United States Patent [19]

Ghilardi et al.

[11] **3,736,944**

[45] **June 5, 1973**

[54] **COMPOSITIONS AND PROCEDURES FOR EFFECTING A PERMANENT WAVE OR SET IN THE HAIR**

[75] Inventors: **Guiliana Ghilardi, Gregoire Kalopissis, Henri Philippe De Beaulieu, Jean-Louis Abegg,** Le Perreux, all of Paris, France

[73] Assignee: **Societe Anonyme dite:** L'Oreal, France

[22] Filed: **Dec. 17, 1971**

[21] Appl. No.: **209,470**

Related U.S. Application Data

[62] Division of Ser. No. 844,645, July 24, 1969, Pat. No. 3,676,546.

[52] **U.S. Cl.** **132/7,** 424/71

[51] **Int. Cl.** **A45d 7/04**

[58] **Field of Search** 132/7; 424/71

[56] **References Cited**

UNITED STATES PATENTS

3,349,000 10/1967 Joos 424/71

Primary Examiner—Hugh R. Chamblee
Assistant Examiner—Gregory E. McNeill
Attorney—Cushman, Darby & Cushman

[57] **ABSTRACT**

A composition for use in the neutralizing stage of a permanent wave operation. The active component of the composition contains an



group where R is hydrogen or lower alkyl. The neutralizing composition can be used with an oxidant which reacts with the active component to increase the temperature of neutralization. The neutralizing composition may be applied to the hair before or after it is placed on rollers.

5 Claims, No Drawings

COMPOSITIONS AND PROCEDURES FOR EFFECTING A PERMANENT WAVE OR SET IN THE HAIR

This application is a division of Ser. No. 844,645 filed Jul. 24, 1969 now U.S. Pat. No. 3,676,546.

The present invention is concerned with certain novel neutralizing compositions and procedures for using the same to effect a permanent wave or set in the hair.

It is known that, in order to confer a durable hair wave, it is necessary to go through a permanent hair setting which is normally carried out in two stages. In the first stage, the hair is treated with reducing agents which usually are thiols so as to reduce the disulphide bridges of the keratin. The hair is then rolled up on hair rollers or wave set rollers, and thereafter treated a second time with an oxidizing solution which reforms the disulphide bridges and thus fixes the keratin fiber in the form which has been given by the rollers. This second operation and the remainder of the treatment is usually called the fixation or neutralization of the permanent.

The oxidizing solutions used for the fixation most often contain oxygenated water, although it is possible to use other conventional oxidizing agents for this operation.

The use of oxygenated water to effect the fixation phase of the permanent is accompained by certain inconveniences in some cases. Thus oxygenated water used at full strength is able to produce significant modifications in the keratin fibers which have already been degraded by the disulphide reduction. This inconvenience is particularly limiting in the case where one desires the effect of a permanent wave which is a variant of the permanent procedure. Accordingly, the hair rolled on the permanent hair rollers is dried most often under a hairdryer immediately after the fixation operation.

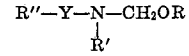
It is known that classic wave set effects are obtained by impregnating the hair with a wave setting lotion, thereafter rolling the hair up on hair rollers and then drying the hair on these rollers. The permanent wave set differs essentially from the classic wave set by the fact that the hair rolled up on the wave set rollers is submitted to a phase of reduction, then to a phase of neutralization before being dried on the same rollers. The oxidizing concentration of the neutralizing mixture is always less than the oxidizing concentration of neutraliziing mixtures for classic permanents.

Nevertheless, if one uses as the neutralizing mixture of a permanent wave set a solution of oxygenated water having a concentration comprising between six and eight volumes and one does not take the precaution of rinsing carefully the hair already rolled on the rollers before drying, one risks a partial discolorization of the hair. This is the reason why it is preferred, in this case, to replace the oxygenated water with compounds such as polythionates which are not as damaging on the keratin fiber. However, because of this, it has been realized that in order to give the hair style and brilliance, a cosmetic resin must be used.

