United States Patent Office

3,025,218

Patented Mar. 13, 1962

1

3,025,218
PERMANENT WAVING OF HAIR ON THE HUMAN HEAD

Robert J. Strain, Stratford, and Philip Tusa, Trumbull, Conn., assignors to Turner Hall Corporation, New York, N.Y., a corporation of New York

No Drawing. Filed Nov. 6, 1958, Ser. No. 772,189
1 Claim. (Cl. 167—87.1)

This invention relates to permanent waving of hair on the human head and, more particularly, to new and improved compositions and processes for the same.

Basically, cold permanent waving of hair on the human head involves softening the hair to render it non-resilient whereby its original shape can be permanently altered, altering the configuration of the hair, as by placing it in waved configuration either before, during or after softening thereof, and then hardening the hair and restoring its resiliency while it is in the new and desired configuration.

Conventionally, in cold permanent waving the hair is softened by application of a waving solution which includes a chemical reducing agent. The reducing agent employed almost universally in cold waving solutions for human hair is the mercaptan thioglycollic acid which is used in the form of its ammonium salt, ammonium thioglycollate. Other mercaptans can be used, however, as can certain members of the class of compounds known as sulfites.

It is generally accepted theory in the hair waving field that the reducing agent softens the hair by breaking the disulfide bonds of the hair keratin which is the basic constituent of the hair. The subsequently applied setting agent functions to rebuild a good portion of the broken disulfide bonds, and conventionally solutions of hydrogen peroxide or alkali perborates or bromates are employed for this purpose.

Keratin is a protein composed of a number of amino acids including cystine, and it is the cystine which includes the disulfide bonds referred to above, the reduced form of this substance being known as cysteine.

The keratin of the hair is surrounded by a thin sheath which is only slightly permeable to water. In order for the reducing agent to effectively act on the keratin, the sheath must be rendered quite penetrable, i.e. broken down and made porous so that the keratin is substantially exposed to the reducing agent. Ordinarily, when hair is wet, even with plain water, it swells slightly; however, when the sheath has been broken down, the degree and rapidity of swelling are much greater, and it has become customary in the hair waving field to define the extent to which the hair keratin is susceptible to attack by the reducing agent in terms of the degree of swelling of the hair instead of in terms of porosity, although as already mentioned swelling is a result of penetration of liquid after the sheath is rendered porous.

The more the sheath has been broken down and the greater its porosity, the more rapidly the hair swells and therefore the more rapidly the reducing agent can soften the hair keratin. As a result, the rate of swelling is conventionally considered to be a good indicator of the rate of softening.

To render the hair sheath penetrable, the waving solution must include an agent which will attack the same, and conventionally this agent is a base, ammonium hydroxide being the preferred one.

As is apparent from the foregoing, the waving solution performs the dual functions of rendering the hair sheath penetrable and attacking the hair keratin. These two functions take place simultaneously and at an accelerating rate since more keratin is exposed as time elapses and

2

the sheath is rendered more porous. The hair swells at an accelerating rate also.

It wil be understood hereinafter herein that the terms "waving agent," "waving solution," "softening agent" and "softening solution" refer to compositions performing the above-mentioned dual functions.

The rapidity with which the reducing solution acts is, as will be pointed out in greater detail hereinafter, very important and is dependent on the strength of the waving agent and the hair on which said agent is used. The word "strength" as used herein with respect to the waving solution means the effectiveness of said solution in softening the hair within commercial time limitations to be discussed hereinafter. This is directly related both to the swelling power of the solution, i.e. its capacity to render the hair sheath porous since this controls the availability of the keratin for reduction, and to the concentration of mercaptan since that affects the inherent capacity of the waving solution to reduce the keratin. Generally, the higher the concentration and/or alkalinity the stronger the solution, but equal strengths can be obtained by lowering the concentration while the pH is raised and vice versa. Thus, the strength of a conventional ammonium thioglycollate solution is controlled by its pH and its concentration.

The rapidity with which the hair sheath is attacked and the extent to which it is rendered porous increases with increase in alkalinity of the waving solution and the time in which the latter is in contact with it, and vice versa. And in the nomenclature of the hair waving art, the rapidity of swelling of the hair and the degree of swelling thereof depend on the alkalinity of the solution, increasing with alkalinity and vice versa. The measure of alkalinity is pH, and it is necessary for the pH to be well on the alkaline side for the waving solution to function within the commercial time limits, i.e. be capable of swelling hair rapidly enough and sufficiently for the keratin to be attacked to the the extent necessary for enough softening for the purposes of permanent waving to occur within said time limits. The solution should not be too alkaline, however, because this could cause destruction of the hair.

All hair does not respond similarly to cold waving solutions. Thus, for example, bleached, dyed and previously waved hair are much more easily softened than normal hair because the aforementioned sheath has already been completely or to some extent destroyed. Such hair is referred to as weak or damaged or porous hair. Generally, hair which has not been previously chemically treated in any way or sunbleached, and which is otherwise in good condition and is of ordinary texture is considered to be normal hair and is rather difficult to soften. So-called resistant hair, on the other hand, is harder to soften than normal hair, because the sheath is more difficult to penetrate.

The use of too strong a waving solution for a particular head of hair can result, as will be explained hereinafter, in the hair being seriously degraded. What this means is that much of the hair keratin is destroyed beyond the ability of setting agents to restore it substantially to its original condition. Such hair is very porous and brittle and not only is the permanent wave unsuccessful because the hair will not retain its shape but in some cases the hair is completely ruined. When hair is degraded beyond a minor amount of degradation inherent in cold permanent waving because the setting agents cannot return it to its exact original condition, the hair is said to be overprocessed.

