

## UNITED STATES PATENT OFFICE

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## PERMANENT WAVING OF HAIR

Ernst O. Schnell, Chicago, Ill.

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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% to 6% or more, by weight, of active ingredients, the latter comprising mono-ammonium thioglycolate, more commonly referred to simply as ammonium thioglycolate ( $\text{HS}-\text{CH}_2-\text{COONH}_4$ ), and an alkaline substance as, for example, ammonia, sodium hydroxide or potassium carbonate. The curls are then formed and, after resaturation, the solution is allowed to remain in contact with the hair, while the latter is wound around the curlers, for about  $\frac{1}{2}$  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 and to eliminate objectionably odors, the initially treated hair is subjected to repeated contact with an aqueous solution of a so-called neutralizer and/or oxidizer, tartaric acid or potassium bromate or mixtures thereof 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/or oxidizer, for example, tartaric acid or potassium bromate or mixtures thereof, 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 com-

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monly 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 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  $\frac{1}{2}$  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 several 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 2 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 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/or 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. The combination of ingredients utilized in 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, automatically controls and regulates the pH of the solution during processing, brings about a stoppage of the reduction reaction, neutralizes the hair, eliminates or reduces objectionable odors, and fixes said wave. 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 alkaline solution containing alkali or ammonium thioglycolates and, in addition, certain water-soluble ammonium salts, hereafter described in detail, 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 about 9.2 to about 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 4 and about 5, the operation is over. The desired pH is readily arrived at by selecting proper proportions of the alkali or ammonium 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 about ½ to 2 hours, for example, the waving operation may be completed and still the pH of the solution may have dropped to only about 7 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 about 5, depending upon the particular ammonium salt and the proportions thereof used in the waving preparation. Where 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 about 5 at the expiration of the selected waving time.

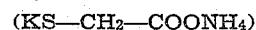
Among the water-soluble, non-reducing ammonium salts which may be utilized in admixture with the alkali or ammonium thioglycolate are ammonium acetate, ammonium bromide, ammonium chloride, ammonium formate, ammonium nitrate, ammonium bisulfate, di-ammonium citrate, mono-ammonium phosphate, ammonium sulfate, di-ammonium tartrate, di-ammonium phosphate, and mixtures of any two or more of said ammonium salts. Such am-

monium salts are characterized by ready solubility in water. I prefer to utilize those which have lower molecular weights, higher percentages of the ammonium radical, and which react acidic in aqueous solutions, those which show in 0.1 mol solutions, a pH of about 4 to about 5, being most desirable. Ammonium chloride, ammonium sulfate, ammonium bisulfate, and ammonium formate, or mixtures thereof, are particularly useful.

It may be noted that it has heretofore been suggested to utilize such ammonium salts as ammonium sulfite and ammonium thiocyanate in permanent wave solutions. Ammonium sulfite is relatively strongly alkaline, has a marked reducing action and is inoperative to accomplish the results achieved by the use of the ammonium salts whose employment in conjunction with the thioglycolates pursuant to the disclosures contained herein constitutes my invention. Ammonium thiocyanate is also unsatisfactory for use in accordance with my invention. The use of these salts in previously known permanent wave compositions is for purposes wholly unrelated to the use of the different ammonium salts employed pursuant to my invention and, as stated, ammonium sulfite and ammonium thiocyanate are unsatisfactory to achieve the results obtained by my present invention.

The alkali thioglycolates, which class of compounds is used generically hereafter to encompass the thioglycolates of sodium, potassium, lithium, magnesium, and ammonium, are employed, as previously stated, in aqueous alkaline solutions. The effect of the incorporation therein of acid-reacting ammonium salts, of the character set forth above (and this is true of the use even of di-ammonium phosphate which has a slightly alkaline reaction and is distinctly not a preferred embodiment of my invention) serves to reduce the alkalinity of the previously prepared alkali metal thioglycolate solution to the desired pH for waving, for example, 9.2 to 9.5, as indicated above, and to accomplish the marked advantages heretofore an hereafter described.

