

1

2

3,433,576

MODIFICATION OF PROTEINACEOUS POLYMERS WITH CARBOXYLIC-CARBONIC ANHYDRIDES

Giuliana C. Tesoro, Dobbs Ferry, N.Y., assignor to J. P. Stevens & Co., Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Mar. 29, 1966, Ser. No. 538,207
U.S. Cl. 8—127.5
Int. Cl. D06m 3/02, 13/20

18 Claims

The present invention relates to a method for the chemical modification of proteinaceous polymers and in its more particular aspects, to the acylation of keratin fibers, especially wool. In its still further aspects, the present invention relates to the method for treating textile fabrics containing wool fibers and blends of wool with other fibers for the chemical modification thereof in order to introduce certain desirable effects into the textile.

Heretofore, many processes have been developed for treating wool in order to enhance the natural properties and characteristics thereof in one way or another. Numerous methods for the chemical modification of wool have been studied, with the objective of introducing selected substituents and cross-linkages or otherwise changing the chemical structure of the keratin molecule by the formation of new chemical bonds, thereby altering the behavior of the fibers in an effort to improve one or more of their inherent characteristics and to improve one or more of the properties of the wool fibers and the final products such as woolen garments. The keratin molecule because it contains a number of reactive functional groups, is capable of undergoing many reactions. However, few reagents selectively combine with specific reactive groups in the keratin molecule and few reagents are capable of reaction with the keratin molecule under relatively mild conditions that will not degrade keratin fiber and/or impair the desirable properties of the fibers and textile products made therefrom. Hence, although capable of reaction with many reagents, the keratin molecule presents many problems to those attempting to introduce substituents therein or to change its chemical structure in order to enhance the properties thereof for the purpose of producing a more commercially attractive material.

It is, therefore, an object of the present invention to provide a method for the chemical modification of proteinaceous polymers to enhance the properties and characteristics thereof.

It is a further object of the present invention to provide improved chemically modified proteinaceous materials, particularly woolen textile fibers and fabrics made therefrom.

It is a further object of the present invention to provide a method for the chemical modification of wool-containing textile fabrics which avoid the shortcomings and drawbacks of prior known methods and compositions.

It is a further object of the present invention to provide a method for the treatment of wool-containing textile materials under mild conditions which avoid undesirable degradation or impairment of the properties of the final product.

It is a still further object of the present invention to provide a method to impart crease retention properties to wool-containing textile fabrics.

In attaining the above objects, one feature of the present invention comprises treating proteinaceous polymers with a mixed carboxylic-carbonic anhydride to introduce substituents into the molecule and to change the chemical structure of the molecule by the formation of new chemical bonds, thereby altering the behavior of the polymers and improving the properties of the textiles made therefrom.

The present invention also includes chemical modification of wool-containing textile fibers, yarns and fabrics with a mixed carboxylic-carbonic anhydride whereby the treated material exhibits improved properties ranging from increased tensile strength to greatly improved retention of creases upon exposure to a moist atmosphere or water.

Another feature of the present invention resides in a method for imparting a durable configuration, such as creases, pleats and the like to wool-containing textile materials by treatment with a mixed carboxylic-carbonic anhydride and thereafter subjecting the treated textile material to heat while maintaining the textile material in the desired configuration.

The above, as well as other objects, features and advantages of the present invention will become apparent from the following detailed description thereof.

According to the present invention there is provided a novel method for the treatment of proteinaceous polymers, particularly keratin fibers such as wool and textile materials containing wool fibers with a mixed carboxylic-carbonic anhydride represented by the structural formula:



wherein:

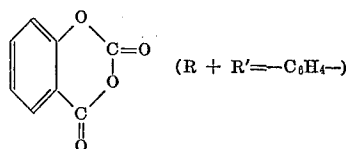
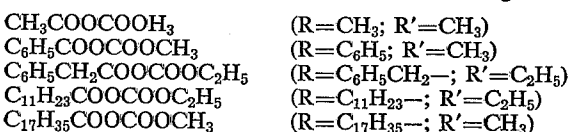
R represents a monovalent organic group such as alkyl, aryl, and aralkyl;

R' is an alkyl group containing from 1 to 4 carbon atoms; and

R+R' taken together may be a divalent cyclic organic group.

