United States Patent

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New York,
Continuation-in-part of application Ser. No. 575,540, Aug. 29, 1966, now abandoned.

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[54] **SIMULTANEOUSLY DEFORMING AND STRENGTHENING HAIR**
9 Claims, No Drawings

[52] **U.S. Cl.** **132/7**
[51] **Int. Cl.** **A45d 7/00**
[50] **Field of Search** 132/7, 5; 161/87.1, 87.2; 424/71, 81, 78, 79; 8/54; 260/77.5, 89.5

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ABSTRACT: Simultaneously deforms hair, e.g., waves or straightens hair and strengthens hair by treating hair with a reducing agent and a vinylic monomer containing acid groups; the vinylic monomer is polymerized during the process.

SIMULTANEOUSLY DEFORMING AND STRENGTHENING HAIR

This application is a continuation-in-part of application Ser. No. 575,540, filed Aug. 29, 1966 now abandoned.

This invention relates to a method for permanently deforming hair and to compositions that are useful for this purpose. More particularly, it relates to hair-deforming compositions and processes that tend to minimize hair damage which ordinarily accompanies conventional hair-deforming procedures.

As used herein, the term "permanently deforming hair compositions" refers to compositions which may be used in cold hair-waving procedures or cold hair-straightening procedures, each being a facet of the same general procedure that involves the softening of the hair by chemical treatment. The cold hair-waving procedure, as is well known in the art, is a mere extension of the cold hair-straightening procedure in which the hair (which if left unwound would tend to become straightened by the action of the treating solution) is wound on a curler to produce a wave.

Although this invention is applicable to any kind of cold permanent deformation of hair, to simplify the discussion thereof, the invention is described particularly with regard to cold permanent waving. It is to be understood, however, that in each case the process described is also applicable to hair straightening as indicated above.

Cold waving generally involves the application of the cold waving lotion to the hair, either before or after the hair has been wound on curlers. The waving lotion is allowed to remain in contact with the hair for a period of time so as to effect a "softening" of the hair. Following this, the hair is usually "hardened" by the application of the so-called "neutralizer."

It is now generally believed that the action of the waving lotion, whose active ingredient is a reducing agent, breaks the disulfide linkage between neighboring hair keratin molecules. This is a damaging action which, if continued in an uncontrolled manner, would result in dissolving some of the hair. The function of the "neutralizer," whose active ingredient is generally an oxidizing agent, is believed to be the reestablishment of the disulfide linkage and the arrest of the action of the waving lotion.

The action of the "neutralizing" agent in reestablishing the disulfide linkage is invariably incomplete. A certain degree of damage, therefore, remains even after the action of the "neutralizing" agent. It has now been found that the apparent hair damage may be minimized or materially reduced by simultaneously cold waving said hair and polymerizing in said hair a water-soluble polymerizable vinylic monomer having acid-forming groups.

It is accordingly an object of the present invention to provide a method for deforming hair with a minimum of apparent hair damage.

It is a further object of the present invention to provide compositions capable of accomplishing the above object.

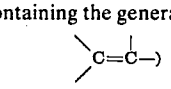
It is also an object of this invention to provide methods and compositions for deforming hair with a minimum of apparent hair damage, involving simultaneously deforming and polymerizing in said hair a water-soluble vinylic polymer having acid-forming groups.

Other and more detailed objects of this invention will be apparent from the following description and claims.

The present invention takes advantage of the fact that the reducing agent of the cold waving solution, either alone or in conjunction with the oxidizing agent of the "neutralizing" solution, causes the polymerization of a vinylic monomer to form long-chain polymers in the hair fibers. The long-chain polymers so formed, in general, are water insoluble and provide a backbone which strengthen the hair fiber. To further insolubilize the polymer formed, a bridging agent is employed, generally in the neutralizing solution, which serves to bridge neighboring polymeric chains in a manner described in more detail below. In a preferred form of this invention, the water-soluble polymerizable monomer comprises a part of the hair-waving lotion.

