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PERMANENT WAVING OF HAIR

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1

My invention is directed to improvements relating to the permanent waving of hair and is particularly concerned with new and useful hair waving preparations and processes of imparting a permanent wave to hair, particularly to hair on the human head.

In accordance with present day practice in the permanent waving of hair on the human head by the so-called cold process, the hair is wetted with an aqueous solution of relatively high alkalinity containing about 5% or more, by weight, of active ingredients, the latter comprising ammonium thioglycolate and an alkaline substance as, for example, ammonia, sodium hydroxide or potassium carbonate. The curls are then formed and the solution is allowed to remain in contact with the hair, while the latter is wound around the curlers, for about 1 to 2½ hours, depending upon the texture of the hair. Thereafter, in order to destroy the activity of said solution and thus protect the hair against damage from unduly long contact with said solution, and in order to make the wave permanent, the initially treated hair is subjected to repeated contact with an aqueous solution of a so-called neutralizer and oxidizer, tartaric acid plus potassium bromate being commonly employed for this purpose. Finally, the hair is rinsed repeatedly with water to remove all traces of the two treating solutions, after which the hair is set and dried.

In recent years, home permanent wave kits have been marketed containing all of the necessary equipment and hair treating materials to enable one to carry out the permanent waving operation in the home, without resorting to the necessity of employing skilled beauty shop operators. Such kits usually include, so far as the hair treating compositions are concerned, a bottle containing an aqueous alkaline solution containing several per cent of ammonium thioglycolate. In a separate envelope, the neutralizer and oxidizer, for example, tartaric acid plus potassium bromate, is packaged and, when the kit is used, the contents of the envelope are dissolved in a stated quantity of hot water and utilized in accordance with the given directions. In a typical instance of the instructions furnished with such kits, the hair, after being shampooed and rinsed with luke warm water and left damp, is thoroughly wetted with the waving solution, or lotion as it commonly is called, containing the ammonium thioglycolate. Individual hair tresses are then blocked off, each tress is again saturated with the waving lotion and then each tress is combed to effect even distribution of the waving

2

lotion. The hair tresses are then wound around the curlers, furnished with the kit, and, after all the tresses are wound, the wound tresses are again saturated with the waving lotion. The hair may or may not then be covered with a cap or turban and allowed to stand for about 1 to 2½ hours, depending upon the texture of the hair. The excess waving lotion is then soaked up with a towel. The tresses while still on the curlers are saturated with the neutralizing and oxidizing solution and allowed to stand for about 5 minutes and the tresses are then blotted or pressed with a towel. The tresses are again saturated with the neutralizing and oxidizing solution and thereafter a period of about 10 minutes is permitted to elapse after which the tresses are gently unwound from the curlers. The neutralizing and oxidizing solution is then poured repeatedly through the hair after which the hair is rinsed with luke warm water for about 1 minute. The hair is then blotted with a towel and, finally, is combed, set and dried. The instructions advise that the hair thereafter be not shampooed for a period of several days, usually 3 to 5 days.

Such procedures, whether carried out by professional operators or in the home by the housewife or the like, have a number of serious objections. In the first place, a number of operations is required and a substantial amount of time must be expended, usually of the order of 3 hours or more, in order to produce a finished wave. The time factor, moreover, depends upon a number of uncertainties in which the human faculty for error of judgment plays a part, such comprising, for example, judging the texture of the hair to be waved and determining the processing times in the light thereof, and making test curls to determine whether the processing times selected are proper. The waving solutions or lotions are usually of such character that, if allowed to remain in contact with the hair for too long a period of time, they tend to cause damage to the hair as, for example, by embrittling the same. The fact that variable factors are involved which the individual user must evaluate enhances the possibility of errors arising with the consequence that, not infrequently, an unsatisfactory wave results or damage to the hair is caused. In an effort to reduce the possibility of human error, charts and other instrumentalities have been devised to enable the user or operator better to judge the processing time and thereby to avoid or lessen the possibility of error. Such means are of only limited usefulness.

In addition to the foregoing disadvantages of

known hair waving preparations and procedures, the hair waving lotions or solutions are, and necessarily must be, marketed as liquids. Because such liquids are subject to deterioration on standing with access to the atmosphere, it is necessary that they be bottled and carefully sealed. If there is leakage or breakage, the solution spoils. Over and above these factors, the necessity for marketing the product in the form of a solution carries the objections of relatively large package size, increased weight and consequent increased shipping charges.

