United States Patent [19]

Kalopissis et al.

[11] **3,757,804**

[45] **Sept. 11, 1973**

[54] **PRODUCT FOR TREATING HAIR**

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

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

[22] Filed: **July 18, 1968**

[21] Appl. No.: **745,667**

[52] **U.S. Cl.** **132/7**, 8/127.51, 8/127.6, 424/70, 424/71

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

[58] **Field of Search** 424/70, 71; 132/7

[56] **References Cited**

UNITED STATES PATENTS

2,372,159	3/1945	Manchey et al.	424/70 X
2,655,923	10/1953	Gallenkamp	424/71 X
2,836,185	5/1958	Hervey	424/71 X
2,836,543	5/1958	Watson	424/71 X
3,068,151	12/1962	Haefele	424/71
3,149,042	9/1964	Habicht et al.	424/70

OTHER PUBLICATIONS

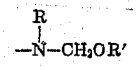
Sagarin, Cosmetics, Science And Technology, Interscience Publishers, Inc., N.Y., p. 609, Sept. 1957.

Wells et al., Cosmetics And The Skin, Reinhold Publishing Corporation, N.Y., p. 475, 1964.

Primary Examiner—Albert T. Meyers
Assistant Examiner—Frederick E. Waddell
Attorney—Holcombe, Wetherill and Brisebois

[57] **ABSTRACT**

New product for treating hair which comprises at least one methylol compound capable of polycondensation or polyaddition which comprises a group responding to the formula:



in which R represents H, a lowr alkyl, hydroxymethyl, or alkoxymethyl, and R′ represents H, or a lower alkyl, said N being attached to a remainder which is sufficiently electrophile to prevent the immediate release of formol; and

an alkaline salt of a sulphur acid in which the sulphur is at the fourth degree of oxidation and capable of forming a stable compound with formol.

1 Claim, No Drawings

PRODUCT FOR TREATING HAIR

This invention relates to new cosmetic compositions for improving the condition of living human hair which has become degraded.

It is well known that living human hair is often degraded either by environmental agents such as sun and sea water, or by chemical treatments such as permanent waving and bleaching.

In practice, these degradations show up in the form of a deterioration in the mechanical properties of the hair and by a roughness which leads to a substantial loss of sheen and attractiveness. Moreover, degraded hair is fragile, and breaks off easily.

It has already been suggested that, in order to improve its mechanical strength and elasticity, the hair be treated with compositions based on dimethylolurea and dimethylol thiourea. Those compositions substantially strengthen the hair, because, in the presence of an acid catalyst, they cause the formation of a resin within the keratinic fiber.

However, such a process is difficult to put into practice because of the poor stability of the said compositions, which liberate substantial quantities of formol, both while they are in storage and during the time required to apply the compositions to the hair and let it act thereon.

Formol is known to be a toxic substance which cannot be applied in any substantial quantity to the scalp without producing undesirable results, so that legislation in force in most countries prohibits the application of compositions containing more than about 0.2 percent formol to the skin or scalp.

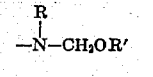
It follows that, for the same reason, the above cosmetic compositions, which are based on dimethylolurea and dimethylolthiourea, cannot be used, because at the time they are applied to the head, they contain concentrations of free formol which are greater than the concentration permitted by law.

It has already been suggested that cosmetic compositions be used which contain methylol compounds which are so stable that the formol concentration does not exceed 0.2 percent. It has also been suggested that methylol compounds be used in cosmetic compositions in admixture with nitrogenous compounds of the amide type, which make it possible to decrease the percentage of free formol in said compositions.

The present invention makes it possible to still further improve the quality of cosmetic compositions in this respect, since the compositions according to the present invention contain almost no free formol, while retaining the advantage of substantially strengthening the hair.

