# United States Patent

**Kalopissis et al.**

[15] **3,678,157**

[45] **July 18, 1972**


## [54] HAIR TREATMENT COMPOSITIONS CONTAINING POLYCONDENSABLE COMPOUNDS


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

[73] Assignee: **Societe anonyme dite: L'Oreal**



[22] Filed: **Oct. 23, 1968**

[21] Appl. No.: **770,074**

[52] **U.S. Cl.**.....**424/71,** 8/127.51, 8/127.6, 132/7, 260/246 B, 260/247.1, 260/247.2 A, 260/295 E, 260/295 G, 424/47, 424/70

[51] **Int. Cl.** .....**A61k 7/10**

[58] **Field of Search**.....260/246, 247.1, 247.2, 247.2 A, 260/553 R; 424/70, 71, 72; 8/116.2, 116.3, 127.51, 127.6



[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,203,493 | 6/1940 | Evans et al. | 8/116.3 |
| 2,203,504 | 6/1940 | Piggott et al. | 260/553 X |
| 2,203,505 | 6/1940 | Piggott et al. | 260/553 X |
| 2,203,506 | 6/1940 | Piggott et al. | 260/553 X |
| 2,220,508 | 11/1940 | Bock et al. | 260/553 X |
| 2,340,046 | 1/1944 | D'Alelio | 260/553 X |
| 3,065,110 | 11/1962 | Hagge et al. | 260/553 X |
| 3,310,539 | 3/1967 | Convert et al. | 260/246 X |
| 3,098,693 | 7/1963 | Sheehan | 424/71 X |

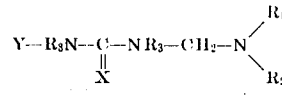


*Primary Examiner*—Albert T. Meyers
*Assistant Examiner*—Vera C. Clarke
*Attorney*—Holcombe, Wetherill & Brisebois



[57] **ABSTRACT**

A composition for treating hair containing a cosmetically effective amount of a polycondensable compound having the formula:



(1)

in which:

Y is selected from the group consisting of H, hydrocarbon chains comprising one to 30 carbon atoms, groups consisting of cosmetic constituents which have —S—S, —SH, —COOH, basic quaternary ammonium, and fatty chain groups,

X is selected from the group consisting of O, S and NH,

$R_1$ and $R_2$ are selected from the group consisting of lower alkyl and together may form a heterocyclic group, comprising nitrogen and/or oxygen atoms,

$R_3$ is selected from the group consisting of H, alkyl, and the two $R_3$ groups may form a heterocyclic group, comprising nitrogen and/or oxygen atoms.


**4 Claims, No Drawings**

# HAIR TREATMENT COMPOSITIONS CONTAINING POLYCONDENSABLE COMPOUNDS

## SPECIFICATION

This invention relates to a cosmetic composition for improving the condition of human hair and imparting thereto properties which are advantageous when the hair is to be subsequently subjected to a cosmetic treatment.

It is known that the hair is more or less degraded by the action of atmospheric agents such as the sun and sea water, and by chemical treatments to which it is subjected, for example, during permanent waving and bleaching.

The effects of such degradation may be to a large extent eliminated by using the compositions according to the present invention.

It has already been proposed that the strength and elasticity of the hair be increased by treating it with compounds which may be polymerized inside the keratinic fiber, and at the same time become attached to the reactive groups of the keratin.

Among the compounds heretofore suggested for this purpose are dimethylolurea and dimethylolthiourea, which have, however, the disadvantage of causing the release of a substantial quantity of free formol, the presence of which in contact with the scalp cannot be tolerated.

It has also been suggested that compounds which are more stable than dimethylolurea and dimethylolthiourea, that is to say, compounds which release much less free formol be used for this purpose.

However, these compounds have in common the characteristic of comprising hydroxymethyl groups which prevent them from being completely stable. Moreover, these products are difficult to prepare in a very pure state, from which it follows that the process of preparing them do not lead to rigorously reproducible results.