In accordance with my invention, the disadvantages such as those outlined above are, in the main, obviated. My invention makes it possible to dispense entirely with the use of the oxidizing and neutralizing treatment. In so doing, much time is saved in carrying out the hair waving process. In the practice of my method, only one processing solution need be employed and the ingredients thereof may be, and most conveniently are, marketed in the form of a dry or solid product thereby substantially simplifying and reducing the cost of packaging and shipping. In use, it is necessary only to dissolve the dry or solid hair wave preparation in water and subject the hair to the action of said solution in the manner hereafter described. The single solution, which does not require the use of elevated temperatures but is advantageously used at ordinary room temperatures, imparts the wave to the hair and fixes said wave without the utilization of any oxidizing and neutralizing agents. It is self-timing in the sense that, after the pH of said solution drops during the treatment of the hair to approximately a certain value, the waving operation is completed.

I have found if the hair is subjected to the action of an aqueous solution containing calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, exceptionally satisfactory results are obtained in the permanent waving of the hair. In view of the fact, among other considerations, that solutions of high alkalinity are objectionable because of possible damage to the hair, I prefer to utilize solutions whose initial pH, that is, whose pH after being prepared and at the time of application to the hair, does not exceed about 10, and, for optimum results, it should be within the range of 9.2 to 9.5. In use, after application to the hair, the pH of the solution steadily decreases and, when the pH falls to below 7, usually between about 5 and about 5.5 or sometimes slightly below 5, the operation is over. The desired pH is readily arrived at by selecting proper proportions of the calcium thioglycolate and the chosen ammonium salt or mixtures of the ammonium salts, as set out hereafter. Where, after the hair tresses have been saturated with the waving solution, the hair is covered with a towel or turban and thus allowed to stand for 1 to 2 hours, for example, the waving operation may be completed and still the pH of the solution may have dropped to only 7.5 or thereabouts. In such cases, when the waving solution is washed from the hair by the rinsing operation with water, the pH will drop to below 7 and usually to below 6, depending upon the particular ammonium salt and the proportions thereof used in the waving preparation. Where, however, the head is left uncovered after the application of the waving solution to the tresses, the pH will drop to below 7 and usually to between about 5 and 5.5 at the expiration of the selected waving time.

Among the acid-reacting ammonium salts which may be utilized in admixture with the calcium thioglycolate are ammonium acetate, ammonium bromide, ammonium chloride, ammonium formate, ammonium nitrate, and mixtures of any two or more of said ammonium salts. Such ammonium salts are characterized by ready solubility in water. They show, in 0.1 mol solutions, a pH of about 4 to about 4.6. Their calcium salts are readily soluble in water. Ammonium chloride and ammonium formate are particularly useful.

I may utilize, together with the calcium thioglycolate and the ammonium salt, a wetting agent in small proportions, usually of the order of about 0.1% to 0.2%, by weight of the dry composition, depending upon the wetting-out properties of the particular agent selected. Where a wetting agent is utilized, one should be selected which does not adversely interfere with the ionic reactions of the compounds, which does not adversely reduce their solubility, and which does not effectively disturb the desired pH operating range. Such agents should be stable in aqueous solutions containing alkali, in aqueous solutions containing acid, and in aqueous solutions containing calicum salts. Typical examples of suitable wetting agents are the alkyl aryl sulfonates as, for example, the products sold under the trade names "Nacconol NR," "Ultra-Wet," "Kreelon" and "Oronite D-40."

The proportions of the calcium thioglycolate and the ammonium salt in the waving preparation are somewhat variable. In general, a molal ratio of one mol of calcium thioglycolate to from about 2 to about 2½ mols of the ammonium salt is satisfactory. Such preparations when dissolved in water have an initial pH on the alkaline side, as previously described, and on standing in the air the pH gradually decreases to a value of from about 3 to about 6, depending upon the particular ammonium salt and the proportions thereof utilized. While calcium thioglycolates may be utilized whose aqueous solutions have particularly high initial pH values, for example pH 11, in such cases the amount of the ammonium salt should be increased.