In the preparation of the alkali thioglycolate solutions, that is, prior to the addition thereto of the aforementioned ammonium salts, I may start, for example, with either thioglycolic acid ( $\text{HS}-\text{CH}_2-\text{COOH}$ ), mono-ammonium thioglycolate ( $\text{HS}-\text{CH}_2-\text{COONH}_4$ ), or mono-sodium thioglycolate ( $\text{HS}-\text{CH}_2-\text{COONa}$ ), all of which are commercially available liquids. I add thereto an amount of a strong alkali or alkaline material, for example, sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, ammonium carbonate, trihydroxyaminomethane, or guanidine carbonate, sufficient substantially, or somewhat in excess thereof, to result theoretically in the formation of the di-alkali metal salt of the thioglycolic acid, that is, a salt in which the hydrogen of both the  $\text{SH}-$  and the  $-\text{COOH}$  radicals of the thioglycolic acid are replaced by alkali metal. Thus, for example, I admix approximately one mol or slightly more of sodium hydroxide or potassium hydroxide with one mol of mono-ammonium thioglycolate. This reaction may be considered as producing, in effect, sodium ammonium thioglycolate ( $\text{NaS}-\text{CH}_2-\text{COONH}_4$ ) or potassium ammonium thioglycolate

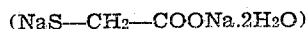


Starting with thioglycolic acid, I may admix one mol thereof with approximately two mols or

slightly more of sodium hydroxide, potassium hydroxide, lithium hydroxide, or ammonium hydroxide, or mixtures thereof, to produce what may be considered as di-sodium thioglycolate, dipotassium thioglycolate, dilithium thioglycolate, and di-ammonium thioglycolate, as the case may be ( $MS-CH_2-COOM$ , where M is alkali metal). It will be appreciated, of course, that instead of single alkalies, mixtures thereof may be utilized. Where sodium carbonate, potassium carbonate, lithium carbonate or ammonium carbonate, or mixtures thereof are used as the alkalies for admixture with the thioglycolic acid, mono-ammonium thioglycolate, or mono-sodium thioglycolate, in such cases, only one-half mol of the carbonates or slightly more is used for each mol of mono-ammonium thioglycolate or mono-sodium thioglycolate; and only one mol or slightly more for each mol of thioglycolic acid; it being clear that, in case of the alkali metal carbonates, there are two alkali metal atoms present in conjunction with the single carbonate radical.

It will thus be seen, and as will be described in even further detail below, that I utilize alkali salts of thioglycolic acid in which the alkali is present in sufficient quantities to replace most or all of the hydrogen of both the  $SH-$  and the  $-COOH$  radicals of the thioglycolic acid with alkali metal or magnesium.

Instead of proceeding in the manner described above, I may employ diammonium thioglycolate, disodium thioglycolate, dipotassium thioglycolate, dilithium thioglycolate, sodium ammonium thioglycolate, potassium ammonium thioglycolate, lithium ammonium thioglycolate, sodium potassium thioglycolate, sodium lithium thioglycolate, potassium lithium thioglycolate, and magnesium thioglycolate, prepared in any of the ways known in the prior art. Disodium thioglycolate



for example, is a solid and may be dissolved in water for use in accordance with the principles of my invention. I claim no novelty herein in methods of preparing the di-alkali metal salts of thioglycolic acid.

The proportions of the aforementioned alkali thioglycolates and ammonium salts utilized in the hair waving preparations of my invention are somewhat variable depending, among other things, upon the degree of alkalinity or acidity of the aforesaid ingredients. In general, good results are obtained with a molal ratio of 1 mol of sodium ammonium thioglycolate or potassium ammonium thioglycolate to about 1 to  $1\frac{1}{2}$  mols of an ammonium salt of a monobasic acid, or to about  $\frac{1}{2}$  to  $\frac{3}{4}$  mol of an ammonium salt of a dibasic acid, or to about  $\frac{1}{3}$  to  $\frac{1}{2}$  mol of an ammonium salt of a tribasic acid. Where a thioglycolate having a particularly high pH is utilized, for example, di-sodium thioglycolate, or magnesium thioglycolate, higher proportions of the ammonium salts should be used, as, by way of illustration, for each mol of such thioglycolate, approximately 2 to 3 mols of an ammonium salt of a monobasic acid, or from 1 to  $1\frac{1}{2}$  mols of a dibasic acid, or from  $\frac{2}{3}$  to 1 mol of a tribasic acid.

Calculating the solutions in terms of their thioglycolic acid content, I find that, for home use, solutions containing from about 3% to about 6% thioglycolic acid, by weight, are satisfactory. For professional use, the solutions may be somewhat more concentrated, containing from about 6% to about 7% or more thioglycolic acid. In general,

solutions containing from about 3 to about 9% thioglycolic acid may be employed, it being understood that, with the less concentrated solutions, containing, for example, from about 3% to about 5% thioglycolic acid, the permanence of the wave will be of diminished degree. With the stronger solutions, whose use is particularly preferred, true permanent waves are obtained, which last, in the ordinary case, until the hair grows out. I find it particularly advantageous to use solutions in which the content of the thioglycolic acid is between  $5\frac{1}{2}$  to  $6\frac{1}{2}$ %. Broadly speaking, solutions with a range of 1% to 10% thioglycolic acid may be used, it being understood, as stated above, that the weaker concentrations are not preferred because of the decreased permanence of the waves produced.