Without being restricted to any theory of action, the formation of the polymer per se in accordance with the present invention is not thought to result in the reestablishment of the ruptured disulfide linkages between keratin molecules. However, the strengthening of the hair, as a result of the polymer formation, compensates for the ruptured disulfide linkages which are not reestablished. The net result is an apparent reduction in the hair damage caused by the action of the cold waving lotion.

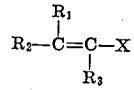
As mentioned above, the polymerizable vinylic monomer (i.e., a monomer containing the general grouping



contains acid-forming groups. The latter are important in one aspect of the present invention in that they provide sites at which neighboring polymer chains may be bridged by means of bridging agents to render the polymer less water soluble. As used herein, the term acid-forming groups is intended to encompass the acid groups per se, the salts of these acids, as well as groups which will be converted into acid groups or salts under the conditions of use of the present invention.

More particularly, the polymerizable vinylic compounds that may be used in accordance with the present invention are water-soluble compounds of the general formula:

(I)



wherein R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, aryl, halide; R_3 is selected from the group consisting of hydrogen, alkyl, carboxyalkyl, aryl and halide and X is selected from the group consisting of acid groups and salts thereof (e.g., COOH, SO_3H). By way of illustration, the following polymerizable vinylic compounds may be mentioned: acrylic acid, sodium acrylate, monoethanolamine acrylate, potassium acrylate, calcium acrylate, methacrylic acid, sodium methacrylate, monoethanolamine methacrylate, potassium methacrylate, calcium methacrylate, itaconic acid, and salts of itaconic acid.

The amount of polymerizable vinylic monomer that may be incorporated in said waving lotion can vary considerably. In general, however, it will constitute between 2 to 20 percent by weight of the waving lotion.

Another usual component of waving lotion utilized in this invention is a reducing agent. Any agent of this character which is effective in rupturing the disulfide linkages between keratin molecules and, either alone or in conjunction with an appropriate oxidizing agent, is capable of causing the polymerization of vinylic monomer can be used in accordance with the present invention. Among the reducing agents that may be employed, there may be mentioned ammonium thioglycollate, sodium bisulfite, ammonium bisulfite, monoethanolamine bisulfite, monoethanolamine thioglycollate, or any of the water-soluble bisulfite or thioglycollate salts well known to those skilled in the art.

The concentration of reducing agent in the waving lotion can also vary considerably. All that is essential is that it be present in sufficient concentration so as to be capable of "softening" the hair in the waving operation and to function in the polymerization of the vinylic monomer. In general, however, it will constitute between 1.5 to 10 percent by weight of the waving lotion.

To facilitate the penetration of active ingredients into the hair fibers, it is advantageous to add a swelling agent to the waving lotion. Any of a number of known materials may be used for this purpose. By way of illustration, the following may be mentioned: urea, NH_4OH, monoethanolamine, NaOH, KOH, triethanolamine, guanidine, thiourea.

The pH of the waving lotion may vary depending upon the particular reducing agent included therein. In general, however, the pH will be in the range of from about 7 to 9.8 for a thioglycollate lotion or 4 to 7 for a bisulfite lotion. If desired, the waving lotion may be buffered at the appropriate pH. Any of a wide variety of buffer systems, well known to those skilled in the art, may be used for this purpose. A sodium acetate-acetic acid buffer system is exemplary of a typical buffer system that can be employed.

The present invention also provides for a "neutralizer" which is an aqueous composition designed to arrest the action of the reducing agent in the waving lotion and reestablish the disulfide linkages of the hair keratin broken by the same. The principal active ingredient in the "neutralizer," which, incidentally, is an oxidizing agent, may perform a dual function in this invention. Where the system is such as to require a redox catalyst system for the polymerization of the vinylic monomer, the oxidizing agent of the neutralizer may provide the oxidizing agent portion thereof. This, together with the reducing agent of the waving lotion, will form the redox couple. Where, however, the reducing agent of the waving lotion is all that is necessary for effecting the polymerization of the vinylic monomer, the oxidizing agent of the "neutralizer" will serve principally to reestablish the disulfide bonds and arrest the action of the reducing agent of the waving lotion.