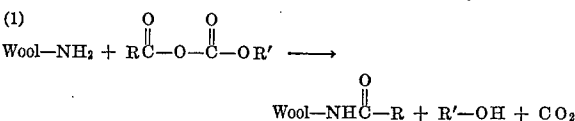
Included as illustrative of R are, for example, alkyl groups from 1 to 18 carbon atoms, phenyl and aralkyl containing 7 to 14 carbon atoms. Divalent cyclic groups include phenylene, cyclo-hexylene, phenylene dimethylene, and the like.

Further illustrative of the mixed carboxylic-carbonic anhydrides included in Formula I that may be used for purposes of the present invention are the following:



As a general rule, compounds wherein R and R' or R+R' represent hydrocarbon groups are preferred.

The reaction of the carboxylic-carbonic anhydrides of Formula I with proteinaceous material such as wool is believed to involve predominantly the primary amino groups in the wool molecule according to the equation:



wherein Wool-NH₂ schematically represents a portion of the wool molecule containing primary amino groups. The course of the reaction postulated above in Equation 1 is indicated by the observation that the acid binding capacity of wool treated with mixed carboxylic-carbonic anhydrides is significantly decreased as compared with untreated wool of identical origin and previous history. Hence in the data reported hereinafter, the reference to acid binding capacity for the wool samples treated in

accordance with the present invention will show a much lower value than those of untreated wool. Acid binding capacity figures thus represent an indication of the extent to which the primary amino groups of the wool molecule have been reacted with the reagents of Formula I. Measurements of acid-binding capacity can be made by any known method.

It has been observed and determined that proteinaceous polymers, particularly wool fibers treated in accordance with the method of the present invention exhibit improved properties and characteristics ranging from increased tensile strength to greatly improved retention of creases upon exposure to a moist atmosphere or water. The latter is a particularly important characteristic from a commercial standpoint inasmuch as it means that fabrics produced from wool fibers treated in accordance with the present invention will tend to retain their intended creases and/or pleats in damp weather or in rainy weather. The imparting of durable creases and pleats to woollen garments represents an important objective and advantage of the present invention.

It will be apparent that the specific improvements imparted to proteinaceous polymers in accordance with the present invention will vary depending upon the structure of the reagent employed and on the extent of the reaction, reaction conditions and the like. In this connection it is generally preferred that the structure of the reagent be such that it is capable of introducing a substituent group which is relatively large. However, within the ranges indicated herein the present invention results in substantial improvements and enhancement of the natural characteristics of proteinaceous materials, particularly wool.

For example, wool treated in accordance with the present invention exhibits improved properties ranging from increased tensile strength to greatly improved retention of creases upon exposure to a moist atmosphere or water depending upon the structure of the reagent employed and the extent of the reaction, especially where the amount of weight increase of a treated wool sample is about 10% or more. In general, however, the amount of weight increase on treated proteinaceous polymer is not narrowly critical and improved properties, such as differential dyeing behavior, are imparted thereto when the weight gain is less than 10%.

In addition to the aforementioned improvements, the chemical modification of wool fibers with mixed carboxylic-carbonic anhydride changes the behavior of the woollen fibers with respect to dyeability. It is, therefore, feasible to obtain a unique effect by blending or mixing treated and untreated wool fibers or yarns in a textile fabric prior to the dyeing thereof. Various pleasing styling effects are obtainable as a result due to the differential dyeing behavior of the treated and untreated fibers in the woollen fabric. Other specific applications which rely on the difference in properties between natural or untreated wool and wool treated in accordance with the methods of the present invention will become apparent to those skilled in the art.

