

1

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HAIR WAVING WITH BOROHYDRIDES

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This invention relates to a method for permanently waving human hair and to a composition therefor and pertains more specifically to the use of alkali metal borohydrides for this purpose.

One object of the invention is to provide a hair-waving composition which may be employed in the form of an aqueous solution or dispersion and which is free from sulfur and from undesirable odor.

Another object is to provide a hair-waving composition which may be employed in aqueous solution over a wide range of concentrations without serious change in the effect of the composition on the hair.

A further object is to provide a hair-waving composition which may be employed in aqueous solution or dispersion over a wide range of alkalinity with little danger of damaging the hair.

Still a further object is to provide a hair-waving composition which may be employed in aqueous solution or dispersion with little danger of over-processing the hair regardless of wide variation in the time of application of the composition to the hair.

Another object is to provide a method and composition for permanently waving human hair suitable for use in the home in the hands of inexperienced operators, where close control of the numerous variable factors is impossible to achieve, with a minimum risk of variation in the effect produced upon the hair.

Another object is to provide a hair-waving composition which may be packaged in the form of a dry powder for sale to the consumer.

Still another object is to provide a hair-waving composition which may be employed in the form of an aqueous solution which is free from ammonia.

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

It has been discovered that alkali metal borohydrides may be employed in hair-waving compositions to attain the foregoing objects. Among the alkali metal salts which may be employed are those of potassium and sodium. Lithium borohydride which is non-ionic in character, unlike the sodium and potassium salts, is not suitable for use in the present invention inasmuch as this compound ignites spontaneously in air. Accordingly, the present invention is limited to those alkali metal borohydrides in which the alkali metal has an atomic weight above 20.

Of these alkali metal borohydrides, sodium borohydride and potassium borohydride, particularly the latter, are preferred. The borohydrides are preferably applied to the hair in the form of an aqueous solution, one of the advantages of the present invention being that a considerable variation in concentration of such an aqueous solution has relatively little effect upon the wave imparted to the hair by use of such a solution. It has been found that solutions varying in molarity from 0.5 to 1.6 may be employed to give satisfactory results, although a concentration from 0.95 to 1.25 is preferred. Solutions which are even more dilute or more concentrated than

2

these ranges may also be employed although the results become less desirable.

Aqueous alkali metal borohydride compositions within the scope of the present invention may vary in pH from about 8.5 to about 11.0 without deleterious or damaging effects on the hair and yet be effective to produce a variety of curl strengths. (By curl strength is meant tightness of the wave produced, varying from very loose to very tight.) Inasmuch as the pH of the solution has relatively little effect upon curl strength or damage within the stated range, control of pH of the solution is not of critical importance.

However, as is well known, high pH solutions (above about 11) tend to have an irritating effect upon the skin; and it is therefore usually desirable to employ solutions having a pH below this value.

The pH of an aqueous solution containing such an alkali metal borohydride varies depending upon the purity of the borohydride employed, and the length of time elapsing after the preparation of the solution. Generally speaking, an aqueous solution of commercial alkali metal borohydride above 90% in purity, when freshly prepared from solid borohydride varies considerably in pH, from about 9.7 to about 11.8. As the solution is allowed to stand, hydrogen gas is evolved as a result of gradual decomposition of the borohydride and, at the same time, the pH of the solution tends to approach a pH range of about 10.5 to 10.8.

Decomposition of aqueous alkali metal borohydride solutions is relatively slow and the rate of evolution of hydrogen is not sufficient to constitute a fire or explosion hazard. However, it is preferred that the aqueous borohydride solutions of the present invention be freshly prepared; i. e., should not be more than five or six hours old—preferably not more than three hours old—at the time they are used. In addition, it is preferable that the dry solid borohydride be stored in sealed containers prior to dissolution in the aqueous medium in order to avoid deterioration through contact with atmospheric moisture.

In order to obtain solutions having a pH below about 9.7, it has been found that special techniques are required. Merely lowering the pH by addition of an acid or of an acidic salt will lead to excessive decomposition of the borohydride and vigorous effervescence of the solution caused by liberation of hydrogen unless the agent employed for reducing the pH is carefully chosen. It has been found that very weak acids, those having a dissociation constant less than 10^{-7} , preferably from 10^{-7} to 10^{-11} , are suitable for reducing the pH of aqueous borohydride solutions without excessive decomposition. Boric acid and amino acids such as glycine, aspartic acid, arginine, asparagine, and the like have been found to be particularly suitable, being employed at concentrations ranging from 0.004 M to 0.16 M so that the molar ratio of the borohydride to the boric acid or amino acid ranges from 400:1 to 3:1.

In addition, it has been found that polyhydric alcohols having more than two hydroxyl groups, such as glycerine and particularly sorbitol or mannitol, are quite effective in reducing the pH of such borohydride solutions without excessive decomposition, probably through the formation of a borate complex. The polyhydric alcohols may be employed in the solution in concentrations ranging from 0.02 to 0.3 M, the molar ratio of borohydride to the alcohol being from 80:1 to 1.7:1. If desired, the sorbitol or mannitol may be employed either alone or in mixture with each other or in mixture with one or more of the above-mentioned weak acids. For particularly low pH values, below 9.0, a combination of boric acid with calcium chloride (the latter in a concentration from 0.02 to 0.2 M) may be employed.

Inasmuch as the borohydride solutions of the present invention have little swelling effect upon the hair, it has been found that superior results can be obtained by employing an agent capable of swelling hair, such as urea, methyl urea, or ethyl urea, together with the borohydride, the swelling agent being preferably employed in a concentration ranging from 0.5 to 3.0 M, the molar ratio between the borohydride and the swelling agent being from 3.2:1 to 0.17:1.

It has also been found that surprisingly good results can be obtained by employing a hair-waving composition containing in the aqueous medium, in addition to the alkali metal borohydride, a conventional thiol or mercaptan hair-reducing agent. Accordingly, the dry borohydride power may be added to a solution of such a conventional hair-reducing agent as a booster. Among the thiol hair-reducing agents which have been found to be most suitable for this purpose are those containing a polar acid group. Particularly preferred are thioglycolic acid and its salts, although other thiols such as cysteine hydrochloride, which contains both a carboxyl and an amine group, may also be employed. A variety of such salts may be employed, such as sodium, potassium, monoethanolamine, ethylene diamine, and other similar salts. It is preferred that ammonium salts such as ammonium thioglycolate be avoided since the presence of ammonium salts in the aqueous solution tends to accelerate decomposition of the borohydride with consequent effervescence of the solution.

Although the concentration of the thiol hair-reducing agent may vary over a considerable range, it has been found that the desired effect is particularly noticeable when the thiol concentration is in the range of 0.1 to 0.6 M, the molar ratio of borohydride to the thiol being from 16:1 to 0.8:1. The molarity is defined in terms of thiol or —SH groups present in the solution, one mole of a dithiol compound in a liter of solution being 2.0 molar with respect to the thiol groups.

The aqueous solutions of the present invention may be employed for waving hair by conventional techniques if desired. The solution may be applied to the hair, which may be either dry or damp, before or after winding upon suitable curling rods, the hair being maintained in wound or curled configuration in contact with the solution for a period of time sufficient to split the disulfide bonds or linkages of the hair keratin and to permit substantial plastic flow of the hair, which may require from 15 minutes to 90 minutes or more. Generally speaking, the drier the hair at the time of application of the lotion, the tighter the curl produced. It is usually preferable to allow the solution to remain in contact with the hair for a period of time between about 30 minutes and about 60 minutes, although one of the principal advantages of the present invention is that considerable variation in the time of hair treatment has little effect upon the resulting hair wave. Following this step, the hair may be thoroughly rinsed with water prior to full development of the wave in order to dilute the borohydride solution in situ on the hair to an extent sufficient to preclude any further substantial chemical reaction of the borohydride upon the hair; the hair is then simply exposed to atmospheric oxygen (while still wound on the curling rods) at ordinary room temperatures for a period of time sufficient to permit full development of the wave. Preferably the hair is allowed to stand in wound form exposed to atmospheric oxygen for a period of from 4 hours up to 12 hours or even longer, although times as short as 2 hours are satisfactory. Conveniently, the hair, following the rinsing step, may be allowed to dry overnight before it is unwound.

If desired, oxidation of the hair to restore the normal disulfide linkages of the hair keratin may be accelerated by the use of a conventional neutralizing agent, i. e., oxidizing agent. When a neutralizing agent is employed, it is preferable to permit the borohydride solution to act

upon the hair for a somewhat longer period of time, up to about 2 hours, than is the case when aerial oxidation is employed. However, with higher concentrations of the borohydride composition, waving times as short as about 30 to 45 minutes may also be used, when a neutralizing agent is employed. If desired, the solution of neutralizing agent may be applied to the hair immediately after rinsing or the rinsed hair may be allowed to remain in wound condition for a period of time up to about two hours after rinsing before application of the neutralizing agent. In employing a chemical neutralizer, the hair need not be rinsed prior to neutralization, but is preferably merely towel-blotted, the neutralizing solution then being applied to the wound hair, preferably in two successive separate applications. Any conventional neutralizer may be employed, such as aqueous solutions of sodium hypochlorite, hydrogen peroxide, sodium perborate, or the like, the concentrations being those commonly employed in this well-known step. Following thorough application of the neutralizer to the hair and after allowing a sufficient period of time, usually about 5 to 30 minutes, for the neutralizer to act, the hair is then thoroughly soaked with neutralizer solution to ensure complete restoration of the disulfide bonds and elimination of any residual waving agent (borohydride) at the surface of the hair.

In addition, it has been observed that satisfactory permanent waves can be obtained merely by applying the borohydride waving solution to the hair and allowing the hair to remain in wound or curled configuration in contact with the previously applied solution for relatively longer periods of time; that is, three hours or longer up to overnight, without rinsing. Upon unwinding the hair after this period of time it may be rinsed or brushed as desired.

It is contemplated that since aqueous solutions of the borohydrides are unstable as described above, the dry solid material in granular form may be supplied directly to the consumer in measured quantities sufficient to make up a predetermined volume of waving lotion. The dry solid borohydride should of course be sealed hermetically in a suitable packaging in order to prevent excessive decomposition or deterioration of the borohydride by contact with the atmosphere. The other ingredients of the waving lotion, such as boric acid or glycine, polyhydric alcohol, swelling agent and/or thiol hair-reducing agent, may be mixed with the solid borohydride prior to preparation of the solution, or the ingredients may be separately dissolved in any desired order in the aqueous medium.

In order to illustrate more clearly the nature of the present invention, but without any intention of limiting its scope, the following specific examples are given:

Example 1

The hair, after shampooing, is parted into tresses in the conventional manner; and the tresses are individually saturated with an aqueous solution of the following composition:

Potassium borohydride	1.26
Boric acid	0.016

The wet tresses are individually wound on conventional curlers, and following the completion of the winding, they are resaturated with the waving solution. The pH of this waving solution as applied to the hair is about 9.6. Thereafter the wound hair is left to process at room temperature for 90 minutes. Following the 90-minute processing time, the wound hair is towel-blotted and thoroughly saturated with a conventional aqueous sodium perborate solution (1%) as a neutralizer. After 5 minutes standing, the hair is again towel-blotted and the neutralizer is poured through the tresses. The hair is then rinsed and dried.

A commercially satisfactory wave of average tightness

5

is obtained by this procedure, the wave being substantially permanent to repeated shampooings.

In order to obtain a lower pH of approximately 8.6, there was added to the waving solution described above 0.18 M of calcium chloride. When this solution was used in the process described in Example 1, the wave obtained was substantially the same, decreasing only slightly after shampooing.

Increase of the concentration of boric acid in the solution first described to 0.064 M lowered the pH from 9.6 to 9.0, but resulted in no change in initial wave. The curl strength of tresses treated with this solution was substantially unimpaired after shampooing.

Example 2

The process described in Example 1 was carried out employing the following aqueous waving solution:

Potassium borohydride.....	M	
Glycine	1.26	
		0.013

The pH of this solution as applied to the hair was 10.0. Strong curls were produced.

Increase of the glycine concentration to 0.08 M lowered the pH to 9.1 and resulted in a commercially satisfactory wave.

Example 3

The same procedure was employed as described in Example 1 using the following aqueous waving solution:

Potassium borohydride.....	M	
Mannitol	1.0	
		0.22

The initial pH of this solution was 9.5. A satisfactory wave was obtained.

Example 4

The following aqueous waving solution was employed in the process of Example 1:

Potassium borohydride.....	M	
Mannitol	1.26	
Glycine	0.22	
		0.007

The initial pH of the solution was 9.6, and a satisfactory wave was obtained.

Example 5

An aqueous waving solution containing 1.6 M sodium borohydride pH 11.0 was employed in the process of Example 1, no other ingredients being present in the solution. The wave obtained was commercially satisfactory.

Substantially identical results were obtained employing a 1.05 M sodium borohydride solution.

Example 6

A hair-waving process was carried out as described in Example 1 using as the waving solution the following aqueous composition:

Sodium borohydride	M	
Urea	1.05	
		2.0

A wave of medium curl strength was obtained.

Example 7

The hair was waved as described in Example 1 with the following waving solution:

Potassium borohydride.....	M	
Urea	0.5	
		3.0

A soft, natural curl was obtained.

Example 8

The following aqueous waving lotion was prepared:

Potassium borohydride.....	M	
Urea	1.0	
		3.0

6

This solution was employed in the process as described in Example 1 except that the hair was allowed to process for only 30 minutes. A satisfactory permanent wave was obtained.

Example 9

The hair was treated with an aqueous solution containing 1.0 M potassium borohydride was described in Example 1. Curls of average tightness were obtained.

Example 10

The hair was treated as described in Example 1 with an aqueous solution containing 1.26 M potassium borohydride, initial pH 10.05. A medium tight wave was obtained.

Example 11

The hair was treated as described in Example 1 with the following wave solution:

Potassium borohydride.....	M	
Urea	1.26	
		1.0

A tight wave was obtained.

Example 12

The hair was treated as described in Example 1. The waving solution employed was an aqueous solution of the following ingredients:

Potassium borohydride.....	M	
Boric acid.....	0.76	
		0.016

The pH of the solution as applied to the hair was 9.6 and a commercially satisfactory wave was obtained.

Example 13

The hair was treated as described in Example 12 with the following waving solution:

Potassium borohydride.....	M	
Boric acid.....	1.5	
		0.016

The pH of the solution as applied to the hair was 9.6 and the wave obtained was very tight.

Example 14

An aqueous solution containing 0.4 M thioglycolic acid was prepared and to this was added sufficient monoethanolamine to neutralize the acid and bring the pH up to 9.6.

To this solution there was added potassium borohydride to make a 1.0 M solution. This waving solution was employed in the process described in Example 1, and a wave of medium tightness was obtained. When the potassium borohydride was omitted from the solution, the wave obtained was somewhat looser.

Example 15

An aqueous solution containing 0.4 M thioglycolic acid was prepared and to the solution was added sufficient ethylene diamine to neutralize the acid and to bring the pH up to 9.6. Potassium borohydride was then added to the solution to give a concentration of 1.0 M potassium borohydride, and the solution was employed in the process described in Example 1. The wave obtained was of medium tightness, as compared with looser waves when the borohydride was omitted from the solution.

Example 16

An aqueous solution containing 0.4 M cysteine hydrochloride was prepared and to it was added sufficient ethylene diamine to bring the pH up to 10.0. There was then added potassium borohydride to give a concentration of 1.25 M potassium borohydride, and the solution was employed in the process described in Example 1. A medium tight wave was obtained.

Example 17

To a 0.4 M aqueous thioglycolic acid solution was added sufficient sodium hydroxide to give a pH of 10.0. Sufficient sodium borohydride was then added to the solution to give a concentration of 1.05 M sodium borohydride, and the solution was employed in the process of Example 1. A loose, natural wave was obtained.

Example 18

An aqueous solution of the following composition was prepared:

Potassium borohydride	-----	1.0
Boric acid	-----	0.016

This solution was used to saturate individual hair tresses following which they were wound upon curling rods and resaturated with the same solution. The hair was covered with a turban and allowed to process for 30 minutes at a temperature of approximately 30° C. At the end of this process time, the hair was thoroughly rinsed with water, then allowed to dry on the curling rods for 18 hours at room temperature while covered with a turban. No neutralizing solution was employed. Upon unwrapping from the curling rods, the hair was found to have very tight curls.

Example 19

The following wave solution was prepared:

Potassium borohydride	-----	1.26
Boric acid	-----	0.016

This waving lotion was employed in the process of Example 18 except that the hair was allowed to remain wound on the curling rods to dry for only 6 hours after rinsing without being covered by a turban, but instead being exposed to the atmosphere. Upon unwinding, the hair was found to have a medium tight wave.

Alternatively, in the above process, the hair after rinsing was allowed to remain wound for 60 minutes, and was then treated with a solution of neutralizing agent as described in Example 1, rinsed and dried. The wave obtained was commercially satisfactory.

Example 20

The shampooed hair tress is dampened with an aqueous solution having the following composition:

Potassium borohydride	-----	0.8
Ethylenediamine thioglycolate	-----	0.3
Boric acid	-----	0.016
Mannitol	-----	0.11
Urea	-----	1.0
pH adjusted with ethylenediamine to 9.6		

The tress is then wrapped on a conventional curler, following which the wound tress is resaturated with the same composition. After processing for 60 minutes, the wound tress is towel-blotted and neutralized in the conventional manner as noted in Example 1. A commercially satisfactory wave, stable to shampooing, was obtained.

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 and modifications within the spirit and scope of the appended claims.

We claim:

1. The method of permanently waving human hair which comprises applying to the hair an aqueous solution comprising an alkali metal borohydride at a molarity of from 0.5 to 1.6 in which the alkali metal has an atomic weight above 20, and maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to permit substantial plastic flow of the hair.

2. The method of permanently waving human hair which comprises applying to the hair an aqueous solu-

tion containing sodium borohydride at a molarity from 0.5 to 1.6, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

3. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.5 to 1.6, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

4. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.5 to 1.6, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, diluting the solution in situ on the curled hair to an extent sufficient to prevent further substantial chemical action on the hair, and maintaining the hair in curled configuration in contact with the dilute solution for a period of time sufficient to permit full development of the wave and restoration of the normal disulfide linkages of the hair through aerial oxidation.

5. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.5 to 1.6, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, diluting the solution in situ on the curled hair to an extent sufficient to prevent further substantial chemical action on the hair, and maintaining the hair in curled configuration in contact with the dilute solution for a period of time sufficient to permit full development of the wave and restoration of the normal disulfide linkages of the hair through aerial oxidation.

6. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.95 to 1.25, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and applying to the hair an aqueous solution of an oxidizing agent to restore the normal disulfide linkages of the hair.

7. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.95 to 1.25, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and applying to the hair an aqueous solution of an oxidizing agent to restore the normal disulfide linkages of the hair.

8. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.5 to 1.6, and a weak acid having a dissociation constant less than 10^{-7} at a molarity from 0.004 to 0.16, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in

curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

9. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.5 to 1.6, and a member of the class consisting of boric acid and glycine at a molarity from 0.004 to 0.16, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

10. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.5 to 1.6, and a member of the class consisting of boric acid and glycine at a molarity from 0.004 to 0.16, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

11. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.5 to 1.6, and a polyhydric alcohol having more than two hydroxyl groups at a molarity from 0.02 to 0.3, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

12. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.95 to 1.25, and a member of the class consisting of sorbitol and mannitol at a molarity from 0.02 to 0.3, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

13. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.95 to 1.25, and a member of the class consisting of sorbitol and mannitol at a molarity from 0.02 to 0.3, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

14. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.5 to 1.6, and a swelling agent for hair selected from the class consisting of urea, methyl urea, and ethyl urea at a molarity from 0.5 to 3.0, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled con-

figuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

15. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.95 to 1.25, and a swelling agent for hair selected from the class consisting of urea, methyl urea, and ethyl urea at a molarity from 0.5 to 3.0, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

16. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing a member of the class consisting of sodium borohydride and potassium borohydride at a molarity from 0.5 to 1.6, and a thiol hair reducing agent at a molarity of 0.1 to 0.6, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

17. The method as defined in claim 16 wherein the thiol hair reducing agent is a salt of thioglycolic acid and the pH of the solution, prior to application of the solution to the hair, has a value from 8.5 to 11.0.

18. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.95 to 1.25, and a thiol hair reducing agent at a molarity of 0.1 to 0.6, maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

19. The method of permanently waving human hair which comprises applying to the hair an aqueous solution containing potassium borohydride at a molarity from 0.95 to 1.25, a member of the class consisting of boric acid and glycine at a molarity from 0.004 to 0.16, a member of the class consisting of sorbitol and mannitol at a molarity from 0.02 to 0.3, a swelling agent for hair selected from the class consisting of urea, methyl urea, and ethyl urea at a molarity from 0.5 to 3.0, and a thiol hair reducing agent at a molarity of 0.1 to 0.6, said solution having a pH value, prior to application of the solution to the hair, from 8.5 to 11.0, and maintaining the hair in curled configuration in contact with said solution for a period of time sufficient to split the disulfide linkages of the hair keratin and permit substantial plastic flow of the hair, and subjecting the hair in curled configuration to the action of an oxidizing agent to restore the disulfide bonds of the hair keratin.

20. A composition comprising an alkali metal borohydride in which the alkali metal has an atomic weight above 20, and a weak acid having a dissociation constant less than 10^{-7} , the molar ratio of the borohydride to the acid being from about 400:1 to 3:1.

21. A composition comprising a borohydride selected from the class consisting of sodium borohydride and potassium borohydride, and a member of the class consisting of boric acid and glycine, the molar ratio of the borohydride to the acid being from about 400:1 to 3:1.

22. A composition comprising potassium borohydride and a member of the class consisting of boric acid and glycine, the molar ratio of the borohydride to the acid being from about 400:1 to 3:1.

23. A composition comprising a member of the class consisting of sodium borohydride and potassium borohydride and a polyhydric alcohol having more than two

hydroxyl groups, the molar ratio of the borohydride to the alcohol being from 80:1 to 1.7:1.

24. A composition comprising a member of the class consisting of sodium borohydride and potassium borohydride and an alcohol selected from the class consisting of sorbitol and mannitol, the molar ratio of the borohydride to the alcohol being from 80:1 to 1.7:1. 5

25. A composition comprising potassium borohydride and an alcohol selected from the class consisting of sorbitol and mannitol, the molar ratio of the borohydride to the alcohol being from 80:1 to 1.7:1. 10

26. A composition comprising a member of the class consisting of sodium borohydride and potassium borohydride and a swelling agent for hair selected from the class consisting of urea, methyl urea, and ethyl urea, the molar ratio of the borohydride to the swelling agent being from 3.2:1 to 0.17:1. 15

27. A composition comprising potassium borohydride and a swelling agent for hair selected from the class consisting of urea, methyl urea, and ethyl urea, the molar ratio of the borohydride to the swelling agent being from 3.2:1 to 0.17:1. 20

28. A composition comprising a member of the class consisting of sodium borohydride and potassium borohydride and a thiol hair reducing agent, the molar ratio of borohydride to thiol being from 16:1 to 0.8:1. 25

29. A composition comprising potassium borohydride and a thiol hair reducing agent, the molar ratio of borohydride to thiol being from 16:1 to 0.8:1.

30. A composition comprising potassium borohydride, a member of the class consisting of boric acid and glycine, 30

the molar ratio of the borohydride to the acid being from about 400:1 to 3:1, an alcohol selected from the class consisting of sorbitol and mannitol, the molar ratio of the borohydride to the alcohol being from 80:1 to 1.7:1, a swelling agent for hair selected from the class consisting of urea, methyl urea, and ethyl urea, the molar ratio of the borohydride to the swelling agent being from 3.2:1 to 0.17:1, and a thiol hair reducing agent, the molar ratio of borohydride to thiol being from 16:1 to 0.8:1.

References Cited in the file of this patent

FOREIGN PATENTS

107,057 Australia _____ Mar. 28, 1939

OTHER REFERENCES

"A Study of Keratin" by Michaelis, in the "Journal of the American Leather Chemist's Assn." for November 1935, pages 557—558—560—561—562. (Copy in Div. 43).

Mellor: "Modern Inorganic Chemistry" (Longmans, Green & Co., New York, N. Y.), 1939, pg. 658, "Compounds of Boron, Boron Hydrides."

Ephraim: "Inorganic Chemistry" (Nordeman, New York, N. Y.), 1943, pp. 763—774.

Krajceman: "Reduction of Organic Compounds With Lithium Aluminium Hydride." *Manuf. Chem.*, April 1951, pp. 147—152 and 156.

Bulletin 502A, "Sodium Borohydride," Metal Hydrides Inc., 12—24 Congress Street, Beverly, Mass. 2 pages.