In terms of parts by weight, for each 100 parts of calcium thioglycolate, from about 69 parts to about 98 parts of ammonium formate, or from about 60 to about 83 parts of ammonium chloride may be used with good results. Where other ammonium salts are employed, the proportions thereof in relation to the calcium thioglycolate may readily be determined in the light of the guiding principles disclosed herein. It may be noted that, where reference is made herein to calcium thioglycolate and certain proportions thereof, said compound is the commercial product which contains three molecules of water of crystallization. If calcium thioglycolate is used in which, for example, all or a part of the water of crystallization has been removed, an allowance should be made for such factor.

The following examples are illustrative of hair waving compositions which fall within the scope of the invention. It will be understood that various other compositions may be made, following the guiding principles and teachings contained herein, and the examples set forth herein are, therefore, in no way to be regarded as limitative of the full scope of the invention. All parts listed are by weight. As previously

stated, the calcium thioglycolate is the product which contains three molecules of water of crystallization.

Example 1

	Parts
Calcium thioglycolate	80
Ammonium formate	55

Example 2

Calcium thioglycolate	80
Ammonium chloride	47

Example 3

Calcium thioglycolate	80
Ammonium bromide	85

Example 4

Calcium thioglycolate	80
Ammonium acetate	67

Example 5

Calcium thioglycolate	80
Ammonium nitrate	69

Example 6

Calcium thioglycolate	80
Ammonium formate	14
Ammonium chloride	35

Example 7

Calcium thioglycolate	80
Ammonium chloride	45
Ammonium bromide	5

Example 8

Calcium thioglycolate	30
Ammonium nitrate	5
Ammonium formate	5
Ammonium chloride	40

Example 9

Calcium thioglycolate	80
Ammonium chloride	55
Wetting agent	0.25

Example 10

Calcium thioglycolate	80
Ammonium formate	60
Wetting agent	0.3

Example 11

Calcium thioglycolate	80
Ammonium formate	77

Example 12

Calcium thioglycolate	80
Ammonium formate	65

Example 13

Calcium thioglycolate	80
Ammonium chloride	65

Example 14

Calmium thioglycolate	80
Ammonium chloride	55

The ingredients are preferably milled, for example, in a stone mill or other suitable equipment, mixed well, preferably in a glass-lined mixer, and then suitably packaged in moisture-proof containers. For best results, the mixing and packaging operations should be carried out in an air-conditioned room under conditions of low relative humidity. The preparations may

be packaged as dry powders in moisture-proof cellophane, cellulose acetate or similar envelopes or other containers. Alternatively, they may be pressed into tablets or the like and packaged in ampoules or in any other desired manner. While the preparations may be marketed in the form of aqueous solutions in carefully sealed bottles or other containers, such represents a definitely less preferred aspect of my invention.

In use, the preparation is dissolved in water at room temperature or somewhat below room temperature to produce a solution containing several per cent, by weight, of the ingredients comprising the dry preparation. For home use, solutions containing from about 9% to about 14%, by weight, of said ingredients are quite satisfactory. For professional use, the solutions may be somewhat more concentrated, for example, from 14% to 20%. In general, aqueous solutions containing from about 5% to about 20% of the hair wave ingredients may be employed, it being understood that, with the less concentrated solutions, for example, from 5% to 9% solutions, the permanence of the wave will be of diminished degree. With the stronger solutions, whose use is particularly preferred, true permanent waves are obtained usually lasting several weeks to several months.

Calculating the calcium thioglycolate in terms of the thioglycollic acid content thereof, I find it particularly advantageous to use solutions in which the content of thioglycollic acid is between 3% and 6% and particularly about 4%. A range of about 1% to 6% may be used, it being understood that the weaker concentrations are not preferred because of the decreased permanence of the wave produced therewith.

The initial steps in the process of waving the hair, in accordance with my present invention, may follow those which have been described above. That is, the hair is initially shampooed, rinsed, and partially dried to leave the hair damp. The combed tresses are then saturated with the waving solution of my present invention, the saturated tresses are combed to effect even distribution of the waving solution, the tresses are wound around the curlers and again saturated with the waving solution, the head may or may not then be covered with a towel or turban, and is then allowed to stand for about 1 to 2 hours or generally until the pH of the solution drops to below 6 and, more particularly, to about 5, according to the exact character of the wave desired. In general, if a loose wave is sought, a period of about 1 hour standing time is adequate. If a medium wave is desired, a standing time of about 1½ hours is usually quite satisfactory. If a tight curl is sought, a standing time of about 2 hours is indicated. It may be pointed out that these times represent a good average irrespective of the texture of the hair being waved. It will be appreciated, however, that the exact time may be varied somewhat from the mean figures given. The excess waving solution is then soaked up with a towel, the curlers are unwound gently, and then the hair is rinsed with luke warm water. Thereafter it is partially dried with a towel, combed, set and dried.