The object of the present invention is to provide a new article of manufacture which is characterized by the fact that it comprises in combination:

1. At least one methylol compound at least partially capable of being polycondensed or poly added which comprises at least one group responding to the formula:



in which:

R represents hydrogen, a lower alkyl, hydroxymethyl, or alkoxymethyl;

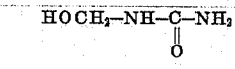
R′ represents hydrogen or a lower alkyl, the nitrogen atom of said group being attached to a remainder which is sufficiently electrophilic to assure the chemical stability of said group, that is to say, to avoid the immediate release of a formol molecule, and

2. At least one alkaline salt of a sulfur acid in which the sulfur is at the fourth degree of oxidation and which is capable of forming a stable combination with formol.

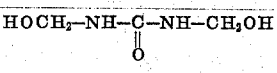
Among the suitable electrophilic groups are alkoxy group or a primary, secondary or tertiary amine to which methylol groups may be attached, but this list is by no means exhaustive.

Among the methylol compounds which may be used in accordance with the invention are:

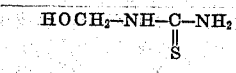
monomethylolurea responding to the formula:



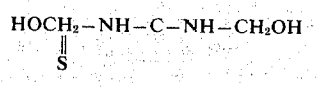
dimethylolurea responding to the formula:



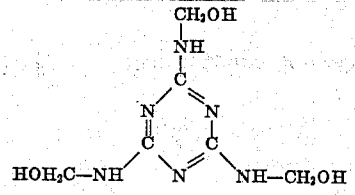
monomethylolthiourea responding to the formula:



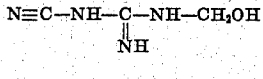
dimethylolthiourea responding to the formula:



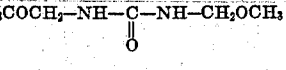
trimethylol melamine responding to the formula:



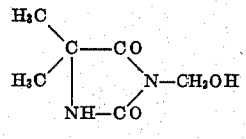
monomethyloldicyandiamide responding to the formula:



bismethoxymethylurea responding to the formula:

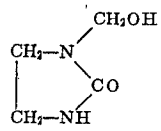


monomethyloldimethylhydantoin responding to the formula:

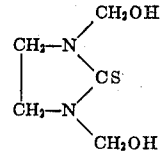


monomethylol ethyleneurea responding to the formula:

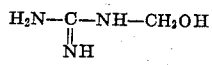
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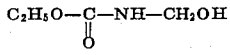
dimethylol ethylene thiourea responding to the formula:



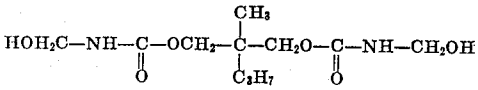
monomethylol guanidine responding to the formula:



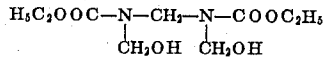
ethyl monomethylolcarbamate responding to the formula:



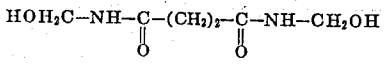
N, N'-dimethylol bicarbamate of (2-methyl-2-propyl) propylene responding to the formula:



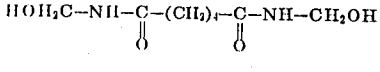
ethyl dimethylol methylene bicarbamate responding to the formula:



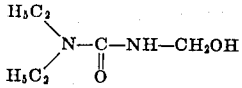
dimethylol succinamide responding to the formula:



dimethylol adipamide responding to the formula:

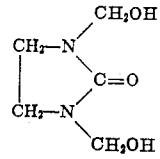


N,N-diethyl-N'-methylolurea responding to the formula:

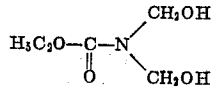


dimethylolethylene urea responding to the formula:

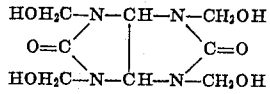
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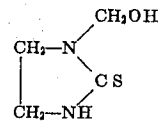
dimethylol ethylol carbamate responding to the formula:



tetramethylol acetylenediurea responding to the formula:



monomethylol ethylene thiourea responding to the formula:



Among the alkaline salts of a sulfur acid in which the sulfur is at the 4th degree of oxidation which are capable of forming a stable combination with formol are the neutral sulfites having the formula SO_3M_2, the acid sulfites having the formula SO_3HM, and the metabisulfites (or pyrosulfites) having the formula $S_2O_5M_2$, in which formulas M represents an alkaline metal.

