium bicarbonate, is present in the stated concentrations. However, because of the difficulty of obtaining pure ammonium carbonate from commercial sources and because of unpredictable variations in purity of commercial ammonium carbonate from one lot to the next, as well as the problems involved in handling this material which tends to cake during storage, we prefer to prepare the lotions of the present invention from ammonium bicarbonate and ammonia, or ammonium hydroxide, as outlined above.

The pH values herein referred to are as measured at 25° C.±0.1° C. (temperature of composition and buffer standard) with a Beckman Model M pH meter equipped with No. 1190–75, Type E, blue tip, high alkali electrodes, standardized with 0.01 M solutions of borax, $Na_2B_4O_7.10H_2O$ (National Bureau of Standards pH Standard to read pH 9.18 at 25° C. and also checked with standard buffers at lower and higher pH, using precise analytical technique in rinsing, wiping of electrodes, etc.

This application is a continuation in part of our copending application Serial Number 100,764, filed June 22, 1949.

Although we have herein described specific embodiments of our invention, we do not intend to limit ourselves solely thereto, but to include all of the obvious variations or modifications within the spirit and scope of the appended claims.

We claim:

1. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and at least 0.1 M material selected from the class consisting of ammonium carbonate and a mixture of ammonium carbonate with ammonium bicarbonate, the solution having a pH in the range 7.7 to 9.0.

2. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and from 0.1 M to 0.9 M material selected from the class consisting of ammonium carbonate and a mixture of ammonium carbonate with ammonium bicarbonate, the solution having a pH in the range 7.7 to 9.0.

3. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and from 0.25 M to 0.6 M material selected from the class consisting of ammonium carbonate and a mixture of ammonium carbonate with ammonium bicarbonate, the solution having a pH in the range 7.7 to 9.0.

4. A liquid composition for the cold permanent waving of hair comprising in aqueous solution at least 0.4 M water-soluble mercaptan and at least 0.1 M material selected from the class consisting of ammonium carbonate and a mixture of ammonium carbonate with ammonium

bicarbonate, the solution having a pH in the range 7.7 to 9.0

5. A liquid composition for the cold permanent waving of hair comprising in aqueous solution 0.4 M to 1.0 M water-soluble mercaptan and from 0.1 M to 0.9 M material selected from the class consisting of ammonium carbonate and mixtures of ammonium carbonate with ammonium bicarbonate, the solution having a pH in the range 8.6 to 8.7.

6. A liquid composition for the cold permanent waving of hair comprising in aqueous solution 0.4 M to 1.0 M ammonium thioglycolate and from 0.1 M to 0.9 M material selected from the class consisting of ammonium carbonate and mixtures of ammonium carbonate with ammonium bicarbonate, the solution having a pH in the range 8.6 to 8.7.

7. A liquid composition for the cold permanent waving of hair comprising in aqueous solution 0.4 M to 1.0 M ammonium thioglycolate and from 0.25 M to 0.6 M material selected from the class consisting of ammonium carbonate and mixtures of ammonium carbonate with ammonium bicarbonate the solution having a pH in the range 8.6 to 8.7.

8. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and from 0.25 M to 0.6 M ammonium carbonate, the solution having a pH of about 8.6 to 8.7.

9. A liquid composition for the cold permanent waving of hair comprising an aqueous solution of a water-soluble mercaptan and at least 0.25 M material selected from the class consisting of ammonium carbonate and ammonium bicarbonate, the solution having been brought to a pH in the range 7.7 to 9.0 with ammonia.

10. A liquid composition for the cold permanent waving of hair comprising in aqueous solution at least 0.4 M water-soluble mercaptan and at least 0.1 M ammonium bicarbonate, the solution having been brought to a pH in the range 7.7 to 9.0 with ammonia.

11. A liquid composition for the cold permanent waving of hair comprising in aqueous solution from 0.4 M to 1.0 M water-soluble mercaptan and a material selected from the class consisting of ammonium carbonate and ammonium bicarbonate present in an amount from 0.25 M to saturation, the solution having been brought to a pH in the range 7.7 to 9.0 with ammonia.

12. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and at least 0.1 M ammonium bicarbonate, the solution having been brought to a pH of about 8.6 to 8.7 with ammonia.

13. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and from 0.25 M to 0.6 M ammonium bicarbonate, the solution having been brought to a pH in the range 7.7 to 9.0 with ammonia.

14. A liquid composition for the cold permanent waving of hair comprising in aqueous solution a water-soluble mercaptan and from 0.25 M to 0.6 M ammonium bicarbonate, the solution having been brought to a pH of about 8.6 to 8.7 with ammonia.

15. A liquid composition for the cold permanent waving of hair comprising in aqueous solution 0.4 M to 1.0 M water-soluble mercaptan and ammonium bicarbonate present in an amount from 0.1 M to saturation, the solution having been brought to a pH of about 8.6 to 8.7 with ammonia.

16. A liquid composition for the cold permanent waving of hair comprising in aqueous solution ammonium thioglycolate and at least 0.1 M ammonium bicarbonate, the solution having been brought to a pH in the range 7.7 to 9.0 with ammonia.

17. A liquid composition for the cold permanent waving of hair comprising in aqueous solution from 0.4 M to 1.0 M ammonium thioglycolate and at least 0.25 M material selected from the class consisting of ammonium carbonate and ammonium bicarbonate, the solution having been brought to a pH in the range 7.7 to 9.0 with ammonia.

18. A liquid composition for the cold permanent waving of hair comprising in aqueous solution from 0.4 M to to 1.0 M ammonium thioglycolate and from 0.25 M to 0.6 M ammonium bicarbonate, the solution having been brought to a pH of about 8.6 to 8.7 with ammonia.

19. The method of permanently waving human hair which comprises treating the hair with an aqueous solution comprising water-soluble mercaptan and at least 0.1 M material selected from the class consisting of ammonium carbonate and a mixture of ammonium carbonate with ammonium bicarbonate, the solution having an initial pH in the range 7.7 to 9.0, and allowing the hair to remain in wound configuration in contact with said solution for a period of time sufficient to soften the hair.

20. The method of permanently waving human hair which comprises contacting the hair with an aqueous solution comprising 0.4 M to 1.0 M water-soluble mercaptan and 0.1 M to 0.9 M material selected from the class consisting of ammonium carbonate and mixtures of ammonium carbonate with ammonium bicarbonate, the solution having an initial pH in the range 7.7 to 9.0.

21, The method of permanently waving hair which comprises contacting the hair with an aqueous solution comprising 0.4 M to 1.0 M ammonium thioglycolate and from 0.25 M to 0.6 M ammonium bicarbonate, the solution having been brought to an initial pH of about 8.6 to 8.7 with ammonia.

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