Mixed carboxylic-carbonic anhydrides of the structure shown in Formula I used according to the methods of the present invention in the treatment of wool are in general known compounds and may be prepared by a number of methods. For example, compounds can be prepared by the reaction of a carboxylic acid and an alkyl chloroformate by the procedure described by Tarbell, D. S. and Longosz, E. J. in the *Journal of Organic Chemistry*, vol. 24, part I, page 774 (1959). The resulting compounds vary in solubility and stability depending on the structure of the terminal groups R and R'. Compounds that are more stable in the presence of moisture are preferred for the treatment of wool inasmuch as they can be used without drying or otherwise treating the wool prior to the acylation treatment.

According to the preferred aspects of the present invention, a keratin material such as wool fiber is treated by

impregnation with a liquid vehicle containing the mixed carboxylic-carbonic anhydrides of Formula I. Wool-containing textile materials can be treated in any form, e.g., fiber, yarn, knitted or woven fabric, and may be blended with other natural or synthetic fibers as well. In general, the fabric should contain about 30% wool content by weight for satisfactory results. As an illustration, the method is carried out by contacting the fiber with the mixed anhydride in the form of a solution in a suitable solvent. Any inert vehicle can be used for this purpose although nonaqueous vehicles which are capable of swelling the keratin or other proteinaceous polymer are preferred. Included among the preferred group of solvents are dimethyl formamide, dimethyl acetamide, and N-methyl pyrrolidone. Hydrocarbon solvents such as benzene, toluene, xylene and halogenated solvents such as perchloroethylene, 1,1,1-trichloroethane and carbon tetrachloride are less effective but also can be employed. The particular solvent vehicle chosen can vary widely and the above are given for the purpose of illustrating the suitable types.

After the wool is contacted with the solution of a mixed anhydride in a suitable solvent, it is thereafter generally heated to accelerate the acylation reaction.

Concentration of the carboxylic-carbonic anhydride reagent in solvent can vary over wide limits depending on other conditions such as temperature and the extent of reaction required. In general, concentrations in the range of 5% to 50% may be used although 10% to 30% are the preferred amounts. All percentages being based on the weight of reagent in solution. Reaction can be carried out and effected by heating the wool in the reagent solution for a given time at a temperature less than the boiling point of the solvent. Alternatively, the wool is impregnated with reagent solution, the excess solution is then removed from the impregnated polymer. Subsequently, the polymer impregnated with the reagent solution is heated in equipment designed to prevent the evaporation of the solvent, such as in a chamber. The process can also be carried out by squeezing out the excess reagent solution from the impregnated polymer, thereafter drying the polymer and baking at the curing temperature in a forced draft oven in the absence of solvent.

The time and temperature required for the reaction to proceed varies greatly with the particular reagent and the solvent system employed. Moreover, these parameters also depend on the method selected for the application of the solution, that is, whether the wool is immersed in excess reagent solution and heated or treated by padding to contain a measured amount of solution. In general, the reaction temperatures can range from about 50° to 150° C. although it is understood that these ranges can be extended. The heating times vary from a few minutes to several hours; generally at higher temperatures the heating time will be adjusted so as to prevent any degradation or adverse effects. Although some reaction takes place between the primary amino groups of the protein molecule and the reagent at room temperature, the reaction is much slower under these conditions.

In accordance with a still further aspect of the invention, a woollen fabric treated in accordance with the hereinabove described process, or a garment made of wool textile material treated as described above has imparted thereto a permanent configuration such as pleats, creases and the like by forming the desired configuration, e.g., pleats in the fabric and while holding or otherwise maintaining the fabric in the desired configuration, subjecting the woollen fabric to a heat creasing operation. Exposure to elevated temperature of up to about 150° C. or more is generally sufficient. It is to be noted that the higher temperature permit short reaction times and that lower temperatures; e.g., 50° C., require longer times. It is believed that the wool molecule is modified by the treatment with the present anhydride and becomes heat

settable as a result thereof. Pleats and creases imparted to fabrics in this manner are durable and result in a product having greater attractiveness from a commercial standpoint.