In accordance with the invention, the concentration of the methylol products may vary within wide limits, but falls generally between 1 and 10 percent, and is in part dependent on the solubility of these products in water and in part on the state of the hair to be treated. Thus bleached hair is preferably treated with lower concentrations than natural hair.

The concentration of the alkaline salt of a sulfur acid capable of producing a stable combination with formol falls between one-fifth and one-fortieth of the concentration of the methylol components and preferably between one-tenth and one-twentieth thereof.

The cosmetic composition according to the invention may take the form of an aqueous or hydroalcoholic solution, may constitute a setting lotion, and may also contain any additives conventionally used in setting lotions.

The composition may also take the form of a gel, cream, or aerosol, and contain surface active agents, swelling agents, dyes, or perfumes.

It is a further object of the present invention to provide a method of packaging the composition characterized by the fact that the methylol products, in the solid state, are packaged separately from a solution contain-

ing the sulfur compounds capable of forming a stable combination with formol, which solution may also contain an acid catalyst.

With this arrangement the powdered methylol products may be dissolved in the acid solution containing the sulfur derivative at the moment of use.

It is also possible to package both the methylol products and the sulfur compounds in the solid state, and various conventional cosmetic additives in an aqueous solution which may contain an acid catalyst. Among the suitable acid catalysts are: phosphoric, sulfuric, lactic and acetic acids.

In all these cases, both the solid and liquid components may also contain other conventional cosmetic ingredients.

The cosmetic compositions according to the invention have the advantage of liberating only an infinitesimal quantity of free formol, since almost all the formol combines with the sulfur compound to form a stable compound having none of the harmful characteristics of free formol.

A further object of the present invention is to provide a method of treating hair characterized by the fact that it is impregnated with a cosmetic, such as has been hereinbefore described, that an acid polymerization catalyst is added if the solution does not already contain it, and that the hair is then dried by the application of heat. The hair may be rinsed before drying.

This leads to a group of reactions inside the keratinic fiber of the hair which tend to create bonds between the fibers and to strengthen the inner parts of the fibers by polymerization of the methylol compounds.

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

EXAMPLE 1

In order to set hair which has previously been bleached in a conventional manner, a powder containing the following components:

dimethylolurea	2 g
polyvinylpyrrolidone/vinyl acetate copolymer	0.4 g

is mixed at the moment of use with 100 cc of an 0.4 percent sodium bisulfite solution.

The resulting solution is applied to the hair, which is set in a conventional manner, with excellent results, especially with respect to the strength of the hair and its ability to hold a wave.

EXAMPLE 2

Under the same conditions as in Example 1, a solution obtained by mixing a powder containing:

dimethylol succinamide	4 g
potassium metabisulfite	0.2 g

and an acidic solution containing:

sulfuric, q.s.p. pH 1.5	
water	100 cc

is applied to bleached hair, which is then set in a conventional manner, yielding excellent results.

EXAMPLE 3

A composition obtained by mixing a powder containing:

monomethylolurea	6 g
monomethylol thiourea	3 g
sodium metabisulfite	0.6 g

with a solution containing:

trimethylcetylammonium bromide	0.1 g
water	90 cc

is applied to natural hair, which is then rolled up on setting rollers. The hair is next impregnated with 2 percent lactic acid solution, and left to dry under a hood. The resulting set shows excellent holding power, and the hair is markedly hardened.

EXAMPLE 4

A solution obtained by mixing a powder containing:

monomethylol dicyandiamide	2 g
disodium sulfite	0.1 g

with an acid solution containing:

lactic acid q.s.p. pH 2,5	
water	100 cc

is applied to bleached hair, which is then set in a conventional manner, and dried under a hood at a temperature of 45°–50° C. Hair treated in this manner is shinier, easier to comb, and has a more agreeable touch than hair which has been bleached, recolored, and set in an identical manner, but without recourse to the process according to the invention.