According to the invention, it has now been surprisingly found that certain compounds having in common the characteristic of a methylol group attached to an atom of nitrogen can be very effectively used to carry out neutralization of keratinous fibers which have gone through the first phase of the permanent operation while at the same time strenghtening the fibers by the

formation of resin within the fibers due to polymerization of the methylol compounds.

Thus, the present invention provides a neutralizing composition to carry out the second phase of the permanent operation which includes a compound having the formula I:

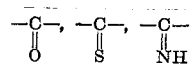


in which:

R represents a hydrogen atom or a lower alkyl radical,

R′ represents a hydrogen atom or alkyl radical, hydroxymethyl or alkoxymethyl or a radical of the type Y-R″

Y represents a radical

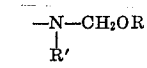


or $-SO_2-$,

or again a radical

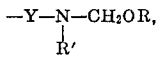


forming with R″ a nitrogen heterocyclic ring which is able to present other groups



R″ represents a hydrogen atom, an alkyl or alkoxy radical, this radical optionally containing amide or carbamate groups optionally substituted on the nitrogen atom by hydroxymethyl groups. R″ may also represent an amino group optionally substituted by an alkyl, cyano, $-CH_2OR$, aryl, alkylaryl such as phenyl or toluyl radical,

the radicals R′ and R″ may also together form a cyclic ring which contains one or more other heteroatoms and/or other groups

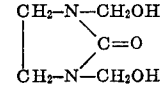


optionally with further substituents such as hydroxyl groups, lower alkyl radicals,

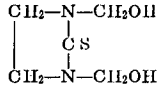
the concentration of the compound in said composition being between 0.5 and 12 percent by weight and the pH of the composition being between 1.5 and 6.

Among the N-methylol compounds which may be used in the neutralizing composition according to the invention, the following examples may be cited:

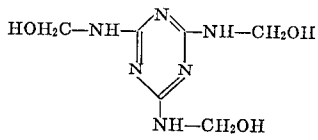
dimethylol ethylene urea of the formula:



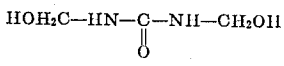
dimethylol ethylene thiourea of the formula:



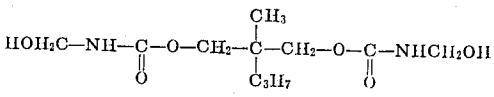
trimethylolmelamine of the formula:



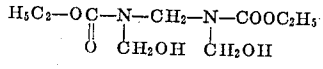
dimethylolurea of the formula:



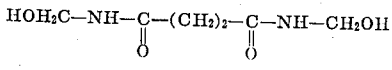
N,N'-dimethylol (2-methyl 2-propyl) propylene bis carbamate of the formula:



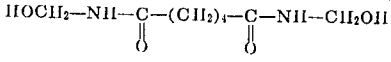
dimethylol methylene bis ethyl carbamte of the formula:



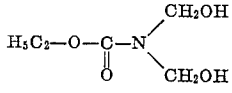
dimethylol succinamide of the formula:



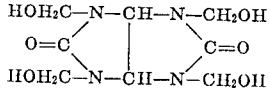
dimethylol adipamide of the formula:



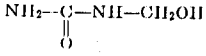
dimethylol ethyl carbamate of the formula:



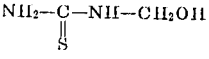
tetramethylol diethyleneurea of the formula:



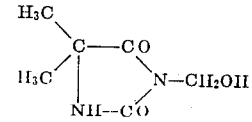
monomethylolurea of the formula:



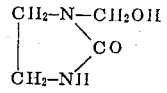
monomethylol thiourea of the formula:



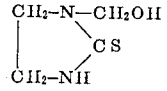
monomethylol dimethylhydantoin of the formula:



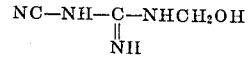
monomethylol ethylene urea of the formula:



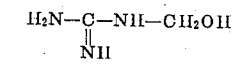
monomethylolethylene thiourea of the formula:



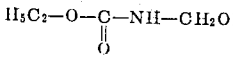
monomethyloldieyandiamide of the formula:



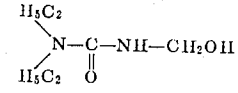
monomethylol guanidine of the formula:



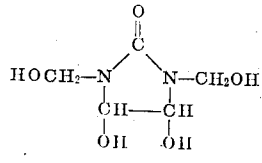
monomethylolethyl carbamate of the formula:



monomethylol diethylurea of the formula:



N,N' -dihydroxymethyl dihydroxyethylene urea of the formula:



The neutralizing composition according to the invention may also include an oxidizing agent utilized in a conventional manner for carrying out of the second phase of the permanent. However, it should be noted that the quantity of such oxidizing agent may be very notably less than the quantity of the same oxidizing agent when used in conventional neutralizing solutions which do not include an N- methylol compound according to the invention. Thus, for example, the neutralizing lotions of the invention may effectively reduce the amount of oxygenated water employed to a concentration of about two volumes.

Particularly unique results are obtained according to the invention by using a neutralizing composition con-

taining a compound of the formula I wherein Y represents the group



It appears that when an oxidizing compound is used in the present compositions or therewith it causes oxidation of the compound of formula I which gives a significant rise in temperature that facilitates neutralization of the permanent. Furthermore, in the case of a neutralizer or permanent wave set, this elevation of temperature of the compound contributes effectually to the drying of the hair.

Accordingly, as a further aspect of the invention, there is provided a composition which can be used to effect the neutralization of a permanent or a permanent wave set, the composition being characterized by the fact that it contains at least one compound of formula I, particularly one in which Y represents the group



and at least one oxidizing compound which is introduced for the purpose of reacting with the compound of formula I so as to give a substantial temperature increase to the composition.

The oxidizing compounds which may be utilized in the composition according to the invention include, for example, oxygenated water, persalts or peroxides such as urea peroxide of the perborate of sodium or ammonium persulfate, sodium percarbonate or salts such as sodium bromate or potassium chlorate.

The quantity of oxidizing compounds which is added at the time composition according to the invention is used to effect the desired temperature rise is such that the moles of the formula I compound wherein Y represents



is between 0.1 and 10 times the number of oxygen molecules added to the composition. It is essential that the mount of oxidizing agent introduced into the composition according to the invention be sufficient to effect an elevation in temperature.

However, in order to keep the emission of heat from being too harsh, it is preferable to utilize a concentration of the compound of formula I and the oxidizing compound less than 1.7 molecules per liter. The quantity of heat released can be regulated by taking into account the conversion of the number of reducing molecules to the number of oxidizing molecules.

The pH of the fixing composition generally is between 1.5 and 6. Nevertheless, where the composition contains dimethylol ethylene thiourea, the pH may be between8.5 and 10.

The neutralizing composition according to the invention is equally able to contain all other conventional agents in the composition in order to make effective the second phase of the permanent or permanent wave set such as cationic compounds, resin, coloring, perfume, surfactant, penetrating agent, pepticide, etc.

The neutralizing composition may be used in the form of an aqueous or alcohol lotion, cream, gel or aerosol.

The fixing composition may be an aqueous solution equally containing another solvent such as butyl-glycol, diethyleneglycol, glycerine, ethyl alcohol. Particularly interesting results are obtained when a mixture containing 25 percent water and 75 percent alcohol is used.

In a preferred operation, the compositions according to the invention are made up in two separate parts to be mixed at the moment of use, the first part containing the compounds of formula I and the second part containing the oxidizing compound.

As an example, the first part can be made up of the compounds of formula I in the form of powder while the second part can be made up of a hydroalcoholic solution of the oxidizing compound.