I may utilize, together with the thioglycolates and the ammonium salts, a wetting agent in small proportions, usually of the order of about 0.02% to 0.1%, by weight of the 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 sodium, potassium, lithium, magnesium, and ammonium salts. Typical examples of suitable wetting agents are the alkyl aryl sulfonates as, for example, the products sold under the trade names "Nacconol NR," "Nacconol FSNO," "Ultra-Wet," "Kreelon" and "Oronite D-40."

I may also utilize small proportions, for example, usually of the order of  $\frac{1}{2}$ % to 2%, by weight, of supplemental ingredients such as so-called clouding agents to impart a cloudiness or turbidity to the wave solutions. Such agents may comprise mixtures of gums, resins and soaps. Typical commercially available clouding agents are those sold under the trade names "Atlas Paragon Blender Cloud," "Stanton's Resin," and "Lamepon 4 C," the latter being a non-ionic condensation product of higher fatty acids and certain proteins. For obtaining smoothness, gloss and sheen, small proportions of sulfonated oils may be employed, sulfonated olive oil being typical.

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.

#### Example 1

|                                            |        |              |
|--------------------------------------------|--------|--------------|
| Mono - ammonium thioglycolate              | (56.7% |              |
| acid <sup>1</sup>                          | -----  | 10.6         |
| Sodium hydroxide                           | -----  | 2.6          |
| Ammonium chloride                          | -----  | 3.48 to 5.22 |
| Water (distilled) to bring up to 100 parts | -----  |              |

<sup>1</sup> The mono-ammonium thioglycolate solution contained 56.7% of acid calculated as thioglycolic acid.

The finished waving solution is an approximately 6% solution calculated on the thioglycolic acid content thereof.

The molal ratio of the contained thioglycolic acid to the ammonium chloride is from about 1:1 to 1:1 $\frac{1}{2}$ .

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## Example 2

|                                                |          |
|------------------------------------------------|----------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6     |
| Sodium hydroxide .....                         | 2.6      |
| Ammonium acetate .....                         | 5 to 7.5 |
| Water (distilled) to bring up to 100 parts     |          |

The molal ratio of the contained thioglycolic acid to the ammonium acetate is from about 1:1 to 1:1½.

## Example 3

|                                                |              |
|------------------------------------------------|--------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6         |
| Sodium hydroxide .....                         | 2.6          |
| Ammonium bromide .....                         | 6.38 to 9.57 |
| Water (distilled) to bring up to 100 parts     |              |

The molal ratio of the contained thioglycolic acid to the ammonium bromide is from about 1:1 to 1:1½.

## Example 4

|                                                |              |
|------------------------------------------------|--------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6         |
| Sodium hydroxide .....                         | 2.6          |
| Ammonium chloride .....                        | 1.74 to 2.61 |
| Ammonium bromide .....                         | 3.19 to 4.78 |
| Water (distilled) to bring up to 100 parts     |              |

The molal ratio of the contained thioglycolic acid to the total ammonium chloride and ammonium bromide is from about 1:1 to 1:1½.

## Example 5

|                                                |        |
|------------------------------------------------|--------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6   |
| Sodium hydroxide .....                         | 2.6    |
| Ammonium formate .....                         | 4 to 6 |
| Water (distilled) to bring up to 100 parts     |        |

The molal ratio of the contained thioglycolic acid to the ammonium formate is from about 1:1 to 1:1½.

## Example 6

|                                                |            |
|------------------------------------------------|------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6       |
| Sodium hydroxide .....                         | 2.6        |
| Ammonium nitrate .....                         | 5.2 to 7.8 |
| Water (distilled) to bring up to 100 parts     |            |

The molal ratio of the contained thioglycolic acid to the ammonium nitrate is from about 1:1 to 1:1½.

## Example 7

|                                                |            |
|------------------------------------------------|------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6       |
| Sodium hydroxide .....                         | 2.6        |
| Ammonium bisulfate .....                       | 3.2 to 4.8 |
| Water (distilled) to bring up to 100 parts     |            |

The molal ratio of the contained thioglycolic acid to the ammonium bisulfate is from about 1:½ to 1:¾.

## Example 8

|                                                |            |
|------------------------------------------------|------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6       |
| Sodium hydroxide .....                         | 2.6        |
| Ammonium sulfate .....                         | 4.3 to 6.4 |
| Water (distilled) to bring up to 100 parts     |            |

The molal ratio of the contained thioglycolic acid to the ammonium sulfate is from about 1:½ to 1:¾.

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## Example 9

|                                                                                 |             |
|---------------------------------------------------------------------------------|-------------|
| Mono-ammonium thioglycolate (56.7% acid) .....                                  | 10.6        |
| Sodium hydroxide .....                                                          | 2.6         |
| Mono-ammonium phosphate (NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> ) ..... | 2.5 to 3.75 |
| Water (distilled) to bring up to 100 parts                                      |             |

The molal ratio of the contained thioglycolic acid to the mono-ammonium phosphate is from about 1:½ to 1:¾.

## Example 10

|                                                                                 |            |
|---------------------------------------------------------------------------------|------------|
| Mono-ammonium thioglycolate (56.7% acid) .....                                  | 10.6       |
| Sodium hydroxide .....                                                          | 2.6        |
| Di-ammonium phosphate ((NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ) ..... | 2.8 to 4.3 |
| Water (distilled) to bring up to 100 parts                                      |            |

The molal ratio of the contained thioglycolic acid to the di-ammonium phosphate is from about 1:½ to 1:¾.

## Example 11

|                                                |        |
|------------------------------------------------|--------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6   |
| Sodium hydroxide .....                         | 2.6    |
| Di-ammonium citrate .....                      | 4 to 6 |
| Water (distilled) to bring up to 100 parts     |        |

The molal ratio of the contained thioglycolic acid to the di-ammonium citrate is from about 1:½ to 1:¾.

## Example 12

|                                                |        |
|------------------------------------------------|--------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6   |
| Sodium hydroxide .....                         | 2.6    |
| Ammonium tartrate .....                        | 6 to 9 |
| Water (distilled) to bring up to 100 parts     |        |

The molal ratio of the contained thioglycolic acid to the ammonium tartrate is from about 1:½ to 1:¾.

## Example 13

|                                                |            |
|------------------------------------------------|------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6       |
| Potassium hydroxide (85%) .....                | 4.3        |
| Ammonium sulfate .....                         | 4.3 to 6.4 |
| Water (distilled) to bring up to 100 parts     |            |

The molal ratio of the contained thioglycolic acid to the ammonium sulfate is from about 1:½ to 1:¾.

## Example 14

|                                                |             |
|------------------------------------------------|-------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6        |
| Sodium hydroxide .....                         | 2.6         |
| Mono-ammonium phosphate .....                  | 2.5 to 3.75 |
| Wetting agent .....                            | 0.02 to 0.1 |
| Clouding agent .....                           | 0.5 to 1    |
| Water (distilled) to bring up to 100 parts     |             |

The molal ratio of the contained thioglycolic acid to the mono-ammonium phosphate is from about 1:½ to 1:¾.

## Example 15

|                                                |            |
|------------------------------------------------|------------|
| Mono-ammonium thioglycolate (56.7% acid) ..... | 10.6       |
| Sodium hydroxide .....                         | 2.6        |
| Ammonium chloride .....                        | 2.6 to 3.9 |
| Ammonium formate .....                         | 1 to 1.5   |
| "Nacconol FSNO" .....                          | 0.03       |
| Clouding resin .....                           | 1          |
| Water (distilled) to bring up to 100 parts     |            |

The molal ratio of the contained thioglycolic acid to the total ammonium chloride and ammonium formate is from about 1:1 to 1:1½.

**Example 16**

|                                            |        |
|--------------------------------------------|--------|
| Thioglycolic acid (72.4%)                  | 8.3    |
| Ammonia (28%)                              | 10     |
| Ammonium bisulfate                         | 2 to 3 |
| Water (distilled) to bring up to 100 parts |        |

The molal ratio of the contained thioglycolic acid to the ammonium bisulfate is from about 1:¼ to 1:¾.

**Example 17**

|                                            |              |
|--------------------------------------------|--------------|
| Thioglycolic acid (72.4%)                  | 8.3          |
| Sodium hydroxide                           | 5.2          |
| Ammonium chloride                          | 3.48 to 5.22 |
| Ammonium formate                           | 4 to 6       |
| Water (distilled) to bring up to 100 parts |              |

The molal ratio of the contained thioglycolic acid to the total ammonium chloride and ammonium formate is from about 1:2 to 1:3.

**Example 18**

|                                            |             |
|--------------------------------------------|-------------|
| Thioglycolic acid (72.4%)                  | 8.3         |
| Potassium hydroxide (85%)                  | 8.6         |
| Ammonium chloride                          | 6.9 to 10.3 |
| Sulfonated oil                             | 1           |
| Water (distilled) to bring up to 100 parts |             |

The molal ratio of the contained thioglycolic acid to the ammonium chloride is from about 1:2 to 1:3.

**Example 19**

|                                             |              |
|---------------------------------------------|--------------|
| Mono-ammonium thioglycolate<br>(56.7% acid) | 14.1         |
| Sodium hydroxide                            | 3.47         |
| Ammonium chloride                           | 4.64 to 6.96 |
| "Lamepon 4 C"                               | 0.2 to 0.3   |
| Clouding agent                              | 0.5 to 1     |
| Water (distilled) to bring up to 100 parts  |              |

The finished waving solution is an approximately 8% solution calculated on the thioglycolic acid content thereof.

The molal ratio of the contained thioglycolic acid to the ammonium chloride is from about 1:1 to 1:1½.

**Example 20**

|                                                                                                |            |
|------------------------------------------------------------------------------------------------|------------|
| Di-sodium thioglycolate<br>( $\text{NaS}-\text{CH}_2-\text{COONa} \cdot 2\text{H}_2\text{O}$ ) |            |
| (96%, solid)                                                                                   | 11.2       |
| Ammonium chloride                                                                              | 6.9 to 8.7 |

For use, said mixture is dissolved in 90 parts of distilled water.

The molal ratio of the contained thioglycolic acid to the ammonium chloride is about 1:2 to 1:2½.

**Example 21**

|                                                                                              |            |
|----------------------------------------------------------------------------------------------|------------|
| Magnesium thioglycolate<br>( $\text{S}-\text{CH}_2-\text{COOMg} \cdot 8\text{H}_2\text{O}$ ) |            |
| (95%, solid)                                                                                 | 16.8       |
| Ammonium chloride                                                                            | 6.9 to 8.7 |

For use, said mixture is dissolved in 90 parts of distilled water.

The molal ratio of the contained thioglycolic acid to the ammonium chloride is about 1:2 to 1:2½.

In the preparation of the hair waving solutions, it is advantageous, in general, initially to

dissolve the alkali in distilled water and then add the necessary amount of thioglycolic acid, mono-ammonium thioglycolate or other thioglycolate to produce the concentration desired as, for example, a solution containing of about 5% to about 7% concentration, calculated as thioglycolic acid. Such solutions are distinctly alkaline and, in general, will have a pH within the range of about 10 to 12.5. Thereupon, the required amount of the aforementioned ammonium salt or salts is added to bring the pH of the solution to the desired value, for example, from about 9.2 to about 9.5. Such supplemental ingredients as wetting agents and clouding agents may be added at any desired stage of mixing. The resulting solutions are then packaged in air-tight bottles or other suitable containers.

Where the alkali thioglycolates are solids and admit of being packaged in dry form, for subsequent solution in water, the dry ingredients are mixed and 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 solid preparations may be packaged in moisture-proof "cellophane," cellulose acetate or similar envelopes or containers, or they may be pressed into tablets or the like and packaged in ampoules or in any other desired manner.

The initial steps in the process of waving the hair, in accordance with my present invention, may follow those which, in general, 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 ½ to 1½ 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 ½ hour standing time is adequate. If a medium wave is desired, a standing time of about 1 hour or slightly more is usually quite satisfactory. If a tight curl is sought, a standing time of about 1½ 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 and is dependent, among other things, on the thioglycolate concentration of the waving solution. The excess waving solution is then soaked up with a towel, the hair is rinsed with lukewarm water on the curlers, then the curlers are unwound gently, and the hair is rinsed again with lukewarm water. Thereafter it is partially dried with a towel, combed, set and dried.

It will be observed that the heretofore employed series of oxidizing and/or 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 also 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 certain 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 comprising a dilute aqueous solution of an alkali thioglycolate, said solution containing an amount of alkali radical sufficient to satisfy the requirement to have said thioglycolic acid present in the form, at least mainly, of a di-alkali thioglycolate, the alkalinity of such solution being represented by a pH in the range of about 10 to about 12.5, and an added non-reducing ammonium salt dissolved in said solution in amounts sufficient to lower the initial pH of said solution to within the range of about 9.2 to about 9.5.

2. A hair wave preparation comprising an aqueous solution of an alkali thioglycolate, said solution containing from about 5% to about 8% thioglycolate calculated as thioglycolic acid, said solution containing an amount of alkali radical sufficient to satisfy the requirement to have said thioglycolic acid present in the form, at least mainly, of a di-alkali thioglycolate, the alkalinity of such solution being represented by a pH in the range of about 10 to about 12.5, and an added non-reducing ammonium salt dissolved in said solution in amounts sufficient to lower the initial pH of said solution to within the range of about 9.2 to about 9.5.

3. A hair wave preparation comprising an aqueous solution of an alkali thioglycolate, said solution containing from about 5% to about 8% thioglycolate calculated as thioglycolic acid, said solution containing an amount of sodium and ammonium sufficient to satisfy the requirement to have said thioglycolic acid present in the form, at least mainly, of sodium ammonium thioglycolate, the alkalinity of such solution being represented by a pH in the range of about 10 to about 10.5, and an added non-reducing ammonium salt dissolved in said solution in amounts sufficient to lower the initial pH of said solution to within the range of about 9.2 to about 9.5.

4. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, from about 5% to 8% thioglycolic acid in the form of a di-alkali metal thioglycolate, and a water-soluble, acid-reacting ammonium salt of a monobasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to said ammonium salt falling within the range of about 1:1 and 1:2.

5. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, from about 5% to 8% thioglycolic acid in the form of a di-alkali metal thioglycolate, and a water-soluble, acid-

reacting, non-reducing ammonium salt of a dibasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to said ammonium salt falling within the range of about 1:½ and 1:¾.

6. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, from about 5% to 8% thioglycolic acid in the form of a di-alkali metal thioglycolate, and a water-soluble ammonium salt of a tribasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to said ammonium salt falling within the range of about 1:½ and 1:½.

7. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, from about 5% to 8% thioglycolic acid in the form of at least one di-alkali metal thioglycolate selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and a water-soluble, acid-reacting ammonium salt of a monobasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to said ammonium salt falling within the range of about 1:1 and 1:1½.

8. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, about 6% thioglycolic acid in the form of at least one di-alkali metal thioglycolate selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and from about 4% to about 6% ammonium formate.

9. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, about 6% thioglycolic acid in the form of at least one di-alkali metal thioglycolate selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and from about 3.5% to about 5.2% ammonium chloride.

10. A hair wave preparation comprising an aqueous solution having an initial pH in the range of about 9.2 to about 9.5, said solution containing, as essential ingredients, about 6% thioglycolic acid in the form of at least one di-alkali metal thioglycolate selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and from about 4.3% to about 6.4% ammonium sulfate.

11. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and an acid-reacting ammonium salt of a monobasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium salt falling within the range of about 1:1 and 1:1½, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

12. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and an acid-reacting ammonium salt of a dibasic acid, the molal ratio

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of the contained thioglycolic acid in said thioglycolate to the ammonium salt falling within the range of about 1:½ and 1:¾, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

13. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and an acid-reacting ammonium salt of a tribasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium salt falling within the range of about 1:½ and 1:¾, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

14. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of disodium thioglycolate and dipotassium thioglycolate, and an acid-reacting ammonium salt of a monobasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium salt falling within the range of about 1:2 and 1:3, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

15. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of disodium thioglycolate and dipotassium thioglycolate, and an acid-reacting ammonium salt of a dibasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium salt falling within the range of about 1:1 and 1:1½, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

16. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of disodium thioglycolate and dipotassium thioglycolate, and an acid-reacting ammonium salt of a tribasic acid, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium salt falling within the range of about 1:¾ to 1:1, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

17. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and ammonium chloride, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium

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chloride falling within the range of about 1:1 and 1:1½, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

18. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and ammonium sulfate, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium sulfate falling within the range of about 1:½ and 1:¾, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

19. A hair wave preparation consisting essentially, as the active ingredients, of at least one member selected from the group consisting of sodium ammonium thioglycolate and potassium ammonium thioglycolate, and ammonium formate, the molal ratio of the contained thioglycolic acid in said thioglycolate to the ammonium formate falling within the range of about 1:1 and 1:1½, said preparation, as a dilute aqueous solution, producing an initial pH between about 9.2 and 10.

ERNST O. SCHNELL.

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