Use of too weak a waving solution, on the other hand, can cause the hair to be underprocessed, i.e. not softened enough, and when this occurs the hair does not take a

good wave in the commercially acceptable time; such waves are unsatisfactory in appearance and longevity.

It is to be understood that the matter of overprocessing and underprocessing and strength of waving solution are intimately related to the time for which the waving solution is allowed to remain in contact with the hair before its action is stopped by removal of it or neutralization of it by a setting agent or the oxygen of the air (which can, itself, act as a setting agent). In other words, a strong solution will not damage weak hair if the solution is used for a short enough time if this is practical, and a weak solution will sufficiently soften resistant hair if it is allowed to remain in contact therewith for a long enough period if this is practical. Since the question of practicality as to time is of fundamental importance, the strength of the solution in relation to the particular hair on which it is to be used is of great importance.

The time for which the softening solution is allowed to remain in contact with the hair varies somewhat in the hair waving field, but certain definite commercially necessary limitations have come to be accepted outside of which the softening solution cannot be used and commercial requirements still be met. In the hair waving process as conventionally practiced, the hair is first saturated with the waving solution and then wound on curlers. After winding, the hair is re-wet thoroughly with said solution, and then it is allowed to "process" for a time, this being known as the "processing time" or "processing period." The time which it takes to reach the beginning of the processing period depends upon the skill of the operator, the particular technique employed and the type and amount of hair the patron has. Usually, it takes from fifteen minutes to one-half of an hour.

During the processing period the softening agent is allowed to work without interruption. The main softening of the hair takes place at this time although a minor amount of softening takes place during the wrapping of the hair. The reason why the amount of softening during wrapping of the hair is minor is that the hair is not covered while the winding is being done and ammonia is rapidly lost so that the pH of the solution drops and its effectiveness decreases. When the hair is resaturated and covered at the beginning of the processing period, however, the full effect of the softening solution is brought to bear and maintained. Thus, the just-mentioned minor softening will not affect the processing period by more than a few minutes. Moreover, the hair which is wrapped last will have been in contact with the waving lotion for hardly any time at all before it is re-wet and the processing period commences. In fact, it is customary to wrap the hardest to wave hair of a particular head of hair first so that it will have a chance to process a little before re-wetting and in this way it is sought to bring all of the hair to a condition before re-wetting where all of it is substantially equally although only slightly softened. Ordinarily, it is the hair at the nape of the neck which is hardest to soften while the hair at the crown is easiest to soften.

The time for processing has been quite definitely set by commercial practice and is very important. Generally, it varies from no processing period at all in so-called instant waving methods to fifteen minutes. One reason for the fifteen minutes upper limit is that it has been found that after approximately fifteen minutes a better wave is not obtained by continued softening because after this point softening begins to adversely affect the hair condition. Also, a long processing period renders the entire waving process too lengthy, patrons obviously not wanting to sit in a beauty parlor for prolonged periods. Since the overall waving process takes a considerable amount of time due to the winding, rinsing, drying of the hair, application of solutions, and the like, it is highly important in this very competitive field that the individual steps take as little time as possible. Still further, because the softening step is the most important one in the entire cold waving process, the operator should be present during the whole processing period and if this period is overlong too much of the operator's time is taken up.

Generally, it is desired to point out that certain routines from the beauty operator's point of view have been developed in the course of experience over the years and the time limitations of the processing period constitute a very important part of this routine. This, in addition to the reasons given above, constitutes another reason why the length of the processing period is quite important.

Conventionally, an attempt is made to provide for the variations in hair condition and type of hair so that the different types can be properly softened in about the same time. This is done by use of three basic hair waving solutions having different strengths, the one having the least strength being for so-called weak or damaged hair, the one having intermediate strength being for normal hair and the strongest one being for resistant hair. In this way, it is sought to wave different types of heads of hair in about the same time without overprocessing or underprocessing.

The different strengths of the three basic waving solutions referred to above are obtainable by varying the pH and/or mercaptan concentration, the pH being controlled by the amount of base present and the concentration of the solution being controlled by varying the number of equivalents of mercaptan present in a given volume. Conventionally, as already mentioned, ammonium hydroxide is the base universally employed to raise the pH to the necessary and desired level. Usually what is done where thioglycollic acid is used as the reducing agent in the waving solution is to react the ammonium hydroxide with the same whereby ammonium thioglycollate is produced and the pH of the solution is raised. As will be pointed out hereinafter, an excess of ammonium hydroxide has to be added above that necessary to completely neutralize the thioglycollic acid because although the pH of ammonium thioglycollate is 6.2 which is much higher than that of thioglycollic acid (which has a pH of 2) it is still not high enough for commercial cold permanent waving, i.e. is not yet in the necessary alkaline range. In practice, the manufacturers of cold wave supplies obtain the different strengths of the aforementioned three basic waving solutions by varying the concentration of thioglycollic acid therein while maintaining the pH substantially constant.

The present cold waving techniques have suffered from a major drawback in that the three basic solutions while satisfactory in a rough way for the majority of heads of hair are really proper for very few (those having normal hair) and in a good many cases quite unsatisfactory.

Another drawback of conventional cold waving processes and compositions is their inadequacy as far as the waving of damaged hair is concerned. Overprocessing is quite frequent with damaged hair even where a weaker solution is used; on the other hand, sometimes in order to avoid this danger the operator is overcareful, with the result that the hair is underprocessed. Generally, in the case of damaged hair the giving of a safe and effective wave has been greatly dependent on the skill of the operator and certain tricks of the trade learned by the operator in the course of his experience rather than upon sure scientific knowledge. Moreover, because the pH is not ordinarily lowered in order to obtain the lower strength in conventional waving solutions for damaged hair, the rate and extent of swelling of the damaged hair and the degradation thereof caused by the alkalinity still are quite high even though such solutions supposedly are appropriate for damaged hair. The same is true where a strong solution is diluted with water because such dilution primarily lowers the thioglycollic acid concentration but reduces the alkalinity very slightly.

The problem represented by damaged hair has become and could become increasingly serious for the individual

patron and the industry as a whole. The reason is that, as already mentioned, there is inevitably some degradation of the hair in the cold waving process and as more women are given permanent waves and the same women receive more waves, the amount and degree of damage to the hair increases. In addition to this, modern beauty trends are towards dyeing and bleaching hair and this, too, is increasing the number of damaged heads of hair. As a result of the foregoing, the necessity of overcoming the problems occurring with the waving of damaged hair is becoming more urgent; indeed, failure to improve methods of waving damaged hair will cause even a further increase in the number of damaged heads of hair.

It is obvious from the foregoing that it is highly desirable to provide hair waving processes and compositions just right for the heads of hair for which they are to be used. Furthermore, it is clear that some further means to control the softening of damaged hair besides merely using a less concentrated reducing solution is needed.

It is a principal object of the present invention to provide a cold waving process and cold waving compositions in which a reducing solution is easily and safely provided for and used with any particular type of hair.

It is another object of the present invention to provide a cold waving process and compositions of the character described which will successfully, safely and uniformly soften all types of hair from the most resistant to the most damaged.

It is a further object of the present invention to provide a cold waving process and compositions of the character described wherein only one basic waving solution is furnished the beauty shop for all types of hair but which is easily and safely in the beauty shop rendered suitable for the particular type of hair on which it is to be used.

It is still another object of the present invention to provide a cold waving process and cold waving compositions of the character described by means of which damaged hair can be safely and easily softened without risk of overprocessing or underprocessing and within the commercially acceptable time limitations.

It is an additional object of the present invention to provide a process of the character described which is simple and inexpensive to practice.

It is still a further object of the present invention to provide a process of the character described which has all of the advantages of conventional cold waving processes but none of the disadvantages thereof.

It is still another object of the present invention to provide a hair waving process and compositions for safely and easily waving damaged hair without risk of overprocessing and within commercially acceptable time limitations.

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

The invention accordingly consists of the series of steps and compositions of matter hereinafter described and of which the scope of application will be indicated in the appended claim.

Pursuant to one aspect of the present invention, there is provided a process for cold waving hair on the human head wherein a single basic cold waving solution having a strength appropriate for resistant hair is furnished to the beauty salon together with the means for easily, safely and accurately reducing its strength in the beauty shop without waste of material or time so as to produce a solution of the proper strength for normal hair and the various degrees of damaged hair including the most damaged which usually is silver blond. This is accomplished by employing an agency to lower the pH of the solution while simultaneously producing a salt in the waving solution which salt inhibits the attack of the base on the hair sheath. By appreciably lowering the pH instead of reducing the thioglycollic acid concentration as is conventional, the heart of the problem of waving damaged hair

is attacked since as already pointed out it is the base in the waving solution which breaks down the hair sheath, and in the case of damaged hair it is this sheath which is quite vulnerable, being already quite porous. Still further, the production in situ of a salt as aforesaid likewise directly aids in preventing overprocessing of damaged hair by slowing up the breakdown of the sheath and thereby reducing the likelihood of occurrence of excess breakdown thereof which would degrade the hair beyond the possibility of being restored by the oxidizing step. The amount of the agency employed is determined by the degree of reduction of strength of the waving solution desired, more of the agency being required for the greater reduction in strength needed for the more damaged types of hair.

The action of a salt in inhibiting attack of the base on the hair sheath is manifested by a slowing up of the swelling of the hair so that softening thereof proceeds at a slower rate. In addition, in the commercial times for softening hair, the extent of breakdown of the sheath and thus softening of the hair is also lessened by the inhibiting effect of salts. The less rapid swelling and lesser extent of swelling of the hair under these circumstances is an observable fact which therefore is referred to herein as describing the result of the presence of salts on the softening process. Accordingly, when the swelling inhibiting effect of a salt on the hair is mentioned herein, it will be understood that what is really referred to is the fact that the rapidity and extent of breakdown of the hair sheath with respect to time and thus the softening of the hair have been slowed up, i.e. inhibited.

The swelling inhibiting effect of salts is undesirable with resistant or normal hair because it slows up the waving process; however, when damaged hair is involved, this effect on the swelling is highly desirable because it aids in preventing overprocessing.

As is apparent from the foregoing, in the first aspect of the present invention, reduction of strength of the waving solution, which as already mentioned refers to the effectiveness thereof with respect to time in the softening of hair, is accomplished by an agency which simultaneously lowers the pH of the waving solution and produces a swelling inhibiting salt in situ therein. Moreover, it is a basic feature of the present aspect of the invention that the more the pH is lowered pursuant to the invention that the more swelling inhibiting salt that is simultaneously produced in situ in the waving solution. This produces the novel and very striking and important result of protecting damaged hair from overprocessing by not only reducing the amount of the substance attacking the hair sheath (the base) but also simultaneously producing an inhibiting substance to slow up said attack; and as the attacking substance is itself reduced in amount as the solution is adapted for more and more damaged hair, the amount of the inhibiting substance is itself increased. Thus, one agency simultaneously and directly overcomes in two ways the basic problem in waving damaged hair, and the agency's effectiveness in both ways increases simultaneously as the amount thereof is increased.

In accordance with the foregoing, the agency employed to reduce the strength of the single basic waving solution provided is a specially selected organic acid or acid salt, either in solid or solution form, which is furnished to the beauty operator along with the waving solution for addition thereto. By "acid salt" is meant a salt which has an available hydrogen ion, and such salts are to be distinguished from salts not having an available hydrogen ion but which, for example because they are salts of a strong acid and a weak base, hydrolyze to give acid solutions. As used in this application, the words "acidic substance" are to be understood as referring to acids and to acid salts of the particular type defined above.

The acid or acid salt is added to the waving solution in particular predetermined amounts in order to reduce the pH of the solution by appropriate increments and

produce enough swelling inhibiting salt to obtain the required solution strength for particular heads of hair. If the acid or acid salt is to be added in solution form, a calibrated pipette preferably is used to make the addition, the calibrations corresponding to particular amounts of specially selected acids or acid salts to be added to the waving solution which amounts will lower the said solution to different pre-selected levels. The beauty operator simply adds enough acid or acid solution according to the marks on the pipette to produce a strength appropriate for the hair with which the waving solution is to be used. The same procedure is followed with solid substances, a calibrated instrument for measuring amounts of solids being employed. In either case, the calibrations themselves, or a table furnished to the beauty shop for use with them, show how much is to be added for the particular type of hair involved. In this way, the basic solution is rendered adaptable for use with a variety of types of hair. In accordance with the present invention, preferably from five to seven different ultimate strength levels are provided for, this ordinarily being sufficient to make the solution adjustable so that it is just about right for almost every type of hair which might be waved. Of course, even more variations than seven can be obtained if desired.

The acids or acid salts usable in the foregoing process are selected in accordance with certain critical factors. Before discussing these, however, it is desired to elaborate to some extent on the chemistry of the waving solution which is believed to be as follows. The thioglycollic acid has two acid groups, to wit: a carboxylic acid group and a sulfhydryl group. Of these the former has the greater attractiveness for hydroxide ions so that when a base is added to thioglycollic acid to raise the pH to the range necessary for commercial cold waving, the carboxylic acid group is neutralized first. As already mentioned, ammonium hydroxide is almost always used to raise the pH, so that ammonium thioglycollate is formed. When more base is added, as is necessary to reach the appropriate pH for commercial cold waving, the additional hydroxide ions are loosely held by the sulfhydryl group which thus remains available for reaction with the hair keratin. The excess ammonium hydroxide above that used to completely neutralize the carboxylic acid group of the thioglycollic acid is known as "free ammonia," this being an accepted term in the art and actually referring to the amount of hydroxide ions present in the excess ammonium hydroxide.

In accordance with the present invention, it has been found that to reduce the strength of the solution to that proper for the poorest type of hair, substantially all of the free ammonia in a conventional cold waving solution for resistant hair must be neutralized. It is not necessary that all of the free ammonia be neutralized for this purpose, however; indeed, this would be highly undesirable since it would lower the pH below the necessary alkalinity required for cold waving. It is readily apparent that the acid or acid salt provided for use with the basic solution must be capable of reducing the pH of the latter to the level appropriate for the most damaged hair by neutralizing substantially all of the free ammonia. Concomitantly, it is highly desirable that the requisite maximum amount of acid or acid salt which might be needed as just set forth be providable within a certain maximum volume limit made important by certain very essential practical, commercial considerations.

Regarding the aforesaid volume limit and the reasons therefor, it is to be pointed out that one of the most important of these considerations is that it is both desirable and highly preferable from a commercial point of view that the addition of the acid or acid salt to the waving solution be carried out in the same bottle in which said solution is furnished. This bottle will have a limited volume, i.e. head space, unoccupied by waving solution and within this volume the addition of the maximum

amount of acid or acid salt that would be necessary (if the reduction in strength required for use of the solution with the most damaged type of hair is sought) must be conveniently possible. A method in which the waving solution had to be poured into a larger vessel before the addition of acid or acid salt would be commercially unfeasible because it would necessitate a messy extra step and extra handling of a potent reactive chemical solution. Moreover, such a procedure would be time consuming and wasteful and would even decrease the accuracy in strength of the waving solution because some of the same would be lost in the transference from the original bottle.

With conventional waving solution bottles usually about 10% of the volume is unfilled, i.e. is available as head space. Ordinarily, 4 oz. bottles of waving solution are furnished, such bottles containing 4 oz., i.e. about 120 cc. of solution, and about 12 cc. of head space—the bottles themselves having a somewhat greater capacity than 4 oz. Although the amount of head space may be varied so that more head space is present, it is not desirable for more than about 30% to be present. The reason for this is that the air above the waving solution tends to oxidize the same and thereby reduce its strength, and, of course, the more air there is the greater the possible reduction in strength. Since the bottles in many cases are not to be used right away, indeed may stand on the shelf for considerable periods of time, the presence of a good deal of air in the bottles could result in unintended substantial reduction of strength, and this is undesirable. In addition, it is not commercially feasible to sell bottles which appear to be less than about three-fifths filled since people tend to feel in such a case that all of the material they were supposed to receive has not been put in or that some has been lost or evaporated, etc. It is to be emphasized that the maximum head space in which a given acid or acid salt must be capable of effecting substantially complete neutralization of the free ammonia is an extremely important factor in the selection of the acid or acid salt because what is involved herein is a practical commercial process.

Although up to 30% head space can be available, as already mentioned, 10% is the most usual amount. Thus, in accordance with the present invention, it is highly important that many of the acids and acid salts be capable of substantially completely neutralizing the free ammonia when the head space is the conventional 10% and even when it is less than that.

Pursuant to the present invention, it has been discovered that the ability of an acid or acid salt to satisfy the above described requirements depends on the equivalent weight of the substance, the dissociation constant of the available acid group of the acid or acid salt, and on the solubility in the waving solution of the reaction product of the acid or acid salt and the ammonium hydroxide of the waving solution.

The equivalent weight of the acid or acid salt should be low enough so that enough equivalents of substance to substantially fully neutralize the free ammonia of the waving solution are providable within the preferred volume limitation on the addition of the particular compound in the least bulky manner.

It has been found pursuant to the present invention that the dissociation constant of the available acid group of the acids and acid salts usable herein should not be lower than 10^{-6}. With respect to the dissociation constant, by "not lower than" is meant "not a smaller number than." By "available acid group" is meant either the only acid group of monobasic acids or that acid group of acid salts and polybasic acids which is available for neutralization of the free ammonia, and wherever the dissociation constant of an acid or acid salt is referred to hereinafter herein it is to be understood that what is referred to is the dissociation constant of the available acid group as just defined.

As to the matter of solubility, the reaction product of the acid or acid salt and ammonium hydroxide should be sufficiently soluble in the waving solution for a clear solution to be obtainable on addition of sufficient acid or acid salt to neutralize substantially all of the free ammonia.

It is readily apparent that strong acids or acid salts, which are totally or almost totally dissociated, can always be used in concentrations sufficient to obtain the desired results if the solubilities in the waving solution of the reaction products formed when they react with the ammonium hydroxide are high enough; however, weaker or partially dissociated acids or acid salts cannot be used unless their dissociation constants are not less than 10^{-6} regardless of solubility. In other words, in the case of the weak acids or acid salts, even if the solubility is high enough so that sufficient equivalent weights of the substance to neutralize substantially all of the free ammonia can be provided within the preferred volume, they still will not be usable if the dissociation constant is less than 10^{-6} because in such case the neutralization reaction would reach equilibrium before substantially all the free ammonia is neutralized and this would necessitate adding more material to drive the reaction further in the direction of neutralization and thereby the volume limitation would be exceeded.

All three of the foregoing factors are interrelated, and the selection of the proper acid or acid salt requires that all of them be considered and satisfied so as to meet the basic requirement that sufficient acid or acid salt be addable in and capable of effecting substantially complete neutralization of the free ammonia in the requisite desired volume.

In addition to the above-mentioned factors there are several other important criteria for the acid or acid salt. Of course, the acid or acid salt must not be a softening agent for the hair. Still further, the acid or acid salt to be added must not react with the sulfhydryl group of the ammonium thioglycollate in one direction only, as, for example, is the case with oxidation or condensation reactions, because this would lower the activity of the reducing solution. Likewise, if an equilibrium reaction occurs between the ammonium thioglycollate and acid or acid salt it must not be such as to render the sulfhydryl group unavailable in the hair waving system. Reduction of activity of the waving solution in these ways is undesirable because it results in a reduction of strength additional to that deliberately caused by the addition of acid or acid salts pursuant hereto and thereby renders the strength uncertain. In fact, the strength might even in some cases be immediately lowered by such undesirable reactions below the level necessary for softening of the particular type of hair involved in the commercially acceptable time.

Other important criteria are that the acids or acid salts must not be harmful to the patron or beauty operator, i.e. toxic or irritating to the skin, malodorous or caustic. Still further, the substances must not be unstable or produce undesirable color reactions.

Examples of acids or acid salts having dissociation constants too low for the present purpose are: diammonium phosphate, disodium phosphate, boric acid and carbonic acid. Exemples of acids or acid salts whose reaction products with ammonium hydroxide are too insoluble in the waving solution are: palmitic acid, stearic acid and oleic acid.

The following are examples of acids which are too toxic or irritating for use herein: formic acid, acrylic acid, crotonic acid, oxalic acid, glycolic acid, carbolic acid and halogenated aliphatic acids such as chloroacetic acid, trichloroacetic acid and iodoacetic acid. Examples of acids which are malodorous or pungent are: propionic acid, butyric acid, valeric acid and caproic acid. Salicylic acid, gentisic acid and trihydroxy benzoic acid are examples of acids which may produce undesirable color reactions, and maleic acid, lactic acid, pyruvic acid and peroxy acids are examples of acids which would be unstable.

Inorganic acids having dissociation constants greater than 10^{-2} would be too caustic in the concentrations necessary. Examples of these are hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid and organic sulfonic acids such as benzene sulfonic acid. By "caustic" what is meant is that it would not be safe for the operator to handle these acids in the concentrations necessary.

The following are examples of acids and acid salts which meet the requirements for practice of the present invention as set forth above: acetic acid, succinic acid, monosodium succinate, glutaric acid, monopotassium glutarate, fumaric acid, monosodium fumarate, gluconic acid delta lactone, tartaric acid, ammonium bitartrate, citric acid, monosodium citrate, monoammonium citrate, tricarballylic acid, aconitic acid, and benzoic acid. Some of these can be used in solution in polar liquids, some in non-polar liquids, and others in solid form. In the latter case, the materials can be used as powders, pellets or the like. Some of these acids and acid salts can be added in various forms whereas others are not capable of being added in proper amount within the desired volume limitation except in certain forms. Thus, for example, citric and tartaric acids can be used in solid form and in solution in polar and non-polar liquids whereas ammonium bitartrate, for example, preferably is only used in solid form and benzoic acid, for example, only in solution in a polar solvent. Acetic acid, of course, only occurs in liquid form and is only used in solution form.

All of the above-referred to acids and acid salts can be added within the maximum head space allowable (30%) and substantially fully neutralize the free ammonia. The following are some of those which are usable even when the head space is only 10%: acetic acid, succinic acid, glutaric acid, fumaric acid, tartaric acid and citric acid. Still further, all of the monosodium salts mentioned on the list above can be used even within the smallest practical head space in commercial preparations.

Some of the acids and acid salts mentioned as usable for the present purposes can be concentrated sufficiently so that with minute additions of the same the full reduction of solution strength is obtainable. However, where a small amount of the substance, whether introduced in solid or liquid form, produces a very great variation in solution strength, it is necessary that the instrument for adding the same be made very accurate. Such instruments are both expensive and difficult for unskilled persons, who are not trained scientists, to use. Accordingly, although permissible, it is not desirable that the substances usable pursuant hereto be used in so concentrated a form that the accuracy of the additions will suffer because of the operator's lack of ability to use a delicate instrument or because a delicate instrument cannot feasibly be furnished.

Referring now in greater detail to the production in situ in the waving solution of swelling inhibiting salts, it has been found that the different salts produced as products of the reaction between the free ammonia and the acidifying substance added as described hereinabove may have different degrees of effectiveness in inhibiting swelling of the hair. In other words, in the case of each acid or acid salt to be added, amounts producing the same reduction in pH in some cases will produce different degrees of reduction in overall strength of the waving solution. As a result, for particular given solution strengths desired for particular types of hair to be waved those acids or acid salts producing salts as products of the reaction with the ammonium hydroxide having lesser swelling inhibiting effect are added in greater amount (to reduce the pH more) than those producing salts having a higher inherent swelling inhibiting effect, and vice versa. The salts produced as a result of the reaction between the free ammonia of the waving solution and the acids and acid salts described hereinabove as examples of those usable in accordance with the present invention all have

the swelling inhibiting effect when produced in sufficient quantity. When the solution is to be used for normal hair, only a small amount of acidifying substance is added and only a small amount of salt is produced in situ, so that the softening process is not noticeably slowed up, the amount of salt produced not being sufficient to appreciably inhibit the swelling of the hair. Of course, when the solution is used for resistant hair, no acidifying substance is added, so no salt is produced in situ at all. On the other hand, however, it has been discovered pursuant to the present invention that on addition pursuant hereto of more acid or acid salt than is necessary to reduce the strength of the solution to that proper for normal hair, a sufficient amount of salt is produced in situ as a reaction product for the swelling inhibiting effect to be present, and to contribute materially to lowering of the strength of the solution to a strength proper for a type of hair more easily softened than normal hair. Of course, as already mentioned the amount of salt produced in situ increases as more acid or acid salt is added so that the swelling inhibiting effect correspondingly rises as the need for it becomes greater.

Referring now to another feature of the first aspect of the present invention, it is to be observed that generally with normal and resistant hair the amount of swelling caused by a given waving solution increases during the softening period with the passage of time and vice versa. With damaged hair there is an initial rapid swelling which is much greater than that of normal hair and this is followed by a slow rise in the amount of swelling. Pursuant to the present invention, it has been discovered that in the presence of sufficient quantities of salts produced in situ by reaction of the ammonium hydroxide of the waving solution with the acids and acid salts usable herein and where the pH of the waving solution is reduced below 9.2 by use of the present invention, the swelling curve (swelling plotted against time) for damaged hair effectively plateaus out prior to overprocessing; this means that further swelling ceases at a point in time during the processing period before overprocessing of the hair has occurred; hereinafter this effect will be referred to as "safety plateauing effect." As a result, in the present process the more damaged hair will be protected against overprocessing not only because of the reduction in pH and because of the swelling inhibiting effect of the salt produced, as previously set forth hereinabove, but additionally because when the pH is reduced below 9.2 and the acid or acid salt is added in the appropriate amount to produce sufficient salt in situ for the safety plateauing effect (as will certainly be the case for the weaker and more damaged types of hair) swelling is stopped completely and prior to overprocessing.

As is apparent from the foregoing, the safety plateauing effect depends on the pH of the waving solution being below 9.2 and enough salt being produced. Inasmuch as some of the salts produced in situ may have different swelling inhibiting capacities, the amounts thereof needed for such plateauing may vary also. It has been found pursuant to the instant invention, however, that if enough acid or acid salt selected in accordance with the foregoing is added to the waving solution to produce in situ in 120 ccs. of said solution at least 0.035 equivalents of salt, said safety plateauing effect will be obtained, i.e. enough salt will be present and the pH will be below 9.2. Addition of lesser amounts of some of said acids and acid salts thereby producing less than 0.035 equivalents of salt in situ, will, of course, in some cases produce the plateauing effect, however.

Although, as mentioned above, the primary factor in reducing the strength of the basic waving solution in the present process is lowering of pH by neutralization of the free ammonia and production of swelling inhibiting salts whereby the capacity of the solution to swell the hair is reduced, a slight reduction of strength may occur also by virtue of dilution (lowering in concentration) of the waving solution resulting from the addition of the acid or acid salt when the volume is increased because of the addition.

Various additives can be employed in the waving solution or be included in the acidifying substances, these comprising wetting agents, clouding agents, perfumes, colors, conditioning agents, emollients or thickeners. Such substances are added to enhance the attractiveness of the waving process as a whole. They are used in minor amounts.

The following are examples showing compositions embodying and usable in accordance with the present invention as described so far. For the purposes of the first four examples there will be considered to be five categories of hair, to wit: resistant, normal or undamaged hair, previously cold waved hair, tinted hair and bleached hair (three shades or more). For the fifth example seven categories are provided, the additional two being bleached (two shades) and silver blond.

In these examples the amounts of the particular acid or acid salt to be added to the particular waving solution for resistant hair in order to produce the solutions appropriate for particular heads of hair have been determined on the basis of the reduction of strength resulting from lowering of pH and the swelling inhibiting effect of the salt produced in situ; also taken into consideration is the reduction in strength caused by any small lowering of the concentration of the thioglycollic acid. In addition, in all of the examples given below enough salt is produced when the pH is below 9.2 for the safety plateauing effect to be present.

Example I

120 ccs. of a basic cold waving solution for resistant hair having a pH of 9.38, a concentration of 7.3% thioglycollic acid and containing 0.73 milliequivalents of free ammonia per cc. is furnished. The head space in the bottle is 12.4 ccs.

Using an acidifying solution containing a 7.1 normal aqueous solution of citric acid, there have been calculated the amounts of the same which must be added for the different types of hair in order to produce the proper strength waving solution for each. These are summarized on the table below.

Type of hair	Cc. of acidifying agent to be added	Milliequivalents free ammonia per cc.	Percent by weight thioglycollic acid	pH
Resistant	0.0	0.73	7.3	9.38
Normal or nondamaged	1.0	0.67	7.25	9.28
Previously cold waved	2.0	0.61	7.20	9.23
Tinted	3.5	0.51	7.10	9.15
Bleached (three shades or more).	7.0	0.30	6.90	8.82

The operator determines the degree of damage or porosity of the person's hair and by use of a pipette calibrated for the above solution, adds the appropriate amount. After shaking the bottle, the solution will have the proper strength for the hair involved and will soften the same within the preferred standard processing time of five to 15 minutes.

Example II

120 ccs. of a basic cold waving solution for resistant hair having a pH of 9.25, a concentration of 8.7% thioglycollic acid and containing 0.73 milliequivalents of free ammonia per cc. is furnished. The head space in the bottle is 12.4 ccs. This softening solution includes protein in accordance with the process and compositions described in Patent No. 2,540,494, dated February 6, 1951, and the higher thioglycollic acid concentration is provided to compensate for the fact that the presence of protein slows up the softening process.

Using an acidifying solution containing a 7.1% normal aqueous solution of tartaric acid, there have been calculated the amounts of the same which must be added for the different types of hair in order to produce the proper strength waving solution for each. These are summarized on the table below:

Type of hair	Cc. of acidifying agent to be added	Milliequivalents free ammonia per cc.	Percent by weight thioglycollic acid	pH
Resistant	0.0	0.73	8.7	9.25
Normal or nondamaged	1.0	0.67	8.65	9.20
Previously cold waved	2.0	0.61	8.57	9.15
Tinted	3.5	0.51	8.5	9.0
Bleached (three shades or more).	7.0	0.30	8.3	8.7

The procedure is the same as in Example I.

Example III

The same waving solution and quantity thereof as for Example I is employed. The head space is 35 ccs.

Using an acidifying solution constituting 2.4 normal benzoic acid in 95 proof ethyl alcohol (10.25 grams benzoic acid in 35 ccs. of alcohol), there have been calculated the amounts of the same which must be added for the different types of hair in order to produce the proper strength waving solution for each. These are summarized on the table below.

Type of hair	Cc. of acidifying agent to be added	Milliequivalents free ammonia per cc.	Percent by weight thioglycollic acid	pH
Resistant	0.0	0.73	7.3	9.38
Normal or nondamaged	3.0	0.64	7.11	9.36
Previously cold waved	6.0	0.56	6.95	9.31
Tinted	10.5	0.46	6.68	9.20
Bleached (3 shades or more)	21.0	0.31	6.33	9.01

The procedure is the same as for the preceding examples.

Example IV

The same waving solution and quantity thereof as for Example I is employed. The head space is 6 ccs.

Using as an acidifying agent the acid salt monoammonium bitartrate in dry form, there have been calculated the amounts of the same which must be added for the different types of hair in order to produce the proper strength waving solution. These are summarized on the table below.

Type of hair	Gr. of acidifying agent to be added	Milliequivalents free ammonia per cc.	Percent by weight thioglycollic acid	pH
Resistant	0.0	.73	7.3	9.38
Normal or nondamaged	1.2	.67	7.25	9.31
Previously cold waved	2.4	.61	7.22	9.24
Tinted	4.2	.52	7.20	9.15
Bleached (3 shades or more)	8.4	.31	7.12	8.8

The procedure is the same as in the preceding examples except that the acid salt is added in solid form and a calibrated instrument for measuring amounts of solid is employed.

Example V

The same waving solution and quantity thereof as for Example I is employed. The head space is 12.4 ccs. Using the same acidifying solution as that for Example I, there are summarized on the table below the amounts of the same which must be added to produce the proper strength waving solution for seven different types of hair.

Type of hair	Cc. of acidifying agent to be added	Milliequivalents free ammonia per cc.	Percent by weight thioglycollic acid	pH
Resistant	0.0	.73	7.3	9.38
Normal or nondamaged	1.0	.67	7.25	9.28
Previously cold waved	2.0	.61	7.2	9.23
Tinted	3.5	.51	7.1	9.15
Bleached (2 shades)	5.0	.42	7.0	8.98
Bleached (3 shades or more)	7.0	.30	6.9	8.82
Silver blond	8.0	.24	6.85	8.6

The procedure is the same as for Examples I, II and III.

It is to be understood that the strength of the basic ammonium thioglycollate waving solution for resistant hair provided pursuant to the aspect of the present invention described so far may vary as to pH and/or thioglycollic acid concentration within the range appropriate for resistant hair. A change in concentration of the original waving solution does not affect the amount of acid or acid salt used in the present process as set forth above.

The use of different mercaptans from ammonium thioglycollate in the waving solution will not change the figures given for the acids and acid salts as set forth herein; however, the use of a different base in said solution will alter these figures and other factors set forth above although the theory of the process will remain the same.

There is set forth below a complete hair waving process, it being understood that prior to performance of the steps set forth below the beauty operator has determined what type of hair it is that she is about to wave and that the waving solution pursuant to the present invention is appropriate for that type of hair.

(1) The hair is blocked off.
(2) The hair is wetted with the waving solution.
(3) The hair is wound up in curlers.
(4) The hair is rewetted with the waving solution.
(5) The hair is allowed to stand for five to fifteen minutes.
(6) The hair is rinsed with lukewarm water.
(7) A setting agent is applied to the hair.
(8) The hair is taken out of the curlers.
(9) The hair is rinsed.

Pursuant to a second aspect of the instant invention, it has been found that the safety plateauing effect for damaged hair referred to above (i.e. plateauing of the swelling curve before overprocessing) can be produced by directly adding salts to the waving solution as long as the pH is below 9.2. Thus, this effect can be produced in conventional cold waving solutions and processes, and, of course, it is highly useful in protecting damaged hair. For these purposes, the waving solution may be one having any of the conventional strengths for damaged hair although the pH must be below 9.2 in each case. As is apparent, all of the salts produced as products of the reaction between ammonium thioglycollate and the acids and acid salts set forth above as examples of those usable in accordance with the first aspect of the invention, are usable pursuant to the aspect now being discussed. The following are examples of other salts usable pursuant thereto: potassium chloride, sodium chloride, potassium bromide, potassium sulfate and ammonium chloride.

As already pointed out, said safety plateauing effect is produced when sufficient salt is present and the pH is less than 9.2. Pursuant to the present aspect of the invention, it has been found that if at least .053 equivalents of salt have been added to 120 ccs. of waving solution said effect will always be produced, although with some salt lesser amounts will produce said effect.

The following are examples showing use of salts to produce said safety plateauing effect on direct addition thereof to cold waving solutions for damaged hair.

Example VI

A waving solution for damaged hair having a pH of

9.15, 8.7% by weight thioglycollic acid, and 1½% by weight casein is employed. Addition of .053 equivalents of potassium sulfate to 120 ccs. of said waving solution will result in the safety plateauing effect being present and the special protection against overprocessing of the damaged hair will be obtained.

Example VII

A waving solution for damaged hair having a pH of 9.15, and a thioglycollic acid concentration of 7.3% by weight is employed. Addition of .03 equivalents of potassium chloride to 120 ccs. of said waving solution will result in the safety plateauing effect being present and the special protection against overprocessing of the damaged hair will be obtained.

It thus will be seen that there are provided compositions of matter and methods for waving hair which achieve the several objects of the invention and are well adapted to meet the conditions of practical use.

As various possible embodiment 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 hereinabove described is to be interpreted as illustrative and not in a limiting sense.

Having thus described the invention, there is claimed as new and desired to be secured by Letters Patent:

In a method of preparing a solution for permanently waving hair cold on the human head wherein the hair is softened by application of a waving solution: that improvement including the steps of providing a waving solution in a container having a head space not exceeding 30% of the volume of the container, said waving solution including a mercaptan reducing agent and excess ammonium hydroxide, having a pH of about 9.2 to 9.4 and in a strength proper for softening resistant hair, providing for addition to said waving solution so as to reduce the strength thereof an acidic substance selected from the class consisting of organic acids and acid salts thereof,

said acidic substance being bland, non-toxic, harmless and substantially inert to the reducing agent of the waving solution, the dissociation constant of the available acid group of said acidic substance being at least 10^{-6}, said dissociation constant and equivalent weight of the acidic substance being such that the amount of said acidic substance which will neutralize substantially all of the excess ammonium hydroxide can be added to the waving solution in the container without exceeding the volume of the container, and then adding to the waving solution in the container a predetermined amount of said acidic substance to reduce the pH strength of said waving solution to a predetermined pH strength, not less than about 8.6, corresponding to a certain type of hair that is more easily softened than resistant hair while simultaneously producing in situ a swelling inhibiting salt by interaction between the acidic substance and the excess ammonium hydroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,577,710	McDonough	Dec. 4, 1951
2,631,965	Schnell	Mar. 17, 1953
2,653,121	Schnell	Sept. 22, 1953
2,688,972	Brown	Sept. 14, 1954

FOREIGN PATENTS

159,395	Australia	Oct. 20, 1954

OTHER REFERENCES

Speakman I, J. Society Dyers and Colorists, vol. 52, 1936, pp. 335–346.

Speakman II, J.S.D.C., vol. 57, No. 3, March 1941, pp. 73–81.

Sagarin: Cosmetics Science and Technology, Interscience Publ. Inc., N.Y. (1957), pp. 610–612.

Valko: J. S. Cos. Chemists, vol. 3, No. 2, August 1952, pp. 108–117.