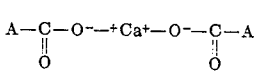
Any of a wide variety of oxidizing agents can be used in the "neutralizer"of the present invention. The only limitations on the oxidizing agents are that they must be capable of "-neutralizing" the action of the reducing agent in the waving lotion and where necessary are capable of forming with this reducing agent a redox system capable of facilitating the polymerization of the vinylic monomer. By way of illustration, the following oxidizing agents may be mentioned: ammonium persulfate, sodium bromate, other soluble persulfates, hydrogen peroxide, sodium pyrophosphate, sodium carbonate peroxide.

The concentration of oxidizing agent in the "neutralizing" agent can also vary considerably. Again, the only limitation is that the concentration be at least sufficient to arrest the action of the reducing agent and reestablish as many of the disulfide bond linkages as possible and also, where necessary, to be present in sufficient amounts to function as a part of the redox catalyst system for polymerizing the vinylic monomer. In general, however, the oxidizing agent will constitute about from 2 to 15 percent by weight of the neutralizer.

In a preferred form of this invention, as mentioned above, the "neutralizer" contains a bridging agent. The bridging agents are used in accordance with the present invention to further insolubilize the polymerized vinylic compound formed.

One of the preferred classes of bridging agents comprises water-soluble compounds (e.g., slats, hydroxides, oxides, etc.) of elements of Group II or III of the Periodic Table capable of yielding multivalent cations (divalent, trivalent, etc. cations). These are believed to function as bridging agents through the formation of a saltlike structure involving the acid groups of neighboring vinylic polymeric chains and the cations of the bridging agents. These bridges can be visualized in the case wherein the polymerizable vinylic compound is a carboxylic acid compound, and the bridging agent is a calcium salt or other calcium compound as follows:

(2)



wherein A is a polymeric chain. Although only one bridge is illustrated in the formula (2) between polymeric chains, it should be understood that there can be many such bridges. By way of illustration, the following compounds can serve as bridging agents which will supply the cationic type bridge: $CaCl_2$, $ZnCl_2$, $BaCl_2$, $Al(SO_4)_3$ and difunctional quaternary ammonium compounds such as: N-Tallow, N-N-dimethyl-N'-N'-N'-trimethyl-1, 3-propylene diammonium chloride (Aliquate 726); N-Tallow-1, 3-propylene-diaminedioleate (Diam 26 Dioleate).

Another class of bridging agent that may be used in accordance with the present invention may be described as agents capable of providing long-chain organic monovalent cations. The mechanism by which these long-chain cations work to provide a bridge between neighboring polymer chains is not quite clear. However, it is believed that this probably involves chain entanglement. By way of illustration, this class of bridging agent may be exemplified by the monofunctional alkyl quaternary ammonium compounds or alkyl primary amines, e.g., cetyl pyridinium chloride; cetyl trimethylammonium chloride; stearyl amine.

The concentration of bridging agent in the "neutralizer" can vary considerably. In general, however, it will constitute between about 0.1 to 5 percent by weight.

The active ingredients utilized in the present invention may be applied in any suitable form. Thus, they may be applied as solutions, gels, creams, foams, lotions, etc.

In addition to the principal active ingredients described above, the compositions of this invention may also contain other ingredients and particularly those which facilitate the application of the active ingredients to the hair. Thus, for example, a surfactant may be included to enhance the wetting property of the ingredients employed.

Although, as described above, the bridging agent is present in the neutralizer, it may instead be incorporated in the waving lotion. However, it is preferred that bridging agents be maintained in the neutralizer. Furthermore, although it is not preferred, the polymerizable vinylic monomer may be incorporated in the "neutralizing" agent along with the bridging agent.