On the other hand, a great many of these compounds are difficult to dissolve in the aqueous solvents generally used in the cosmetic field.

In order to at least partially eliminate these disadvantages, it has been suggested that one might use, instead of the hydroxymethyl derivatives themselves, particular derivatives of these compounds obtained in a known manner by condensing them with secondary amines in accordance with the Mannich reaction.

The compounds produced in accordance with this reaction are more soluble, more stable, and easier to prepare than the corresponding hydroxymethyl compounds and are thus appreciably more satisfactory when used for the cosmetic purpose of strengthening the hair.

On the other hand, this method of treating the keratin of the hair also seeks to introduce into the hair reactive groups having a particular cosmetic value, at the same time that it strengthens the hair.

Specifically, cosmetic compounds having disulfide bonds have been chemically attached to the hair. This supplement to the S—S bonds improves the behavior of the hair and affects the action of the fiber with respect to the chemical reactants customarily used in the cosmetic field, such as reducing solutions containing mercaptans or sulfites, or oxidizing agents containing hydrogen peroxide, for example.

In like manner cosmetic compounds having carboxylic groups have been attached inside the hair. These additional acid groups greatly increase the affinity of the fiber for basic dyes.

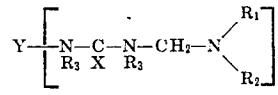
On the other hand, basic groups, or even fatty chains, have been introduced into the hair in order to increase the affinity of the hair for acid dyes, or improve the sheen and "feel" of the hair over a substantial period of time.

It has now been discovered that these different purposes may be served by using compounds having in their molecule both a function capable of causing polycondensation and a second function serving the other cosmetic purposes outlined above. In this manner, when this type of product is polycondensed in a conventional manner inside the keratin, the result



is to simultaneously achieve both the desired cosmetic effect and improved properties with respect to their mechano-elastic behavior.

It is the object of the present invention to provide a composition for treating or modifying the keratin of the hair essentially characterized by the fact that it comprises a cosmetically effective amount of a polycondensable compound having the formula:



(I)

in which:

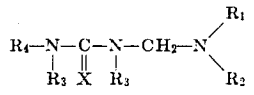
Y is selected from the group consisting of H, hydrocarbon chains comprising one to 30 carbon atoms, groups consisting of cosmetic constituents which have —S—S—, —SH, —COOH, basic quaternary ammonium, and fatty chain groups,

X represents oxygen, sulfur, or —NH,

$R_1$ and $R_2$ represent lower alkyl groups and may form part of a heterocyclic ring,

$R_3$ represents a hydrogen atom or an alkyl radical, and the two $R_3$ groups may be connected together to form a heterocyclic ring comprising nitrogen and/or oxygen atoms.

In one particular embodiment of the invention, the composition for treating or modifying the keratin of the hair comprises at least one polycondensable compound corresponding to the formula:



(II)

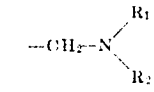
in which:

X represents oxygen, sulfur, or —NH,

$R_1$ and $R_2$ represent lower alkyl groups and may form parts of a heterocyclic ring, comprising nitrogen and/or oxygen atoms,

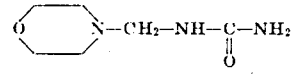
$R_3$ represents hydrogen, or an alkyl radical, and the two $R_3$ groups may be connected together to form a heterocyclic ring, comprising nitrogen and/or oxygen atoms,

$R_4$ represents hydrogen, an alkyl radical, or a radical corresponding to the formula:

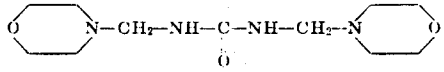


Among the polycondensable compounds which may be used in the composition according to the invention are:

monomorpholinomethylurea, having the formula:



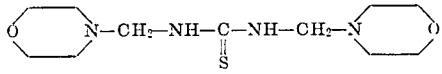
dimorpholinomethylurea, having the formula:



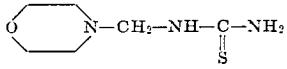
1. A composition for treating human hair comprising a solution in a solvent selected from the group consisting of water and hydroalcoholic solutions, of 0.5 to 12% by weight of a polycondensable compound selected from the group consisting of morpholinomethylurea quaternized with methyl iodide and methexymethylureidomethyl pyridinium chloride.

