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PERMANENT HAIR WAVING

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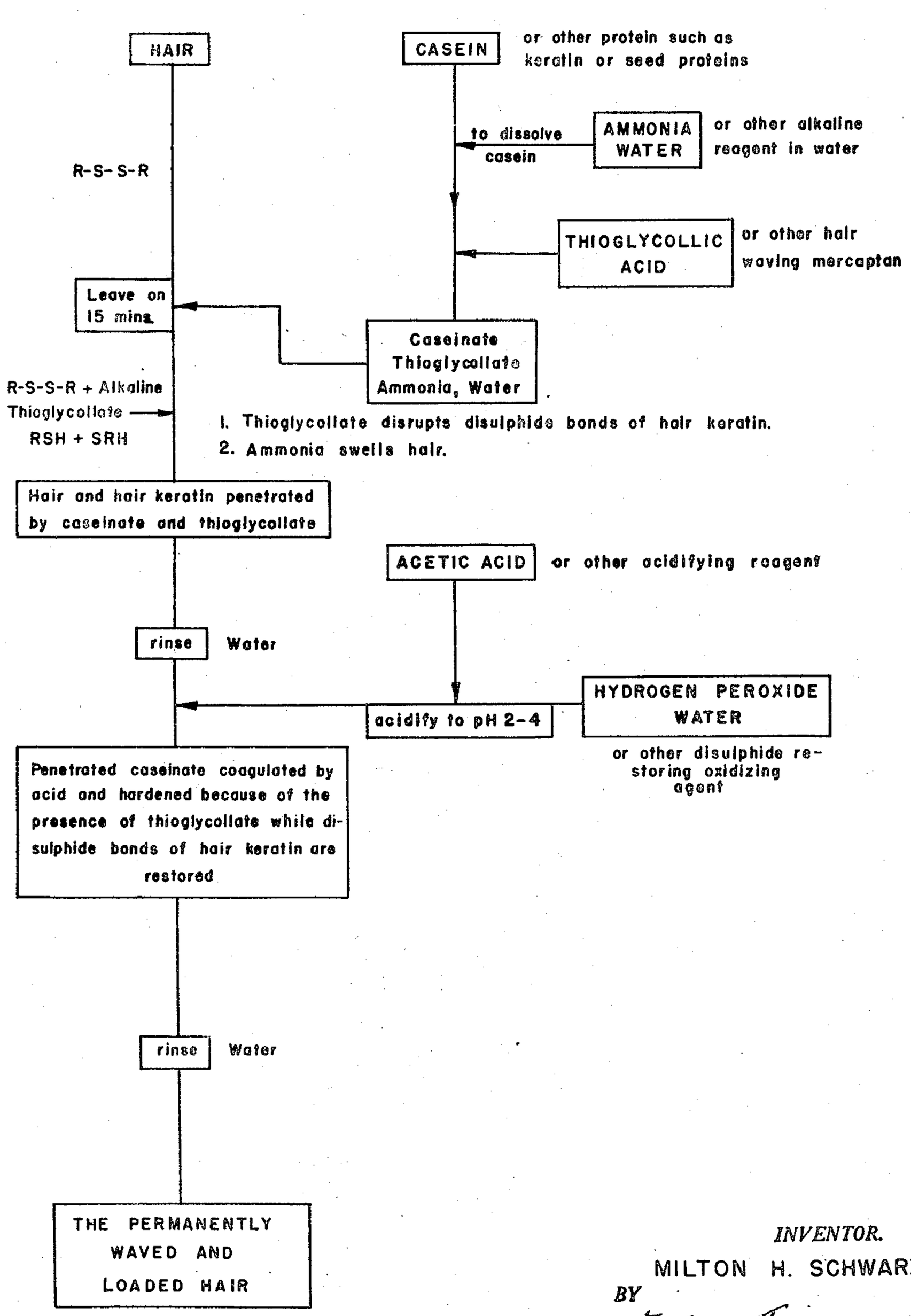

INVENTOR.

MILTON H. SCHWARZ

BY

Elyon Burkhart

ATTORNEY

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PERMANENT HAIR WAVING

Milton H. Schwarz, Stamford, Conn.