In treating hair, in accordance with the present invention, the respective compositions can be applied in any of several procedures well known to those skilled in the art. In one preferred procedure, the hair to be waved is wrapped on a curler. The hair is then wet with a waving lotion containing the reducing agent and the water-soluble polymerizable vinylic monomer. The hair so wetted is allowed to remain in contact with said waving lotion for a period of from about 5 to 30 minutes.

The hair is then rinsed with water and neutralizer is applied. The neutralizer is maintained in contact with the hair for about 2 to 15 minutes after which time the hair is again rinsed with water.

The following examples are further illustrative of the present invention. It should be understood, however, that the invention is not limited thereto.

EXAMPLE 1

The following procedure was used on some bleached hair which has a tensile modulus index of 5.1.

A swatch of hair was wrapped on a waving mandrel such as is used in the procedure of Kirby [D. H. Kirby, Proc. Scientific Section TGA, p. 12, No. 26 Dec. 1956)]. The swatch was then wet with a solution containing:

7.5 g.	Urea
7.5 g.	$NaHSO_3$
5.0 g.	Sodium Acrylate
50.0 ml.	H_2O

After 15 minutes the hair was rinsed with water and wet for 10 minutes with a solution containing:

1.0 g.	$(NH_4)_2S_2O_8$
2.0 g.	$CaCl_2$
10.0 g.	Sodium Acetate
40.0 ml.	H_2O

The wet waving efficiency was found to be 59 percent, and the tensile modulus index was 4.1. A sample of the same starting hair was treated the same way, except that in the first solution the sodium acrylate was replaced by sodium acetate. In this treatment the wet waving efficiency was 63 percent, but the tensile modulus index was 3.3.

EXAMPLE 2

A. Waving lotion containing monomer

21.6 g.	(60%) aqueous ammonium thioglycollate.
8.0 ml.	(28%) aqueous NH_4OH.
20.0 g.	Sodium acrylate.
3.0 ml.	Glacial acetic acid q.s. to 200 g. with distilled water pH 8.0.

B. Control waving lotion

21.6 g.	(60%) ammonium thioglycollate.
8.0 ml.	(28%) NH_4OH.
20.0 g.	Sodium acetate.
3.0 ml.	Glacial acetic acid q.s. to 200 g. with distilled water pH 8.0.

Neutralizer

2.0 g. Ammonium persulfate
2.0 g. $CaCl_2$
10.0 g. Sodium acetate
40.0 ml. Distilled water

For the purposes of comparison, two waving lotions, A and B, were applied for 5 minutes to some bleached hair (modulus index 4.5) on mandrels. Waving lotion A is representative of the present invention. Without rinsing, the neutralizer was applied to the two batches of hair. After 15 minutes of neutralization, the hair was rinsed with water and the wet and dry waving efficiencies measured. The tensile modulus index of the hair so treated was also measured.

RESULTS

	Monomer lotion A	Control lotion B
Wet waving efficiency, percent	62	57
Dry waving efficiency, percent	43	41
Tensile modulus index	3.6	2.5

It is seen that the monomer lotion gives a slightly better wave and leaves the hair stronger.

EXAMPLE 3

C. Waving Lotion Containing Monomer

7.5 g. Urea
7.5 g. Sodium Bisulfite
5.0 g. Sodium Methacrylate
50.0 ml. H_2O

D. Control Lotion

7.5 g. Urea
7.5 g. Sodium bisulfite
5.0 g. Sodium acetate
50.0 ml. H_2O

Neutralizer

1.0 g. Ammonium persulfate
2.0 g. $CaCl_2$
10.0 g. Sodium acetate
40.0 ml. H_2O

Some bleached hair (modulus index 4.6) was wrapped on mandrels and wet with the two waving lotions, C and D. In this case, waving lotion C is representative of the present invention. The lotions were left on for 15 minutes, rinsed off with water and then neutralized for 15 minutes. After neutralization, the hair was rinsed again with water and dried.

RESULTS

	Monomer lotion C	Control lotion D
Wet waving efficiency, percent	67	49
Dry waving efficiency, percent	67	41
Tensile modulus index	4.0	2.0

It is seen that the monomer lotion gives a significantly better wave and leaves the hair much stronger.

EXAMPLE 4

E. Waving lotion containing monomer

Grams:	
8.4	Ammonium thioglycollate.
10.0	Methacrylic acid.
13.2	(28%) ammonium hydroxide q.s. to 100 g. with water pH 9.3.

F. Control lotion

8.4	Ammonium thioglycollate.
6.9	Glacial acetic acid.
15.2	(28%) ammonium hydroxide q.s. to 100 g. with water pH 9.3.

Neutralizer

1.0	Ammonium persulfate.
2.0	$CaCl_2$.
0.2	Acetic acid q.s. to 100 g. with water.

Two swatches of normal brown European hair (modulus index 11.0) on waving mandrels were treated with the control lotion F and monomer waving lotion E respectively for 10 minutes. Waving lotion E is representative of the invention. The swatches were rinsed with water and treated with the neutralizer for 5 minutes.

The monomer lotion treated swatch had a wet waving efficiency of 50 percent and a tensile modulus index of 6.9, whereas the control lotion treated swatch had a wet waving efficiency of 46 percent and a tensile modulus index of 5.3.

EXAMPLE 5

In another experiment two swatches of the same batch of normal brown hair were treated with the same monomer and control waving lotions as in example 4 respectively for 10 minutes, rinsed with water and then neutralized with the following neutralizer for 5 minutes:

Neutralizer

Grams:	
2.0	Sodium bromate.
0.5	Sodium pyrophosphate.
0.5	Sodium tripolyphosphate q.s. to 100 g. with water.

	Monomer lotion E	Control lotion F
Wet waving efficiency, percent	57	47
Dry waving efficiency, percent	46	38
Tensile modulus index	6.9	5.8

It is seen that the monomer lotion gives a better wave and leaves the hair stronger.

EXAMPLE 6

A swatch of curly hair was treated with a solution containing the following:

A. Hair Straightening Lotion Containing Monomer

7.5 g. Urea
7.5 g. $NaHSO_3$
5.0 g. Sodium Acrylate
50.0 ml. H_2O

The material was permitted to remain on the hair for 15 minutes during which time, at 5 minute intervals, the hair was combed. After the 15 minute period, the hair was rinsed with water and wet for 10 minutes with a solution containing:

B. Neutralizer

1.0 g. $(NH_4)_2S_2O_8$
2.0 g. $CaCl_2$
10.0 g. Sodium Acetate
40.0 ml. H_2O

This treatment caused the straightening of the curly hair.

EXAMPLE 7

The procedure of example 6 was followed, excepting that the "Hair Straightening Lotion" and the "Neutralizer" employed were as follows:

A. Hair straightening lotion containing monomer

21.6 g. (60%) aqueous ammonium thioglycollate.
8.0 ml. (28%) aqueous NH_4OH.
20.0 g. Sodium acrylate.
3.0 ml. Glacial acetic acid q.s. to 200 g. with distilled water pH 8.0.

B. Neutralizer

2.0 g. Ammonium persulfate
2.0 g. $CaCl_2$
10.0 g. Sodium acetate
40.0 ml. Distilled water

Equivalent results were obtained.

EXAMPLE 8

The procedure of example 6 was followed, excepting that the "Hair Straightening Lotion" and the "Neutralizer" employed were as follows:

A. Hair Straightening Lotion Containing Monomer

7.5 g. Urea
7.5 g. Sodium Bisulfite
5.0 g. Sodium Methacrylate
50.0 ml. H_2O

B. Neutralizer

1.0 g. Ammonium Persulfate
2.0 g. $CaCl_2$
10.0 g. Sodium Acetate
40.0 ml. H_2O

Equivalent results were obtained.

EXAMPLE 9

The procedure of example 6 was followed, excepting that the "Hair Straightening Lotion" and the "Neutralizer" employed were as follows:

A. Hair straightening lotion containing monomer

Grams:
8.4 Ammonium thioglycollate.
10.0 Methacrylic acid.
13.2 (28%) ammonium hydroxide q.s. to 100 g. with water pH 9.3.

B. Neutralizer

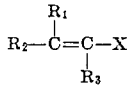
1.0 Ammonium persulfate
2.0 $CaCl_2$.
0.2 Acetic acid q.s. to 100 g. with water.

Equivalent results were obtained.

Although the invention has been described with reference to specific forms thereof, it will be understood that many changes and modifications may be made without departing from the spirit of this invention.

What I claim is:

1. A process for simultaneously permanently deforming hair and polymerizing therein a vinylic monomer which comprises treating said hair with a reducing agent and a polymerizable vinylic monomer; said vinylic monomer being a compound of formula:

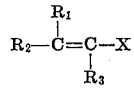


in which R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, aryl and halide; R_3 is selected from the group consisting of hydrogen, alkyl, carboxyalkyl, aryl and halide and X is an acid group or a salt thereof; said reducing agent being effective to rupture disulfide linkages between keratin molecules and to deform said hair and to polymerize said vinylic monomer; said reducing agent being selected from the group consisting of water-soluble bisulfite and thioglycollate salts.

2. A process according to claim 1 including neutralizing the action of said reducing agent with an oxidizing agent.

3. A process according to claim 2 wherein said polymerization is effected by means of the redox couple formed by said reducing agent and said oxidizing agent.

4. A process for deforming hair comprising treating said hair with a first composition comprising a reducing agent and a water-soluble polymerizable vinylic monomer containing an acid group or salts thereof, allowing said composition to remain in contact with said hair for sufficient time to cause the softening of said hair; and then treating said hair with a second composition containing an oxidizing agent capable of rehardening said hair and a bridging agent whereby long-chain polymers of said vinylic monomers bridged by said bridging agents are formed in said hair; said vinylic monomer being a compound of formula:



in which R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, aryl and halide; R_3 is selected from the group consisting of hydrogen, alkyl, carboxyalkyl, aryl and halide and X is an acid group or a salt thereof; said reducing agent being effective to rupture disulfide linkages between keratin molecules and to polymerize said vinylic monomer.

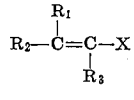
5. A process according to claim 4 wherein said hair is wound on a mandrel during treatment whereby the hair is waved.

6. A process according to claim 4 wherein the hair treated is curly hair and the hair is combed periodically during treatment whereby the curly hair is straightened.

7. A process according to claim 4 wherein said reducing agent comprises about 1.5 percent to 10 percent by weight of said first composition; said vinylic monomer comprises about 2 percent to 20 percent by weight of said first composition; said oxidizing agent comprises about 2 percent to 15 percent by weight of said second composition and said bridging agent comprises about 0.1 percent to 5 percent by weight of said second composition.

8. A process according to claim 4 wherein said reducing agent is selected from the class consisting of sodium bisulfite and ammonium thioglycollate; said vinylic monomer is sodium acrylate; said oxidizing agent is ammonium persulfate and said bridging agent is calcium chloride.

9. A process for simultaneously deforming hair and polymerizing therein a vinylic monomer which comprises treating said hair with a reducing agent and a polymerizable vinylic monomer, and bridging the polymeric chain so formed with a bridging agent whereby the solubility of said polymer is reduced; said vinylic monomer being a compound of formula:



in which R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, aryl and halide; R_3 is selected from the group consisting of hydrogen, alkyl, carboxyalkyl, aryl and halide and X is an acid group or a salt thereof; said reducing agent being effective to rupture disulfide linkages between keratin molecules and to polymerize said vinylic monomer.