2. A composition according to claim / which also contains an acid catalyst selected from the group consisting of acetic acid, lactic acid, phosphoric acid, monosodium phosphate and monopotassium phosphate.

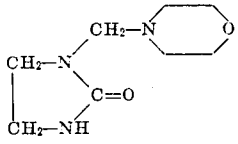
dimorpholinomethylthiourea, having the formula:



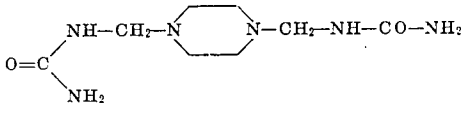
monomorpholinomethylthiourea, having the formula:



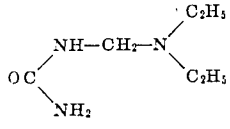
monomorpholinomethylethyleneurea, having the formula:



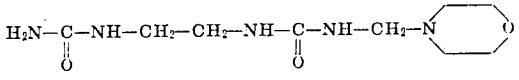
1,4-bis(carbamidomethyl)piperazine, having the formula:



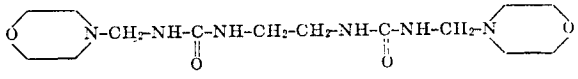
diethylaminomethylurea, having the formula:



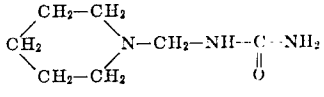
monomorpholinomethylethylene diurea, having the formula:



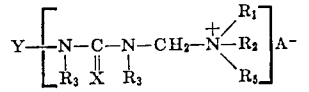
dimorpholinomethylethylene diurea, having the formula:



piperidinomethylurea, having the formula:



In one embodiment, the composition according to the invention comprises a group having the formula:



(III)

in which:

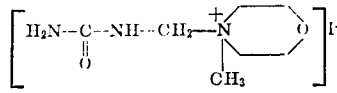
X, $R_1$ $R_2$ $R_3$ and Y have the significances set forth in formulas I and II,

$R_5$ represents an alkyl radical or a radical having a function or chemical bond imparting a cationic property to the nitrogen and,

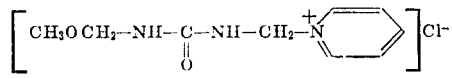
$A^-$ represents an anion of the halide or sulfate type.

Among the polycondensable compounds of this type which may be used in the composition according to the invention are:

morpholinomethylurea quaternized with methyl iodide having the formula:



methoxymethylureidomethyl pyridinium chloride having the formula:

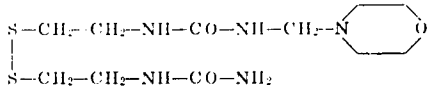


In a preferred embodiment of the invention the group according to the above formula I is attached to a group having a chemical function which is especially reactive with respect to conventional cosmetic reagents, which group is hereinafter referred to as the "cosmetic constituent" and corresponds to group $R_4$ in formula II.

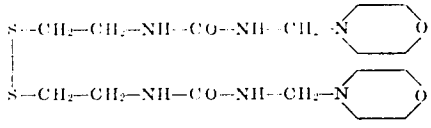
Among the cosmetic constituents suitable for use in carrying out the present invention are those groups having a disulfide function, a thiol function, a carboxylic acid function, a basic or quaternary ammonium function, or a fatty chain.

Among the cosmetic constituents which may be used in compositions according to the invention are:

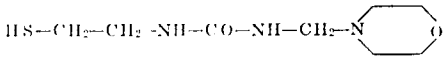
(N-carbamyl-N'-morpholinomethylcarbamyl)cystamine, having the formula:



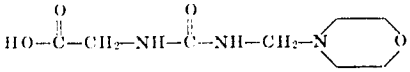
N,N'(morpholinomethylcarbamyl)cystamine, having the formula:



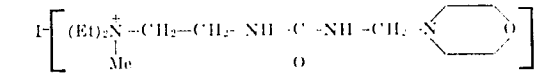
N(morpholinomethylcarbamyl)cystamine, having the formula:



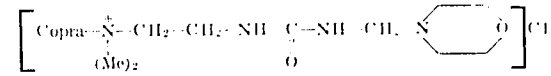
N(morpholinomethylcarbamyl)glycine, having the formula:



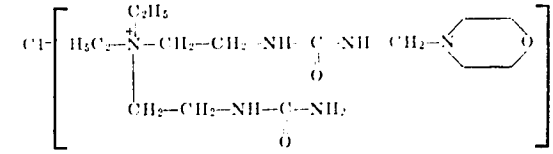
(diethyl-methyl-morpholinomethyl-ureidoethyl)ammonium iodide having the formula:



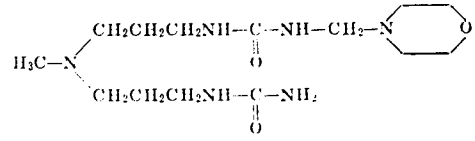
(dimethyl-copra-morpholinomethyl-ureidoethyl)ammonium chloride having the formula:



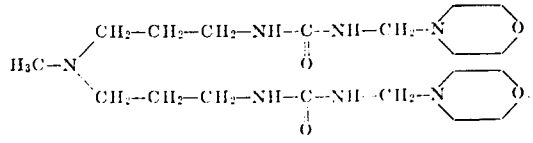
[N-(morpholinomethyl)-ethylurea-diethyl-ethylurea]ammonium chloride having the formula:



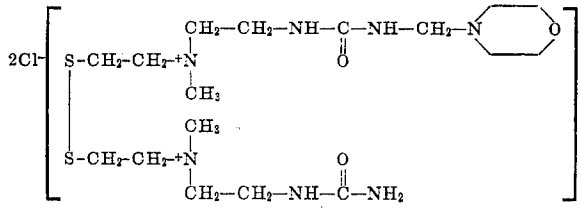
(methyl-propylurea-N-(morpholinomethyl)propyleneamine, having the formula:



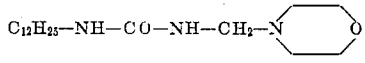
methyl di-[N-(morpholinomethyl)propylurea]amine having the formula:



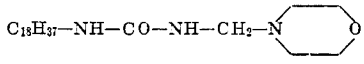
(N-dimethyl-ethylurea-N'-dimethyl-morpholinomethylureidoethyl) having the formula:



N=dodecyl-N'-(morpholinomethyl) urea



N-octadecyl-N'-(morpholinomethyl)urea

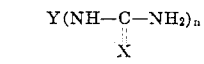


In a preferred embodiment of the invention the cosmetic compositions are in the form of aqueous or hydroalcoholic solutions containing 0.5 to 12 percent by weight and preferably 2 to 4 percent by weight of at least one polycondensable compound such as has been hereinbefore described. These cosmetic compositions may have a pH of 1.5 to 10.

The cosmetic compositions according to the invention may also contain an acid catalyst which may be either a mineral or an organic acid, such as phosphoric acid, acetic acid, etc, or an acid reaction salt such as monosodium and monopotassium phosphate capable of promoting the polycondensation of these compounds with the keratinic fiber when heated.

The cosmetic compositions according to the invention may also contain nitrogenous compounds of the urea family and in particular ureins, which may have cosmetic constituents of the type defined above attached to their nitrogen atoms.

Such ureins can correspond to the following formula



in which

X is selected from the group consisting of O, S, NH,

$n = 1$ or 2

Y is a chemical group which has cosmetic properties selected from the group consisting of disulfide, carboxylic acid, tertiary amine, quaternary amine, fatty chain and —SH groups.

The composition may also take the form of a gel, cream, or aerosol. It may also contain any conventional cosmetic additives, such as surface-active agents, penetrating agents, perfumes, resins, etc.

In accordance with the invention, the cosmetic composition may be packaged in two phases destined to be mixed at the moment of use on the hair, one phase being solid and containing the polycondensable compounds and the other phase being aqueous or hydroalcoholic and containing the acid catalyst and any conventional cosmetic additives.

In particular, the solid or aqueous phase of the cosmetic composition packaged in this manner may also contain a salt of sulfurous acid, such as sodium metabisulfite.

A further object of the present invention is to provide a new process for treating hair characterized by the fact that the hair is impregnated with the above composition, and dried by the application of heat, possibly after having been rinsed.

In a first method of carrying out this process, the cosmetic composition does not itself contain the acid catalyst necessary to cause polycondensation of the polycondensable compounds in the keratinic fiber, and this acid catalyst is instead applied directly to the hair either before or after applying the composition according to the invention.

In another method of carrying out this process, a cosmetic composition which does contain the acid catalyst is applied directly to the hair, which is then dried as previously described.

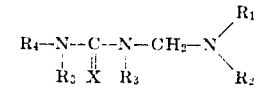
The treatment according to the invention makes it possible to substantially strengthen the keratinic fiber of the hair by



forming a polycondensate inside the hair which also becomes attached to the reactive groups of the keratin. In this manner it makes it possible to obtain sets of excellent quality when the hair is treated while wound up on setting rollers.

On the other hand, when the polycondensable compounds also comprise cosmetic constituents, the treatment according to the invention also makes it possible to carry out subsequent cosmetic treatments, such as bleaching, dyeing, permanent waving, etc., under greatly improved conditions.

It is a further object of the present invention to provide, as a new article of manufacture, compounds corresponding to the formula:



(II)

in which

X, $R_1$, $R_2$, $R_3$ are as defined above, and

$R_4$ represents a cosmetic constituent as hereinbefore defined.

The present invention comprises, in particular, the following new compounds:

N-(carbamyl-N'-morpholinomethylcarbamyl)cystamine, N,N'-(morpholinomethylcarbamyl)cystamine, N-morpholinomethylcarbamyl)cysteamine, N-(morpholinomethylcarbamyl)glycine, (diethyl-methyl-morpholinomethyl-ureidoethyl) ammonium iodide, (dimethyl-copra-morpholinomethyl-ureidoethyl) ammonium chloride, [N-(morpholinomethyl) ethylurea-diethyl-ethylurea]ammonium chloride, methyldi-[N-(morpholinomethyl)propylureahamine, methyldi-[N-(morpholinomethyl) propylurea]amine, and (N-dimethyl-ethylurea-N'-dimethyl-morpholinomethyl ureidoethyl) cystamine dichloride, the formulas for which compounds have been given above.

It is also an object of the present invention to provide a process for preparing the above-described new compounds, which process is characterized by the fact that, in a first step, a urein is prepared which contains the cosmetic constituent defined above by reacting a cyanate or an alkaline thiocyanate with a primary amino hydrochloride so that the nitrogen of the amine becomes attached to the cosmetic constituent.

In a second step, a reaction of the "Mannich" type such as described in "Organic Reactions" vol. 1, ch. 10, p. 303 and Houban Weyl XIV/2, pp. 342–354 is carried out by reacting the urein which has thus been formed with a secondary amine in the presence of formol, the reaction being carried out in aqueous solution, either at room temperature or at a temperature of about 50° to 60°C.

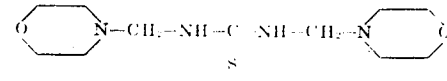
In an alternative process according to the present invention a tertiary amine is quaternized with a halogeno-ethylurea, so that the nitrogen of the amine becomes attached to a cosmetic constituent.

In a second step in this alternative process the urein compound obtained in the first step is reacted with a secondary amine in the presence of formol, as hereinbefore described.

In order that the invention may be better understood, several examples will now be described, purely by way of illustration.

## EXAMPLES OF PREPARATION

1. Preparation of dimorpholinomethylthiourea

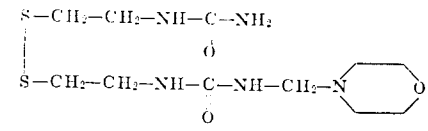


1 mol of thiourea is dissolved in two mols of formol in an aqueous 30 percent solution, at a temperature of 40°–50°C.

This is cooled below 20°C and 2 mols of morpholine are added slowly while keeping the temperature between 15° and 20°C. This is then cooled to −10°C until the dimorpholinomethylthiourea crystallizes out. (This takes at least 24 hours.)

The result is a white crystalline solid which melts at 130°C. The yield of the reaction is 90 percent.

2. Preparation of (N-carbamyl-N'-morpholinomethylcarbamyl) cystamine



1 mol of N,N'-dicarbamyl-cystamine, 1 mol of formol in an aqueous 30 percent solution, 1 mol of morpholine and 500 cc of distilled water are mixed while stirring.

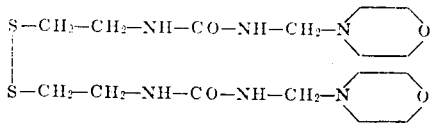
The resulting reaction is exothermic but it is nevertheless necessary to heat the mixture to 50°–55°C to dissolve the reagents. The mixture is then permitted to revert to the ambient temperature and cooled to −15°C. The reaction product solidifies, and is dried under vacuum on $P_2O_5$.

It is a white crystalline product. The yield of the reaction is better than 90 percent.

Total amines 3.0 meq/g Theoretical 2.96 meq/g

Tertiary amines 2.7 meq/g Theoretical 2.96 meq/g

3. Preparation N,N'-(morpholinomethylcarbamyl)cystamine.

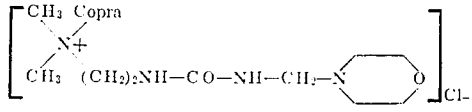


1 mol of N, N'-dicarbamyl cystamine, 2 mols of formol in an aqueous 30 percent solution, 2 mols of morpholine and 500 cc of distilled water are mixed together while stirring.

These are heated at about 55°–60°C until they are completely dissolved. After cooling, the mixture is evaporated under vacuum at a temperature below 40°C. The residue is a white crystalline product. The yield of the reaction is greater than 90 percent.

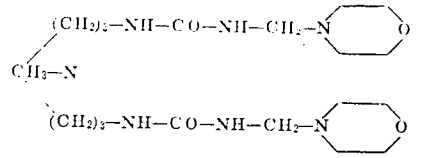
Tertiary amines 4.0 meq/g Theoretical - 4.6 meq/g

4. Preparation of (dimethyl-copra-morpholino-methylureidoethyl) ammonium chloride.



1 mol of (dimethyl-copra-ureidoethyl) ammonium chloride, prepared by quaternization of dimethyl-copra with chloroethylurea, is dissolved in distilled water. 1 mol of formol in an aqueous 30 percent solution is then added. Morpholine is then added slowly, while stirring. The reaction is exothermic. The temperature is kept near 50°C. When the temperature falls, the reaction mixture is evaporated until dry. This is redissolved by heating it in 2,400 cc of ethanol, and the mixture is then again evaporated until dry. The resulting product is a yellow oil, which after mixing with ether and vacuum drying, forms a translucent light-colored paste. The yield of the reaction is 87 percent.

5. Preparation of C².



1 mol of N-methyl-dipropylurea, 2 mols of formol in an aqueous 30 percent solution, and 2 mols of morpholine are mixed while stirring, and then heated for 30 minutes at 50°C. The reaction mixture is evaporated until dry, and after washing several times with ether and vacuum drying on $P_2O_5$, the result is a white crystalline product.

The yield of the reaction is 82.5%.

Total amines 6.57 meq/g Theoretical 7.0 meq/g

Tertiary amines 6.32 meq/g Theoretical 7.0 meq/g

## EXAMPLES OF APPLICATION

EXAMPLE I:

A head of hair is first bleached with a conventional oxidizing composition, rinsed, and dried. The hair is then impregnated with the following solution:

| | |
|---|---|
| monomorpholinomethylthiourea | 2 g |
| polyvinylpyrrolidone/vinyl acetate copolymer | 0.4 g |
| acetic acid, q.s.p. | pH=2.8 |
| water, q.s.p. | 100 cc |

A head of hair is then set and dried under a hood for 30 to 40 minutes at a temperature of about 45°–50°C. The hair is markedly hardened and is easily arranged. The tips of the hair appear to be in good condition. The set is springy, and lasts well.

EXAMPLE II:

A solution having the following composition is applied to natural hair which has first been washed and dried:

| | |
|---|---|
| 1,4-bis(carbamidomethyl)piperazine | 4 g |
| water | 100 cc |

The hair is then wound up on setting rollers and carefully impregnated with a 2 percent lactic acid solution. The hair is left to dry under a hood at about 45°C and a set of excellent quality results.

EXAMPLE III:

Hair which has been strongly bleached is impregnated with a solution obtained by mixing, at the moment of use, a powder containing:

| | |
|---|---|
| monomorpholinomethylurea | 6 g |
| urea | 1 g |

with 100 cc of a phosphoric acid solution diluted to a pH of 2.5.

The hair is dried while keeping the temperature between 40° and 45°C for about 30 minutes.

Hair which has thus been treated is permanently waved in a conventional manner. The results of this permanent are excellent, whereas it is usually impossible to give a satisfactory permanent wave immediately after bleaching.

EXAMPLE IV:

The following composition is applied to hair which has just been bleached in a conventional manner.

| | |
|---|---|
| (dimethyl-copra-morpholinomethyl-ureidoethyl ammonium chloride | 1 g |
| N-methyl di-[N-(morpholinomethyl)propylureagamine | 1 g |
| acetic acid, q.s.p. | pH = 2.5 |
| water | 100 cc |

The hair is then set in a conventional manner and excellent results are obtained with respect to resilience and holding power, as well as the condition, feel and sheen of the treated hair.

EXAMPLE V:

A solution having the following composition is applied to hair which is to be strongly bleached.

| | |
|---|---|
| N,N'-(morpholinomethylcarbamyl) cystamine | 4 g |
| phosphoric acid q.s.p. | pH = 2.5 |
| water q.s.p. | 100 cc |

The hair is then dried under a hood for about 30 minutes at a temperature of about 45°C.

The hair is then bleached with a conventional oxidizing agent. The quality of hair which has been thus bleached after being first treated in accordance with the invention is excellent, under both humid and dry conditions.

EXAMPLE VI:

The first step of a conventional permanent wave is carried out using the following composition:

| | | |
|---|---|---|
| N-(morpholinomethylcarbamyl)cystamine | | 1.3 g |
| N,N'-(morpholinomethylcarbamyl)cystamine | | 4 g |
| monoethanolamine, q.s.p. | pH = 9.5 | |
| water q.s.p. | 100 cc. | |

The hair is impregnated with this solution, wound up on rollers of the usual diameter, and again saturated with this solution. It is then left for 15 minutes under a plastic cap at room temperature. The hair is then rinsed, after which an aqueous solution of hydrogen peroxide at 6 volumes is applied. This solution has been brought to a pH of 1.5 by adding phosphoric acid.

The hair is then put under a hood and dried in a conventional manner. The result is a set of excellent quality, which lasts well, with the hair shiny with a very soft "feel."

EXAMPLE VII:

Natural hair, or hair which has first been bleached is permanently waved, using the following self-neutralizing composition:

| | | |
|---|---|---|
| thioglycolic acid | | 2 g |
| (N-carbamyl-N'-morpholinomethyl-carbamyl)cystamine | | 7 g |
| ammonia q.s.p. | pH = 9.5 | |
| water q.s.p. | 100 cc | |

and then keeping the hair wound up on rollers of small diameter, under a cap, for about 15 minutes.

The hair is then rinsed with a 2 percent lactic acid solution and set in conventional manner.

The result is a permanent which imparts excellent cosmetic properties to the hair, improving its sheen and giving it an agreeable feel.

The hair is springy and the wave lasts well when exposed to the weather.

What is claimed is:

1. A composition for treating human hair comprising a solution in a solvent selected from the group consisting of water and hydroalcoholic solutions of 0.5 to 12 percent by weight of a polycondensable compound selected from the group consisting of morpholinomethylurea quaternized with methyl iodide and methoxymethylureidomethyl pyridinium chloride.

2. A composition according to claim 1 which also contains an acid catalyst selected from the group consisting of acetic acid, lactic acid, phosphoric acid, monosodium phosphate and monopotassium phosphate.

3. A composition for treating human hair comprising a solution in a solvent selected from the group consisting of water and hydroalcoholic solutions, of 0.5–12 percent by weight of a polycondensable compound selected from the group consisting of

(N-carbamyl-N'-morpholinomethylcarbamyl)-cystamine;
N,N'-(morpholinomethylcarbamyl)cystamine;
N-(morpholinomethylcarbamyl)cysteamine;
N-(morpholinomethylcarbamyl)glycine;
(diethyl-methyl-morpholinomethyl-ureidoethyl) ammonium iodide;
(dimethyl-copra-morpholinomethyl-ureidoethyl) ammonium chloride;
[N-(morpholinomethyl)ethylurea-diethyl-ethylurea]ammonium chloride;
methyl-propylurea N-(morpholinomethyl)propylurea amine;
methyl di-[N-(morpholinomethyl)propylurea] amine;
(N-dimethyl-ethylurea-N'-dimethyl-morpholinomethylureidoethyl)cystamine dichloride;
N-dodecyl-N'-(morpholinomethyl)urea; and
N-octadecyl-N'-(morpholinomethyl)urea.

4. The composition according to claim 3 which also contains an acid catalyst selected from the group consisting of acetic acid, lactic acid, phosphoric acid, monosodium phosphate and monopotassium phosphate.

* * * * *

UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,678,157 Dated July 18, 1972

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

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, add

--Claims priority, application Luxembourg 54,745, October 26, 1967--

Signed and sealed this 15th day of January 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

8

FORM PO-1050 (10-69)

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

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,678,157 Dated July 18, 1972

Inventor(s) Gregoire Kalopissis et al

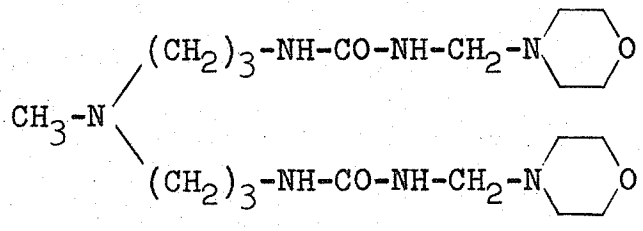
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, delete lines 70-75.

Column 3, delete lines 1-4.

Column 7, line 60, delete "$C^2$" and insert therefor --methyl-propylurea-N-(morpholinomethyl) propylurea amine--.

lines 61-67, delete the structural formula and insert therefor--



Signed and sealed this 8th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents



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