EXAMPLE 5

Bleached hair is first washed with a cationic acid shampoo and dried. The hair is then impregnated with a solution obtained by mixing a composition obtained by mixing a powder containing:

dimethoxymethylurea	3 g
polyvinylpyrrolidone/vinyl acetate copolymer	0.5 g
sodium metabisulfite	0.3 g

with a solution containing:

ethyl alcohol	25 cc
trimethylcetylammonium bromide	0.1 g
perfume	0.1 g
water	75 cc

The hair is rolled up on curlers, again saturated with this solution and dried under a hood for 30 to 40 minutes at about 45° C. The hair becomes strong and flexible and holds the set well.

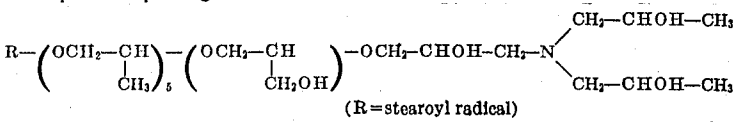
EXAMPLE 6

Bleached hair is treated with a composition obtained by mixing a powder containing:

methoxymethyl dicyandiamide	1 g
monomethylol dicyandiamide	1 g
polyvinylpyrrolidone/vinyl acetate copolymer	0.3 g
sodium metabisulfite	0.01 g

with a solution containing:

a compound responding to the formula:



(R=stearoyl radical) 0.1 g.

phosphoric acid q.s.p. pH 2.5
water 100 cc

The hair is rolled up on curlers and set in a conventional manner.

Excellent results are obtained.

EXAMPLE 7

Strongly bleached hair is treated with a composition obtained by mixing a powder containing:

monomethylolurea	8 g
monomethylol ethyl carbamate	1 g
sodium metabisulfite	0.8 g

with a solution containing:

acetic acid q.s.p. pH 3	
water	100 cc

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

Hair which has just been treated in this way is then permanently waved in a conventional manner. The results of this permanent waving are excellent, whereas a conventional permanent wave carried out immediately after strongly bleaching hair without treating the hair in accordance with the invention is generally unsatisfactory.

While the illustrative Examples show the use of sodium metabisulfite, it should be understood that similar results are obtained with other alkaline salts, such as potassium, or with other sulfur acid salts such as neutral sulfites, acid sulfites, etc.

What is claimed is:

1. A process for improving the condition of human hair which has become degraded comprising applying to said hair an effective amount of an aqueous solution of (1) a methylol compound selected from the group consisting of monomethylolurea, dimethylolurea, monomethylolthiourea, dimethylolthiourea, trimethylol melamine, monomethylol dicyandiamide, bismethoxymethylurea, monomethylol dimethylhydantoin, monomethylol ethylene urea, monomethylol ethylene thiourea, dimethylol ethylene thiourea, monomethylol guanidine, ethyl monomethylol carbamate, N,N'-dimethylol bicarbamate of (2-methyl-2-propyl) propylene, ethyl dimethylol methylene bicarbamate, dimethylol succinamide, dimethylol adipamide, N,N-diethyl-N'-methylolurea, dimethylol ethylene urea, dimethylol ethylol carbamate, tetramethylol acetylenediurea and their mixtures and (2) an alkaline salt of a sulfur acid selected from the group consisting of sulphite, bisulphite and metabisulphite of sodium and potassium, said alkaline salt being present in amounts of one-fifth to one-fortieth of the amount of said methylol compound, in the presence of an acid catalyst selected from the group consisting of phosphoric acid, sulfuric acid, lactic acid and acetic acid in amounts sufficient to polymerize said methylol compound, and drying said hair.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,757,804 Dated September 11, 1973

Inventor(s) Gregoire Kalopissis; Jean-Louis Abegg; Giuliana Ghilardi; and Henri Philippe deBeaulieu

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:

Foreign Application Priority Data

July 27, 1967 France 115,918

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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

DETACH HERE BEFORE MAILING THE TYPED CERTIFICATE TO THE PATENT OFFICE

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,757,804 Dated September 11, 1973

Inventor(s) 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:

Col. 2, between lines 30 and 34, the structural formula should read:

$$HOCH_2 - NH - \underset{\underset{S}{\|}}{C} - NH - CH_2OH$$

Col. 4, lines 9-10 should read:

dimethylol ethyl carbamate responding to the formula

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents