

[54] **PERMANENT WAVING OF HAIR WITH QUATERNARY AMMONIUM ALKYLATING AGENTS AND AMMONIUM THIOGLYCOLATE**

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Related U.S. Application Data

[63] Continuation of Ser. No. 598,959, Dec. 5, 1966, abandoned, which is a continuation-in-part of Ser. No. 212,158, July 24, 1962, abandoned.

[52] **U.S. Cl.**..... **132/7**, 8/127.51, 260/248.5, 260/249.5, 260/249.6, 260/249.7, 424/71, 424/72

[51] **Int. Cl.**..... **A45d 7/06**

[58] **Field of Search**..... 424/71, 72; 8/127.51; 132/7

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

1,150,943 7/1963 Germany 424/72

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[57] ABSTRACT

A method of permanently waving keratin substrates, such as hair, by applying thereto keratin softening agents and a quaternary ammonium halide salt keratin alkylating agent. Quaternary ammonium halide salts that make suitable keratin alkylating agents are mono, bis and tri quaternary reaction products or mixtures thereof selected from the group consisting of the reaction products of (1) hexamethylenetetramine and cyanuric chloride; (2) hexamethylenetetramine and 1,4-dichlorobutene; (3) hexamethylenetetramine and p-bis-chloromethylbenzene; and (4) triethanolamine and cyanuric chloride.

5 Claims, No Drawings

PERMANENT WAVING OF HAIR WITH QUATERNARY AMMONIUM ALKYLATING AGENTS AND AMMONIUM THIOGLYCOLATE

This application is a continuation of U.S. Pat. application Ser. No. 598,959, filed Dec. 5, 1966; which is a continuation-in-part of U.S. Pat. application Ser. No. 212,158, filed July 24, 1962; both now abandoned.

The present invention relates to the permanent shaping of keratin substrates, and more particularly to improvements in the permanent waving of living hair.

Conventional permanent waves involve two steps. In the first step, a reducing agent, such as ammonium thioglycolate, is applied to the keratin substrate to split the disulfide links in the keratin into free thiol groups to make shaping, such as waving, of the substrate possible. In the second step, the shape is permanently fixed by reconstituting the disulfide links through the application of an oxidizing agent. In an alternate procedure, the shape is fixed by blocking the thiol groups by the application of a mono- or bifunctional alkylating agent. This procedure involves two steps. In the treatment of wool, for instance, it has been proposed to use mono- and bifunctional organic halides in organic solvents as alkylating agents, but this system cannot be used for living hair. Other methods of this type utilize aqueous solutions of quaternary ammonium salts which may be decomposed to produce an alkyl group resulting in an S-alkylation. The decomposition of the quaternary ammonium salt on the substrate and the resultant alkylation depend on the constitution of the compound which must be able to undergo the reaction mechanisms examined by Ingold et al. (Journal of the Chemical Society of London 1928, 3,125; 1929, 2,375; 1933, 66; and 1933 526) and by Snyder and Speck, Journal of the American Chemical Society 61, 668, 1939.

I have now found that novel, water-soluble, readily decomposable and non-toxic mono- and polyquaternary ammonium compounds for this purpose may be obtained from tertiary aliphatic or alicyclic di- or polyamines or alkanolamines and acyclic or cyclic mono- or polyhalogen compounds containing a conjugate double bond. The preferred halogen compound is 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride). The invention covers a method of permanently waving keratin substrates, such as hair, by applying thereto keratin softening agents and a quaternary ammonium halide salt keratin alkylating agent. Quaternary ammonium halide salts that make suitable keratin alkylating agents are mono, bis and tri quaternary reaction products or mixtures thereof selected from the group consisting of the reaction products of (1) hexamethylenetetramine and cyanuric chloride; (2) hexamethylenetetramine and 1,4-dichlorobutene; (3) hexamethylenetetramine and p-bis-chloromethylbenzene; and (4) triethanolamine and cyanuric chloride.

More specifically the new compounds of this invention are (1) mono, di and tri hexamethylenetetramine cyanuryl chloride; (2) mono, di and tri triethanolamine cyanuryl chloride; (3) mono and di hexamethylenetetramine butene chloride; and (4) mono and di hexamethylenetetramine para-bis-methylbenzene chloride.

The alkylating agents of the invention are produced by reacting a solution containing stoichiometric amounts of the components in anhydrous polar solvents or suspensions thereof. The reaction product is recovered as a solid. Typical methods of forming the

reaction products of this invention are illustrated by examples 1 to 4 below.

Examples 1 to 12 relate to preferred di or bis-quaternary ammonium salts, but it should be noted that the mono and tri quaternary ammonium salts may also be used to alkylate keratin substrates. Furthermore the mono, bis and tri quaternary salts may be used individually or in various mixtures to alkylate the keratin substrate. Austrian Pat. No. 174,377 also illustrates other methods of producing the mono, bis and tri quaternary ammonium salts of this invention.

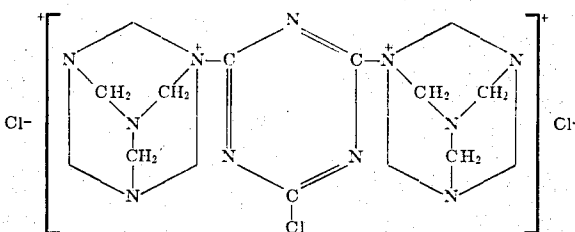
The quaternary ammonium alkylating compounds of the present invention may be used in a one-step process of permanently shaping keratin substrates, such as the permanent waving of living hair, since said component will effect S-alkylation on the hair keratin only at an elevated temperature by decomposition of said compound in the aqueous alkaline solution conventionally used in the permanent waving of hair without causing premature alkylation of the thioglycolate reducing agent. In view of the stability of the quaternary ammonium compounds of this invention in thioglycolate solutions, these alkylating agents may be put into the permanent wave solution and stored at ambient temperatures for extended periods of time. This is an additional advantage in using these compounds since it simplifies handling and application.

The optimum pH range of the permanent wave solution is 8 to 10 and the preferred molar ratio concentration of the keratin softening agent, for instance ammonium thioglycolate, to the quaternary ammonium compound is 0.5-1 : 1.

While in no way limited thereto, the method of preparing some of the quaternary ammonium salts of this invention will be illustrated by examples 1 to 4.

EXAMPLE 1

Preparation of the bis-quaternary ammonia salt obtained by reacting hexamethylenetetramine and cyanuric chloride, having the formula:

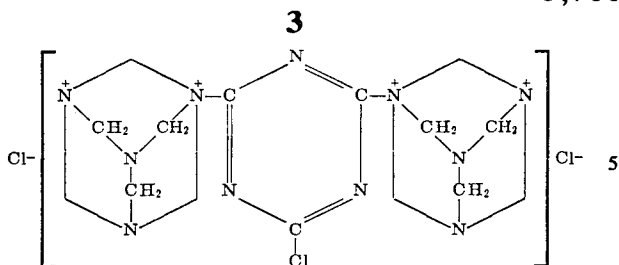


The hexamethylenetetramine was dried in an oven for 5 hours at 110° C. Then 28 grams of hexamethylenetetramine was dispersed in 60 cc. of dioxane.

A solution containing 20 g. of cyanuric chloride in 40 cc. of dioxane was prepared. This solution was added to the hexamethylenetetramine suspension while cooling to room temperature. The resulting mixture was stirred until the odor of cyanuric chloride disappeared completely. After drying the reaction mixture, a yellow powder was obtained. The yield was 40 percent and the product had a fusion point of 189° C.

EXAMPLE 2

Preparation of the bis-quaternary ammonia salt obtained by reacting triethanolamine and cyanuric chloride having the formula:



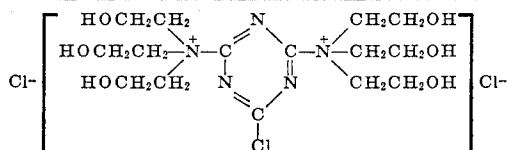
A solution of 30 g. of triethanolamine was dissolved in 60 ml (milliliters) of methylethyl acetone.

A solution of 20 g. of cyanuric chloride was dissolved in 40 cc. of dioxane. The cyanuric chloride solution was added drop by drop to the triethanolamine solution while the mixture was continuously stirred and cooled to ambient temperature until the odor of cyanuric chloride completely disappeared.

After drying the reaction mixture, a colorless powder was obtained. The yield was 70 percent and the product had a fusion point of 152° C.

EXAMPLE 3

Preparation of the bis-quaternary ammonia salt obtained by reacting hexamethylenetetramine and 1,4-dichloro-2-butene, having the formula:



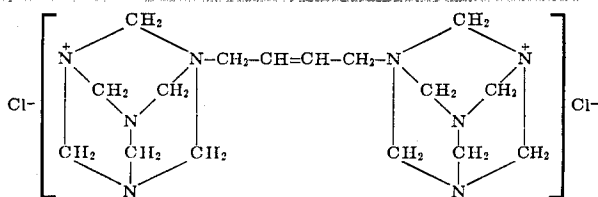
The hexamethylenetetramine was pulverized and dried in an oven for 5 hours at 110° C. A suspension of 28 g of the dry substance is prepared in 50 ml. of dioxane, and 15 g. of 1,4-dichloro-2-butene are added to the suspension.

The mixture was left for 8 days in a closed bottle. At the end of this time, a thick, yellowish mass was formed. The dioxane was dried and the residue was washed several times with methyl ethyl acetone to eliminate the excess dichlorobutene.

A 60 percent yield of a yellow powder was obtained which had a fusion point of 157° C.

EXAMPLE 4

Preparation of the bis-quaternary ammonia salt obtained by reacting hexamethylenetetramine and para-bis-chloromethylbenzene, having the formula:



The hexamethylene tetramine was pulverized and dried in an oven for 5 hours at 110° C. A suspension of 28 g. of dried hexamethylenetetramine was prepared in 50 ml. of methylethyl acetone. Next 20 g. of para-bis-chloromethylbenzene was dissolved in just the necessary amount of dioxane and this solution was added to the preceding suspension. The mixture was kept in a tightly closed bottle for 3 days. The residue was then dried and washed with methylethyl acetone and ether.

Sixty-five percent of the desired compound was obtained in the form of a white powder, having a fusion point of 212° C.

Examples 5 to 12 illustrate how the quaternary ammonium salts of this invention may be used to alkylate or permanently wave keratin substrates.

EXAMPLE 5

100 ml of a 10 percent ammonium thioglycolate solution was adjusted with ammonia to a pH of 9. 1.5 of urea and 6.5 of the bis-quaternary ammonium salt of hexamethylenetetramine and cyanuric chloride of Example 1 were dissolved in the solution. Untreated strains of hair were impregnated with the solution, wound on curlers and subjected to the effects of the solution for 15 minutes at ambient temperature. The temperature was thereupon raised for 5 minutes to 55° C. The hair was then carefully rinsed and dried.

EXAMPLE 6

100 ml of a 10 percent ammonium thioglycolate solution was adjusted with ammonia to a pH of 9.5 and 1.5 of urea and 7.5 g of the bis-quaternary ammonium salt of triethanolamine and cyanuric chloride of Example 2 were dissolved in the solution. The hair was treated with this solution as in Example 5.

EXAMPLE 7

Untreated strains of hair were impregnated with the thioglycolate solution of Example 5, wound on curlers and subjected to the effects of the solution of 15 minutes at ambient temperature. The bis-quaternary ammonium salt of Example 5 was then added to the solution on the hair and the temperature was raised for five minutes to 55° C. The hair was then carefully rinsed and dried.

EXAMPLE 8

The procedure was the same as in Example 7 but the ammonium salt of Example 6 was used.

EXAMPLE 9

Example 6 was repeated but the ammonium salt was substituted by the bis-quaternary ammonium salt of hexamethylenetetramine and 1,4-dichloro-2-butene of Example 3. The hair was treated as in Example 5.

EXAMPLE 10

Example 9 was repeated but the ammonium salt was added only shortly before the temperature was raised.

EXAMPLE 11

Example 6 was repeated but the ammonium salt was substituted by the bis-quaternary ammonium salt of hexamethylenetetramine and p-bis-chloromethyl benzene of Example 4. The hair was treated as in Example 5.

EXAMPLE 12

Example 11 was repeated but the ammonium salt was added only shortly before the temperature was raised. In all examples, the hair received a good permanent wave of soft hand.

Using the standards of alkali solubility of Am. Dye-stuffs Rep. 25, 542 (1936), the following values were obtained:

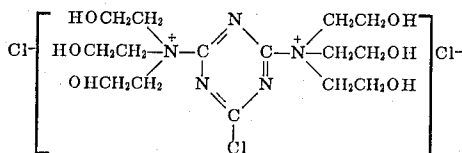
Untreated Hair	Hair Treated According to Example	Conventional
% 5	5, 6, 7, 8, 9, 10, 11, 12	
	5.7, 5.8, 7.0, 6.0, 4.3, 8.4, 4.9, 8.8	10.2

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What is claimed is:

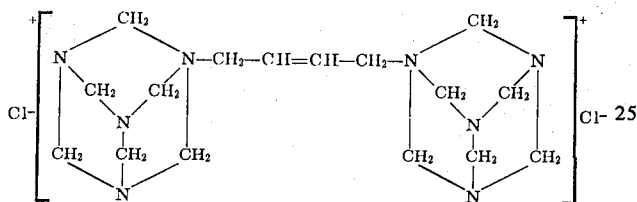
1. A composition for facilitating the permanent shaping of keratin substrates comprising an aqueous ammoniacal solution, having a pH of 8 to 10, of a keratin reducing amount of ammonium thioglycolate and a keratin alkylating amount of a quaternary ammonium compound alkylating agent selected from the group consisting of

1. bis-quaternary ammonium salt of hexamethylenetetramine and cyanuric chloride of the formula



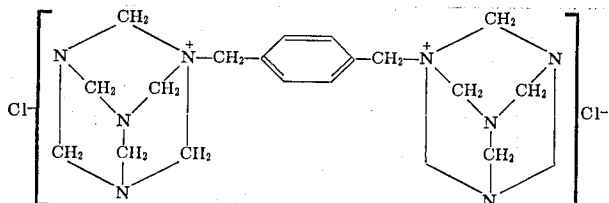
having a fusion point of 189° C;

2. bis-quaternary ammonium salt of triethanolamine and cyanuric chloride of the formula



having a fusion point of 152° C;

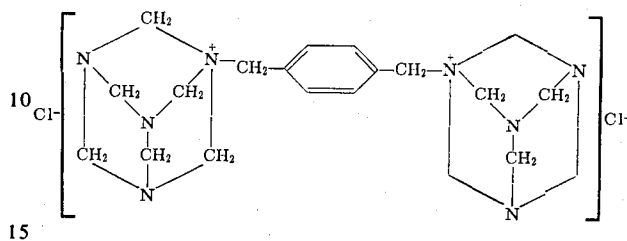
3. bis-quaternary ammonium salt of hexamethylenetetramine and 1,4-dichloro 2-butene of the formula



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having a fusion point of 157° C; and

4. bis-quaternary ammonium salt of hexamethylenetetramine and para-bis-chloromethylbenzene of the formula



having a fusion point of 212° C, the ratio of the molar concentration of ammonium thioglycolate to the quaternary ammonium compound alkylating agent being 0.5:1 to 1:1.

2. The composition of claim 1 having a pH of 9.

3. The composition of claim 2 which also contains urea.

4. A method of permanently shaping living hair comprising the steps of applying to the hair in amounts effective to facilitate the shaping of said hair the composition of claim 1, shaping the hair, keeping said composition on the hair for about 15 minutes at ambient temperature, then raising the temperature to about 55° C, keeping said composition on the hair for about 5 minutes at 55° C, rinsing and then drying the hair.

5. The composition of claim 3 wherein said ammonium thioglycolate is present in amounts of about 10 weight percent, said urea is present in amounts of about 1.5 g and said quaternary ammonium compound alkylating agent is present in amounts of about 6.5 to 7.5 g per 100 ml of said composition.

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