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This invention relates to the permanent waving of hair on the human head. In its preferred embodiment my invention pertains to "cold" permanent waving, that is to say, to permanent waving without an external source of heat. More particularly my invention is concerned with cold permanent waving wherein a mercaptan is employed as an agent for relaxing the hair. A mercaptan is an organic compound containing an SH group attached to a carbon atom.

The mercaptan process of cold permanent hair waving presently is well known. It consists in treating a tress of hair, before or after shaping the same in a desired form, e. g. by winding, with an alkaline aqueous solution of a mercaptan. This has the effect of reducing, i. e. breaking, the disulphide bonds in the keratin of the hair with consequent softening or relaxing of the hair. A suitable period of time conventionally is allowed to enable this action to bring the hair to a desired degree of plasticity. Thereafter, the hair is treated with a solution of an oxidizing agent which will substantially restore the disulphide bonds and elasticity of the hair, leaving the hair however in the altered shape in which it has been arranged.

Any mercaptan will react with the keratin of the hair to effect reduction of the disulphide bonds into SH groups. Nevertheless, it is well known in the art that certain of the mercaptans e. g. the substituted mercaptans (a mercaptan containing a group in addition to the SH group) are more desirable to employ for this purpose. For example, some of the simple mercaptans are odorous and/or toxic.

Pursuant to my invention, I contemplate the use of any mercaptan which is suitable for hair waving and which will be referred to hereinafter as a "hair waving mercaptan." By way of example and without limiting my invention thereto, the following are hair waving mercaptans: mercaptans with carboxylic groups—e. g., thiolactic acid, thiocitric acid, mercapto acetic acid (thioglycollic acid); mercaptans containing amino groups—e. g., B-amino ethyl mercaptan and B-mercapto ethylmethylamine; mercapto carbinols—e. g., B-mercapto ethanol, mercapto acetaldehyde, mercapto dimethylketone and homologues, such as cyclic, benzenoid and other derivatives of these compounds; monomercapto monohydric substituted compounds—e. g., thioglycerol; polymercapto monohydric substituted compounds—e. g., trithiohexitol; and polymercapto polyhydric substituted compounds—e. g., tetraglycoldimercaptan. The alkaline salts of all of these compounds also can be employed. Of these I have found thioglycollic acid, thiolactic acid, thioglycerol, B-mercapto ethanol and their alkaline salts to be the most satisfactory. It will be understood that when the mercaptan is acidic

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and in alkaline solution it reacts to an alkaline salt of the mercaptan provided in the solution.

An aqueous mercaptan reducing solution conventionally has a basic pH and usually is brought to this condition by the addition of a sufficient quantity of a soluble alkaline compound having a pH greater than 7. Such a compound will hereinafter be referred to as an "alkaline reagent." Examples of alkaline reagents follow, it being understood that the same are in no way limitative: water soluble alkali metal hydroxides and alkaline salts of such metals—e. g., hydroxides, carbonates, borates, phosphates, citrates and tartrates of sodium and potassium; ammonium hydroxide and derivaties—e. g. ammonium hydroxide, amines, such as ethylamine and methylamine, alkylolamines, such as mono-, di-, and tri-ethanolamine, substituted alkylolamines, such as diethyl- and phenyl ethanolamines, and quarternary bases obtained by substituting one or more of the hydrogens of ammonium hydroxide, such as tetramethylammonium hydroxide. Of these I have found ammonium hydroxide, triethanolamine, borax, sodium carbonate and sodium hydroxide to be highly satisfactory.

It also is presently understood that it is desirable to control the reducing solution so that the pH of the same ranges between certain optimum values and so that the hair waving mercaptan and alkaline reagent are present within certain optimum proportions. Thus, it is considered that the preferred pH range is from 7.0 to 10.0 with excellent results being secured at 9.2. An effective concentration of the hair waving mercaptan usually is not greater than 15% by weight. The concentration of the alkaline reagent is so selected as to neutralize any acidity of the mercaptan and to obtain the requisite pH. Also it is possible to employ hair waving mercaptans of a basic nature, for instance mercapto-ethylamine to act both as the hair waving mercaptan and the alkaline reagent.

Oxidizing agents in the setting solution which restore the disulphide bond may be of any known and conventional type and are used in aqueous solution. Essentially, these consist of typical oxidizing compounds which are characterized by their non-harmful effect when applied to hair on the human head, their non-toxicity and their absence of explosive or fire-hazardous qualities when dry. Exemplificative but not limitative of such oxidizing agents are the following: salts of oxidizing acids—e. g., bromates and iodates of sodium and potassium; hydrogen peroxide and its salts—e. g., ammonium sulfate peroxide, urea peroxide and pyrophosphate peroxides, carbonate peroxides and perborates of sodium and potassium; metal substitutes for hydrogen peroxide which, when dissolved, will give active oxygen in

aqueous solution—e. g., calcium, magnesium and zinc peroxides; salts of persulfuric acid—e. g., ammonium, sodium and potassium persulfates; organic peroxides and substituted peroxides—e. g., acetyl peroxide, benzoyl peroxide and perbenzoic acid. I have found that hydrogen peroxide, sodium perborate, sodium persulfate, urea peroxide, potassium bromate and potassium iodate give excellent results.

It is the principal object of my invention to improve the foregoing method of permanently cold waving of hair by providing a solution which increases the luster, body, strength and texture of the hair and the permanency of the wave.

Other objects of my invention in part will be obvious and in part will be pointed out hereinafter.

In general, my invention comprises the provision of a cold waving solution which enables a deposit of a protein to be made within the hair concomitantly with permanent cold waving thereof by the mercaptan process. More particularly, the protein is one which is soluble in an alkaline solution and will precipitate in an acid solution. Typical of such proteins are those in the class consisting of keratin, casein and seed proteins, such as soybean protein, linseed protein, cotton seed protein, corn protein and peanut protein.

I have found that the deposit of such proteins within the hair lends itself particularly well to performance in conjunction with the mercaptan cold waving process hereinabove described.

Essentially, I deposit a protein of the type specified by treating the hair with an alkaline solution within which there are dissolved both the protein and a hardening agent. The hair at the time of such treatment should not only be swelled but it should be in a chemically reduced state, that is to say, the disulphide bonds must be changed to SH groups, inasmuch as this permits the protein to penetrate within the hair structure due to the swelling of the hair and within the structure of the keratin itself due to the rupture of the disulphide bonds. After the proteinaceous solution has penetrated the hair, the protein is coagulated from the penetrated solution, being deposited in the process within the hair structure. The thus deposited protein is hardened during coagulation and thereby acts as a resinous solid which increases the body, luster, strength and texture of the hair and the permanence of the wave.

The protein employed is placed in solution by dissolving the same in an aqueous alkaline solvent so that this solvent serves the joint functions of enabling the protein to enter solution and of swelling the hair. I have discovered that the very alkaline solution which normally is used as the waving, i. e. reducing, solution in the mercaptan cold waving of hair will suffice to dissolve the protein. Hence, it is not necessary to prepare a special alkaline solution. In other words, the proteinaceous solution constitutes at least one protein from the class mentioned and an aqueous solution of at least one of the alkaline reagents hereinabove described, an alternative being a solution to which the proper pH has been imparted by use of a basic mercaptan. The term "dissolved," as used herein in connection with protein, denotes that the protein has reacted in solution with the alkaline reagent to form the more soluble alkaline salt of the protein.

I also have discovered that all mercaptans, and, therefore, all hair waving mercaptans will serve as hardening agents for a coagulated protein of the class mentioned. When these mercaptans are present an effect on the proteins is produced similar, for example, to that of an aldehyde; hence it is not necessary to employ any additional hardening agent. Moreover, as noted earlier, the presence of the hair waving mercaptan in the waving, i. e. softening, solution causes the disulphide bond of the keratin to be separated and thus permits an intimate penetration of the keratin molecule by the proteinaceous solution. Accordingly, pursuant to my invention, the hair first is treated with an aqueous solution containing at least one protein of the class mentioned, at least one hair waving mercaptan and at least one alkaline reagent, the latter being optional only if the mercaptan is sufficiently basic. It will be appreciated by those skilled in the art that, if desired, solubilizing agents may be employed to induce solution of any one of these three substances, if the same are not readily soluble to the extent required. Examples of suitable solubilizing agents are: wetting agents—e. g., alkyl aryl sulphonates such as triethanolamine lauryl sulfate and organic solvents—e. g., alcohols such as ethanol and isopropanol, ketones such as acetone and methylisobutyl ketone, benzenoids such as benzene and xylol and glycols such as propylene glycol and ethylene glycol. A small quantity only of wetting agents, e. g. ½% by weight, should be used—just enough for solubilizing purposes, or they will tend to wash the hair.

The amount of mercaptan and of the alkaline reagent and the type of mercaptan and alkaline reagent used are controlled wholly by the known requirements of cold hair waving, that is to say, these two constituents either as to amount or kind are not affected insofar as the presence of the protein or its subsequent deposit are concerned. The amount of the protein present in solution can vary within wide limits. I have found that when from 1 to 5% by weight of protein is present, good results are secured; the best results being obtained when about 1½% by weight of protein is employed. However, noticeable effects are obtained when even less protein is used, down as low for example as $\frac{1}{10}$ of 1% by weight. Moreover, amounts of protein greater than 5% by weight can be present. In the latter case, however, there is simply a waste of protein, as I have observed that increasing the amount of protein present to greater than 5% by weight does not appreciably affect the amount of protein deposited within the hair; that is to say that about 5% by weight of protein present in the waving solution enables me to obtain substantially the maximum deposit of protein within the hair. The presence of additional protein in the solution does not markedly increase the deposit of protein within the hair. Moreover, where amounts of protein greater than 5% by weight are used in the waving solution, there is a tendency for some of the protein to deposit as a slime on the external surface of the individual hair strands. Although this does not harm the hair and can easily be rinsed or washed off, it is a wasteful use of the protein.

It also is to be noted that as the amount of protein is raised the first waving solution increases in viscosity and as larger amounts of protein are present, for instance in the neighborhood of 25% by weight, the solution becomes too viscous for conventional use in the manner of an ordinary softening solution in a mercaptan cold hair waving process.

I have observed that the amount of protein deposited increases with the time of treatment by the waving solution and have noted that the rate of increase of deposit appears to approximate the rate of dissociation of the disulphide bond. Furthermore, I have observed that the maximum deposit of protein appears to occur at about the same time that the hair is properly relaxed for waving; in other words, when the dissociation of the disulphide bond has taken place to the extent which is considered proper for mercaptan cold hair waving.

It may be mentioned here that where a 1½% by weight protein solution is used, a deposit of protein in the hair equal to about 15% by weight of the hair is obtained if the waving solution is permitted to stay on long enough for proper mercaptan cold hair waving, for instance from 5 to 15 minutes, depending on the nature of the hair to be waved and the nature of the hair waving constituents of said solution. An increase of the protein content to 5% by weight in solution results in a deposit of approximately 20% by weight of protein in the hair.

The setting or neutralizing solution includes at least one of the usual disulphide-restoring oxidizing agents of a type and in an amount conventionally employed. The presence of this agent has no effect on the coagulation of the protein.

In addition, the setting solution includes at least one acidifying reagent, i. e., a reagent which causes the setting solution to have an acidic pH. It is within the scope of my invention to obtain an acidic pH by using an acidic oxidizing agent such for instance as potassium bromate or potassium iodate. However, I obtain maximum deposit of protein when the pH of the setting solution is below the isoelectric point of the particular protein employed. In the even that the protein is casein, which is the preferred protein used in accordance with my invention, the isoelectric point is from 4.1 to 4.6 depending upon the method used to prepare the casein which is employed.

The acid to be used in the setting solution must not be irritating nor toxic in the quantities used. It must not disaffect the wave action, which has been accomplished by the mercaptan solution. It is recommended that the quantity of acid used in the setting solution be limited to a quantity required to establish a pH range in the solution of from 2 to 4. At this point, there is maximum deposit of the protein within the hair. A lower pH value may cause irritation on the scalp and may influence the waving results and hair condition. If the pH of the solution is above 4, the pH is within the isoelectric range of most proteins and results in the precipitation of a lesser quantity of protein. As the pH of the setting solution is increased from the range of isoelectric points to pH 7 the deposit of protein becomes much smaller. When the pH is above 7, there is no deposit whatsoever. The following are suitable acidifying reagents, it being understood that the same are in no wise limitative: organic acids, mono- or poly-carboxylic—e. g., malonic, succinic, maleic, acetic, propionic, butyric, and crotonic; organic acids with hydroxy groups—e. g., lactic, citric, tartaric, malic, and glycollic; inorganic acids—e. g., sulfuric, hydrochloric and phosphoric; acid salts—e. g., potassium or sodium, acid tartrate, citrate, or phthallate. The preferred acidifying reagents are citric, tartaric, sulfuric, phosphoric and acetic acids.

The presence of the mercaptan which has permeated the hair together with the protein in the proteinaceous solution causes the coagulated protein to harden as it is precipitated, thus enhancing its resinous nature and causing the protein itself to deposit as a resin in the general shape of a filament having the contour of and coextensive with each hair strand. This functions to enhance the permanency of the wave.

I believe that under the conditions present, at least some of the protein molecules link with the cysteine molecules, thus increasing the molecular weight and strength of the subsequent keratin molecule obtained upon oxidation by the setting solution.

It now will be appreciated that in the waving solution, the alkaline reagent serves a triple function, to wit: (1) it provides a pH of the proper value to enable the hair waving mercaptan to rupture the disulphide bond of the keratin molecule; (2) it swells the hair structure (while ordinarily this is not desirable because of its tendency toward roughening the hair, pursuant to the present invention, this function has advantages and any unfavorable effects are mitigated by the deposit of the hardened protein within the hair, so that not only is the hair not rendered harsh, but its softness and sheen actually are improved); and (3) it provides a pH of such value as to enable the protein to go into solution and thereby penetrate the hair structure when the latter swells.

The hair waving mercaptan operates to achieve four different effects, to wit: 1, it acts in a conventional manner to break the disulphides of the keratin molecule into SH groups of the cysteine molecules; 2, it serves by its presence as an intimately dispersed hardening agent for the subsequently deposited protein; 3, it enables the protein to penetrate the molecular structure of the keratin molecule itself; 4, it is believed that because of the rupture of the disulphide links into SH groups, some casein molecules bond with the keratin molecules when the latter are restored by oxidization upon treatment of the hair with the setting solution.

I have given below specific examples of various waving and setting solutions which may be used satisfactorily in practicing my invention:

WAVING SOLUTIONS

I

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Casein	15 gr.	
Thioglycollic acid	64 gr.	

In this and all following examples the protein is dissolved in the alkaline reagent and water prior to the addition of the mercaptan although this may be reversed, i. e. the mercaptan and alkaline dissolved before the protein. After the solution has been prepared, a final adjustment is made for desired pH by small additional corrections of the mercaptan and alkaline reagent.

II

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Soya bean protein	15 gr.	
Thioglycollic acid	64 gr.	

III

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Casein	15 gr.	
Thioglycerine	90 gr.	

IV

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Soya bean protein	15 gr.	
Thioglycerine	90 gr.	

V

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Soya bean protein	15 gr.	
Thiolactic acid	90 gr.	

VI

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Casein	15 gr.	
Thiolactic acid	90 gr.	

VII

Thioglycollic acid	60 gr.	pH 9.2
Sodium hydroxide (cp. pellets)	28 gr.	
Casein	14 gr.	
Water	840 gr.	

VIII

Plural alkaline reagents

Casein	15 gr.	pH 9.3
Thioglycollic acid	60 gr.	
Tetraethanolamine	25 gr.	
Ammonia water (26–28%)	85 gr.	
Water	730 gr.	

IX

High casein content

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Casein	50 gr.	
Thioglycollic acid	64 gr.	

X

Plural proteins

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Casein	7.5 gr.	
Soya bean protein	7.5 gr.	
Thioglycollic acid	64 gr.	

XI

Plural hair waving mercaptans

Ammonia water (26–28%)	90 gr.	pH 9.3
Water	800 gr.	
Soya bean protein	15 gr.	
Thioglycollic acid	32 gr.	
Thioglycerine	45 gr.	

SETTING SOLUTIONS

I

Hydrogen peroxide (100 vol.)	10 ml.	pH 2
Citric acid anhydrous	4 gr.	
Water	q. s.–pt.	

II

Potassium bromate	32 gr.	pH 2
Tartaric acid	13 gr.	
Water	q. s.–pt.	

III

Urea peroxide	21 gr.	pH 2
Hydrochloric acid (conc.)	2¼ ml.	
Water	q. s.–pt.	

IV

Sodium perborate (monohydrate)	10 gr.	pH 3
Acetic acid (glacial)	25 ml.	
Water	q. s.–pt.	

V

Sodium perborate (monohydrate)	10 gr	pH 4
Hydrochloric acid (conc.)	6.0 ml.	
Water	q. s.–pt.	

VI

Sodium perborate (monohydrate)	10 gr.	pH 2
Sulfuric acid (conc.)	1.5 ml.	
Water	q. s.–pt.	

VII

Multiple acidifying reagents

Hydrogen peroxide (20 vol.)	60 ml.	pH 3
Citric acid anhydrous	2 gr.	
Tartaric acid	2 gr.	
Water	q. s.–pt.	

If desired, a buffering salt can be employed to stabilize the pH. An example of a solution containing such a salt follows:

VIII

Hydrogen peroxide (20 vol.)	60 ml.	pH 3
Sodium acetate	4 gr.	
Acetic acid (glacial)	2 gr.	
Water	q. s.–pt.	

It will be noted that according to the concentration state of the compositions employed, the pH may vary slightly and can be adjusted.

It also is to be observed that the usual rinses, e. g. water rinses, may be practiced after treatment of the hair with the waving and setting solutions. Rinsing in a conventional manner after treatment with the softening solution does not appear to noticeably reduce the amounts of protein and mercaptan which penetrated the hair strands during treatment with this solution. Precipitation of like amounts of similarly hardened protein occur within the hair both when rinsing is not practiced and when a simple rinsing is performed before application of the setting solution.

When rewaving hair previously waved in accordance with my invention no noticeable change in protein content takes place. This is particularly useful in matching a newly waved portion of a hair tress to a previously waved portion.

The term "shaping" as used herein denotes mechanically changing the contour of the hair so as to give it a wave shape or straighten the same.

The flow sheet is derived from specific examples set forth above in the specification as well as the generic teachings thereof and is not to be considered as a limitation upon the invention any more than are the specific examples.

It thus will be seen that I have provided a permanent waving solution and a method which achieve the several objects of my invention and are well adapted to meet the conditions of practical use.

As various possible embodiments might be made of the above invention and as various changes might be made in the embodiments above set forth, it is to be understood that all matter herein described is to be interpreted as illustrative and not in a limiting sense.

Having thus described my invention, I claim as new and desire to secure by Letters Patent:

1. In combination in compositions for permanently cold waving hair on the human head, a first aqueous solution including an alkaline reagent for swelling hair, a hair waving organic mercaptan for disrupting the disulphide bonds of the hair keratin and penetrating the swelled hair and disrupted keratin thereof, and a protein which is soluble in an alkaline solution and precipitates in an acid solution, said protein being dissolved in said first solution so as to penetrate the swelled hair and disrupted keratin; and a second subsequently applicable aqueous solution including an oxidizing agent for substantially restoring the disulphide bonds of the hair keratin and an acidifying reagent other than the oxidizing agent for imparting to the second solution a pH below the isoelectric point of the protein so as to precipitate the penetrant protein which simultaneously is hardened because of the presence of the penetrant organic mercaptan.

2. In combination in compositions for permanently waving hair on the human head wherein disrupted keratinous disulphide bonds resulting from the initial application of a waving solution subsequently are restored by treatment with a second solution including an oxidizing agent: a first composition including an alkaline reagent for swelling hair, a hair waving organic mercaptan for disrupting the disulphide bonds of the hair keratin and penetrating the swelled hair and disrupted keratin thereof, and a protein which is soluble in an alkaline solution and precipitates in an acid solution, said protein being dissolved so as to penetrate the swelled hair and

disrupted keratin; and a second composition for subsequent application to the hair in the solution including the oxidizing agent, said second composition including an acidifying reagent other than the oxidizing agent, for imparting to the solution a pH below the isoelectric point of the protein, so as to precipitate the penetrant protein which simultaneously is hardened because of the presence of the penetrant organic mercaptan.

3. A method of permanently cold waving hair on the human head, said method comprising swelling the hair with an aqueous waving solution containing an alkaline reagent, at the same time disrupting the disulphide bonds of the hair keratin with a hair waving organic mercaptan in said solution and penetrating the swelled hair and disrupted keratin thereof with said mercaptan and with a protein dissolved in said alkaline solution, shaping the hair, and then substantially restoring the disulphide bonds of the hair keratin with an aqueous setting solution containing an oxidizing agent while simultaneously precipitating the dissolved penetrant protein with an acidifying reagent other than the oxidizing agent in said setting solution which reagent imparts thereto a pH below the isoelectric point of the protein and hardening the precipitated protein because of the presence of the penetrant organic mercaptan.

4. A method of permanently cold waving hair on the human head, said method comprising swelling the hair with an aqueous waving solution containing an alkaline reagent, at the same time disrupting the disulphide bonds of the hair keratin with a hair waving organic mercaptan in said solution and penetrating the swelled hair and disrupted keratin thereof with said mercaptan and with casein dissolved in said alkaline solution, shaping the hear, and then substantially restoring the disulphide bonds of the hair keratin with an aqueous setting solution containing an oxidizing agent while simultaneously precipitating the dissolved penetrant casein with an acidifying reagent other than the oxidizing agent in said setting solution which reagent imparts thereto a pH below the isoelectric point of the casein and hardening the precipitated casein because of the presence of the penetrant organic mercaptan.

5. A method of permanently cold waving hair on the human head, said method comprising swelling the hair with an aqueous waving solution containing an alkaline reagent, at the same time disrupting the disulphide bonds of the hair keratin with a hair waving organic mercaptan in said solution and penetrating the swelled hair and disrupted keratin thereof with said mercaptan and with a protein dissolved in said alkaline solution up to 5% by weight of said solution, shaping the hair, and then substantially restoring the disulphide bonds of the hair keratin with an aqueous setting solution containing an oxidizing agent while simultaneously precipitating the dissolved penetrant protein with an acidifying reagent other than the oxidizing agent in said setting solution which reagent imparts thereto a pH below the isoelectric point of the protein and hardening the precipitated protein because of the presence of the penetrant organic mercaptan.

6. In a method of permanently cold waving hair on the human head, in which method the hair is shaped and treated with a waving solution containing an alkaline reagent which swells the hair and a hair waving organic mercaptan which disrupts the disulphide bonds of the hair keratin and penetrates the swelled hair and disrupted keratin thereof, and in which method the hair thereafter is treated with a setting solution containing an oxidizing agent for substantially restoring the disulphide bonds of the hair keratin: that improvement including the steps of penetrating the swelled hair and disrupted keratin with a protein dissolved in the alkaline waving solution, precipitating the dissolved penetrant protein with an acidifying reagent other than the oxidizing agent in the setting solution which reagent imparts thereto a pH below the isoelectric point of the protein and hardening the precipitated protein because of the presence of the penetrant organic mercaptan.

7. In a method of permanently cold waving hair on the human head, in which method the hair is shaped and treated with a waving solution containing an alkaline reagent which swells the hair, a hair waving organic mercaptan which disrupts the disulphide bonds of the hair keratin and a dissolved protein which with the mercaptan penetrates the swelled hair and disrupted keratin thereof and in which method the hair thereafter is treated with a setting solution containing an oxidizing agent for substantially restoring the disulphide bonds of the hair keratin: that improvement including the steps of precipitating the dissolved penetrant protein with an acidifying reagent other than the oxidizing agent in the setting solution which reagent imparts thereto a pH below the isoelectric point of the protein and hardening the precipitated protein because of the presence of the penetrant organic mercaptan.

MILTON H. SCHWARZ.

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