It will be observed that the series of oxidizing and neutralizing treatments are unnecessary in the practice of my process. In addition to the substantial saving of time and effort which is involved in producing a permanent wave, the practice of my invention eliminates the difficulty arising from the uncertainty of determining

processing times when utilizing heretofore known waving compositions and procedures. In the case of my invention, this is for all practical purposes self-regulating. It follows, therefore, that the practice of my invention is much safer than the heretofore known methods and brings about greater assurance of uniformity of satisfactory results. In this general connection, it may be noted that dyed hair and hair of light shades, which are well known to be particularly susceptible to discoloration when using heretofore known hair waving preparations, can be given a permanent wave without adverse effect upon the dye or the natural light shades when treated in accordance with my present invention. Indeed, in many cases, the dye tends to become even more permanently fixed and such hair appears to acquire a new life and luster.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A hair wave preparation, in the form of a solid product, said composition consisting essentially, as the active ingredients, of calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, said preparation, when dissolved in water to form a dilute solution, producing an initial pH in excess of 9 but not exceeding about 10.5.

2. A hair wave preparation consisting essentially, as the active ingredients, of calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, said preparation being in the form of an aqueous solution containing from about 9% to about 20%, by weight, of said ingredients, said solution having an initial pH between about 9.2 and 9.5.

3. A hair wave preparation, in the form of a solid product, said composition consisting essentially, as the active ingredients, of calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, said preparation containing said ingredients in a molal ratio of one mol of calcium thioglycolate to approximately two to two and one-half mols of said ammonium salt and adapted, when dissolved in water to form a dilute solution, to produce a solution having an initial pH in excess of 9 but not exceeding about 10.5.

4. A hair wave preparation, in the form of a solid product, said composition consisting essentially, as the active ingredients, of calcium thioglycolate and ammonium chloride in a molal ratio of one mol of calcium thioglycolate to from approximately two to two and one-half mols of ammonium chloride, said preparation, when dissolved in water to form a dilute solution, producing an initial pH between about 9.2 and about 10.

5. A hair wave preparation, in the form of a solid product, said composition consisting essentially, as the active ingredients, of calcium thioglycolate and ammonium formate in a molal ratio of one mol of calcium thioglycolate to from approximately two to two and one-half mols of ammonium formate, said preparation, when dissolved in water to form a dilute solution, producing an initial pH between about 9.2 and about 10.

6. A hair wave preparation consisting essentially, as the active ingredients, of calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, said preparation being in the form of a dilute aqeous solution which, when freshly prepared, has an initial pH not exceeding 10, the molal ratio of the calcium thioglycolate to the ammonium salt present in said solution being 1 to approximately 2 to 2.5.

7. A hair wave preparation consisting essentially, as the active ingredients, of calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, said preparation, in the form of a dilute aqueous solution, having an initial pH in excess of 9 but not exceeding about 10.5.

8. A hair wave preparation consisting essentially, as the active ingredients, of calcium thioglycolate and a water-soluble acid-reacting ammonium salt whose anion forms water-soluble calcium salts, said ingredients being present in a molal ratio of one mol of calcium thioglycolate to from approximately two to two and one-half mols of said ammonium salt, said preparation, in the form of a dilute aqueous solution, having an initial pH in excess of 9 but not exceeding about 10.5.

9. A hair wave preparation, in the form of a solid product, said preparation consisting essentially, as the active ingredients, of calcium thioglycolate and at least one ammonium salt selected from the group consisting of ammonium acetate, ammonium bromide, ammonium chloride, ammonium formate, and ammonium nitrate, said preparation, when dissolved in water to form a dilute solution, producing an initial pH between about 9.2 and 10.

10. A hair wave preparation consisting essentially, as the active ingredients, of calcium thioglycolate and at least one ammonium salt selected from the group consisting of ammonuim acetate, ammonium bromide, ammonium chloride, ammonium formate, and ammonium nitrate, said ingredients being present in a molal ratio of one mol of calicum thioglycolate to from approximately two to two and one-half mols of said ammonium salt, said preparation, in the form of a dilute aqueous solution, having an initial pH in excess of 9 but not exceeding about 10.5.

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