The compounds according to the present invention may also contain polymers for hair setting and particularly cationic polymers.

The present invention also provides a new procedure to effect the second stage of a permanent operation or permanent wave set, characterized by soaking the hair after it has been set with the help of a composition such as described above.

In the first method preferred according to the invention, the neutralizing composition is applied to the hair which has been previously set on rollers after which the hair is dried on the rollers with help of heat, for example, by means of a hairdryer. This method presents important advantages over the permanent setting technique previously used. First of all, it is not necessary to rinse the neutralizing mixture before drying the hair. The methylol compounds present in the mixture are capable of polymerizing with or in the keratinic fibers which as a result strengthens the fibers and augments the hold of the set.

In a second method which is preferred according to the invention, the neutralizing composition is applied on the hair before it is set on the rollers, then it is dried with heat under a hairdryer. This method presents the advantage of being more simple, since it is easier to impregnate the hair with the fixing lotion before the hair is rolled on the rollers.

Another important method contemplated by the present invention for effecting the second stage of the neutralization of the hair permanent wave operation is characterized by impregnating previously reduced hair with a mixture including at least one compound of the formula I in which Y represents



to which there is added at the time of use an oxidizing compound which reacts with the compound of formula I in which Y represents



to give a notable rise in temperature of the mixture with the advantages indicated above.

In a variant of the procedure described here, neutralization of the permanent wave set may be carried out in an equally effective manner by applying first the mix-

ture having the compound of formula I in which Y represents



and then applying immediately after a mixture having an oxidizing agent.

In the particular situation where the fixation of the permanent wave set is effected with the help of a composition giving rise to a release of heat on the hair, it is necessary to acidify the hair at the end of the fixation reaction in the case where the oxido-reduction reaction is conducted in a solution having a neutral or basic pH in a manner to effect the formation of a polymer on the hair.

It is equally possible in this way to acidify the hair before the application of the composition.

The following examples are given for purposes of illustration:

EXAMPLE 1

Hair was given a shampoo and thereafter placed in rollers. Each roller was saturated with a reducing mixture of the following formula:

ammonium thioglycolate	9.5 g
ammonium bicarbonate	12 g
perfume	0.2 g

This mixture was left on the hair with a plastic hair covering for 15 minutes. The hair was then rinsed of this solution and a neutralizing mixture according to the invention and having the following formula was applied to each roller:

dimethylol ethylene urea	5 g
glycerine	0.5 g
phosphoric acid q.s.p. pH 2.5	
coloring	0.2 g
water q.s.p.	100 cc

The hair was then dried under a dryer and there was obtained a permanent wave characterized by an excellent hold, the hair being vigorous, shiny, very lightly lacquered and easy to style.

There was not the least trace of discoloration, contrary to what would happen if a nautralizing composition of oxygenated water of six to eight volumes were used and the hair was dried without rinsing.

EXAMPLE 2

The same procedure was used as indicated in Example 1, a permanent wave set being effected by utilizing in order to effect the first stage of the permanent the following formula:

ammonium thiolactate	9 g
monethanolamine	2.5 g
triethanolamine laurysulfate	0.5 g
coloring	0.01 g
perfume	0.4 g

To effect the neutralization of the following formula was used:

dimethylol ethyleneurea	5 g
dimethylammonium cetyl bromide	0.5 g
oxygenated water	2 volumes
formic acid q.s.p. pH 2	
phenacetin	0.05 g
water q.s.p.	100 cc

The results obtained were the same as those indicated in Example 1.

EXAMPLE 3

After shampooing, the following reducing mixture was applied to bleached hair:

ammonium thioglycolate	8 g
ammonium bicarbonate	6 g
wax 700 AO	4 g
perfume	0.3 g
water q.s.p.	100 cc

This mixture was in the form of a cream.

The mixture was left on the hair, free of hair covering for 15 minutes. The hair was then rinsed and the following neutralizing lotion was then applied:

dimethylol ethylene thiorea	5 g
ethyl alcohol	20 g
vinylpyrrolidone/vinyl acetate copolymer	1 g
cetyl trimethylammonium bromide	0.5 g
lactic acid q.s.p. pH 2	
coloring	0.01 g
water q.s.p.	100 cc

The hair was then rolled on rollers and dried under the hair dryer. The results obtained are a permanent wave of excellent hold, hair that is shiny, easy to comb out and style and presenting a certain lacquer.

The technique of setting described in this example has the advantage over the others of being easier since the hair is not rolled on the rollers until after it has been soaked with the neutralizing solution.

EXAMPLE 4

The same procedure was used as described in Example 3, the bleached hair being soaked with the following reducing formula:

thioglycolic acid	6 g
ammonia q.s.p. pH 8.7	
sodium salt of dithiodiglycol	10 g
carbopol	4 g
perfume	0.3 g
water q.s.p.	100 cc

This composition was used in the form of a gel. The mixture was left on the hair with a plastic hair covering for 10 minutes. The hair was then rinsed and soaked with a neutralizing solution of the following formula:

dimethylolethylene urea	5 g
silicone oil (huile)	0.3 g
peptisant	0.5 g
perfume	0.1 g acetic acid q.s.p. pH 1.5
water q.s.p.	100 cc

A permanent wave set was obtained with the same characteristics as that described in Example 3.

EXAMPLE 5

The hair is shampooed and then rolled on the rollers. Each roller is then saturated with a reducing composition of the following formula:

ammonium thioglycolate	9.5 g
ammonium bicarbonate	12 g
perfume	0.2 g
water q.s.p.	100 cc

This mixture is left on the hair (under a plastic hair covering) for 15 minutes. The hair is rinsed and then a neutralizing composition is applied that has been pre-

pared at the moment of use by dissolving 1 g of dimethylol ethylene thiourea or a solution containing:

cetyl-trimethyl-ammonium bromide	0.3 g
phenacetin	0.05 g
sulfate of oxyquinoleine	0.0125 g
ethyl alcohol	10 cc
oxygenated water q.s.p.	2 volumes
lactic acid q.s.p. pH 9	
water q.s.p.	100 cc

It is observed that the temperature of the mixture increases, which accelerates the drying of the permanent wave set. A set was obtained showing excellent hold, with the hair being terse, shiny, very lightly laquered and easy to style.

EXAMPLE 6

On a natural head of bair, a cold permanent according to the conventional technique is realized.

The reducing solution used for the first phase of the permanent is as follows:

ammonium thioglycolate	9 g
mono-ethanolamine q.s.p. pH 9.5	
perfume	0.3 g
water q.s.p.	100 cc

This solution is left in contact with the hair rolled on the adequate rollers for 15 minutes. After rinsing, a neutralizing composition is applied to the rollers, this solution being prepared at the moment of use by mixing a powder containing:

dimethylol ethylene thiourea	3 g
sodium bromate	13.3 g
sodium perborate	12.7 g

with a solution containing:

cetyl trimethylammonium bromide	0.7 g
formic acid	1 g
water q.s.p.	100 cc

This composition is left on the hair for several minutes; it is observed that the temperature of the composition rises. The rollers are then taken out of the hair and the head of hair is left as such for 5 to 10 minutes and is then rinsed.

A permanent giving an excellent hold is thus obtained.

EXAMPLE 7

A permanent for hair dyed with the help of an oxidizing agent coloring follows the conventional treatment. The reducing solution used for the first phase of the permanent has the following composition:

ammonium thioglycolate	5.5 g
ammonium bicarbonate	5 g
perfume	0.2 g
water q.s.p.	100 cc

The fixing solution is prepared at the moment of use, using 4 g of dimethylol ethylene thiourea in a solution containing:

cetyl trimethylammonium bromide	0.7 g
para ethoxy-acetanilide	0.05 g
sulfate of oxyquinoleine	0.0125 g
citric acid	0.125 g
oxygenated water q.s.p.	9.8 vol.
water q.s.p.	100 cc

Each roller is impregnated with the fixing solution and the temperature of the solution is augmented. A permanent of excellent quality is equally obtained in this case.

Example 8

The same operation as indicatd in example 6 is used; a neutralizing composition is obtained by dissolving, at the moment of use, 3.4 g of dimethylolthiourea in a solution containing:

citric acid	0.15 g
para ethoxy-acetanilide	0.05 g
sulfate of oxyquinoleine	0.01 g
dimethyl-dilaurylammonium chloride, as a 75% solution in isopropanol	0.3 g
H_2O_2 q.s.p.	9.8 vol.
water q.s.p.	100 cc

The temperature of the neutralizing composition is elevated from the application on the rollers and facilitates the fixation of the permanent.

EXAMPLE 9

The same procedure as indicated in example 6 is used, a hair permanent utilizing a neutralizing composition that is prepared at the moment of use by dissolving 8 g of dimethylol ethylene thiourea in a solution containing:

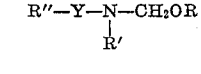
sodium percarbonate	15 g
cetyl trimethylammonium bromide	0.4 g
water q.s.p.	100 cc

The temperature of the neutralizing composition in augmented out of the application on the rollers and facilitates the fixation of the permanent.

Various modifications may be made in the invention as described above without deviating from the scope thereof as defined in the following claims wherein:

We claim:

1. A process for effecting the second phase of a permanent or permanent wave set operation of the hair in which the hair is soaked, after previously being reduced, with a composition including at least one active compound of the following formula:

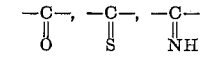


in which:

R represents hydrogen or lower alkyl,

R′ represents hydrogen, alkyl, hydroxymethyl or alkoxymethyl or a radical or type — Y — R″,

Y represents

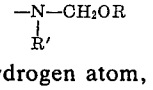


or $-SO_2-$,

or a radical

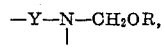


forming with R″ a nitrogen heterocyclic ring able to present other groups



R″ represents a hydrogen atom, an alkyl or alkoxy radical, this radical optionally containing amide or carbamate groups optionally substituted on the nitrogen atom by hydroxymethyl groups. R″ may also represent an amino group optionally substituted by an alkyl, cyano, $-CH_2OR$, aryl alkylaryl such as phenyl or toluyl radical,

the radicals R′ and R″ form together a ring which includes one or more other hetero atoms and/or other groups



and a carrier for said compound, said compound comprising between 0.5 and 12 percent by weight of the compositon and the pH of said composition being between 1.5 and 6.

2. A process according to claim **1** in which the neutralizing mixture is applied on the hair after it has been put on permanent wave rollers, the hair being thereafter dried.

3. A process according to claim **1** in which the neutralizing mixture is put on the hair before it is put on rollers after which the hair is put on rollers and dried.

4. A process according to claim **1** where the hair is soaked, after previously being reduced, with a solution containing said active compound where Y represents



in conjunction with the application of an oxidant which reacts on said active compound to raise the temperature and facilitate the neutralization reaction.

5. A process according to claim **4** characterized by the fact that the head of hair is acidified in the case where the oxido-reduction reaction contains a solution having a neutral pH or basic for the purpose of effecting the polymerization of said active compound.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,736,944 Dated June 5, 1973

Inventor(s) Guiliana Ghilardi, Gregoire Kalopissis, Henri Philippe De Beaulieu and Jean-Louis Abegg

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading, please insert --

Foreign Application Priority Data

July 25, 1968	Luxembourg	56,584
July 9, 1969	Luxembourg	59,072--

Signed and sealed this 23rd day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE 1969 O-366-334