The examples which follow illustrate the acylation reaction of wool with specific mixed carboxylic-carbonic anhydrides according to the present invention. Although the amount of reagent that is applied to the fabric samples is not narrowly critical, as mentioned hereinbefore, it is preferred that for optimum crease retention enhancement of fabric the amount of reagent deposited upon the fabric should give at least a 10% weight increase. It is understood that each of the mixed carboxylic-carbonic anhydrides illustrated above could be employed in the following examples.

In the following examples which serve to illustrate the present invention without limiting it in any way, the method used to evaluate crease retention in water was as follows:

Samples of 8 inch (warp) by 4 inch (filling) were creased with a 15-second steam, 45-second bake cycle on a Hoffman press (80 pounds line steam pressure). The crease was made parallel to the warp. The permanence of the crease to relaxation was evaluated by immersing the creased swatch open and with the crease vertical in a deep beaker of water containing 0.1% non-ionic wetting agent at 25° C. Each sample was suspended in the water by clips for 30 minutes and then withdrawn, dried by towel blotting and conditioned at 65% relative humidity and 21° C. for 16 hours. Thereafter the samples were rated for crease retention. The scale used for the ratings was 5.0 indicating a perfect crease to a zero for no crease. Untreated samples gave the rating of 0.0 to about 0.5, thus showing substantially no crease retention.

Example I

A sample of plain weave woolen fabric in the ready-to-dye state was kept in a conditioned room (21° C., 65% R.H.) overnight and weighed on an analytical balance. The weighed sample was dried in a forced draft oven at 60° C., rinsed in methanol and dried again. The pre-dried sample was immersed in a 20% solution of lauroyl-ethyl carbonic anhydride in dimethyl formamide (hereinafter referred to as DMF) (fabric-to-liquor ratio: 1 to 16), for 6 hours at 90° C. The sample so treated was rinsed in DMF, washed in water and dried. The sample was placed in a conditioner room (21° C., 65% R.H.) overnight and again weighed on analytical balance to determine the weight increase due to the treatment. The weight increase was 14.8%. Only 0.8% of the added weight was lost after 2 hours extraction in boiling CCl₄, showing that chemical bonding had been achieved.

The acid binding capacity and the crease rating of the treated sample and of an untreated control, each having been subjected to the same preconditioning, were as follows:

Sample	Acid Binding Capacity (meq./g.)	Crease Rating
Treated.....	0.21	3.5
Untreated.....	0.7	0.3

Example II

A sample of plain weave woolen fabric in the ready-to-dye state, conditioned, weighed and pre-dried, as described in Example I, was padded with a 40% DMF solution of lauroyl-ethyl carbonic anhydride using a laboratory padded and setting the rolls at such a pressure as to give 106% wet pickup. The padded sample was dried at 65° C. and then cured at 150° C. for 15 minutes in a forced draft laboratory oven. The sample so treated was rinsed in DMF and washed in water. The treatment resulted in 4.1% weight gain.

In order to get a higher weight gain the treated sample was exposed to the same treatment again. The second treatment gave 6.6% additional weight gain. The total weight gain was thus 10.7% corresponding to an overall reaction yield of about 20%. The acid binding capacity of the treated sample was 0.45 meq./g. compared to 0.75 meq./g. for an untreated control.

Example III

Example II was repeated, but the treatment was carried out by two subsequent paddings. In the first padding the wet pickup was 104%. After the first padding the sample was dried at 60° C. and then padded again with the reagent solution. The wet pickup was only 52% in the second padding. The sample was dried, cured and rinsed as specified in Example II. The treatment with two subsequent paddings resulted in 7.4% weight gain, corresponding to about 18% yield for the reaction.

In order to obtain a higher weight gain, the treated sample was exposed to the same treatment a third time. The treatment yielded 6.3% additional weight gain. The total weight increase was thus 13.7%.

Example IV

A sample of plain weave woolen fabric in the ready-to-dye state was conditioned, weighed and pre-dried as specified in Example I. The pre-dried sample was padded with a 40% DMF solution of benzoyl ethyl carbonic anhydride, setting the rolls at such a pressure as to give 126% wet pickup. The sample so treated was kept at room temperature for 10 minutes, then rinsed in DMF, washed in water and dried.

Such a treatment resulted in a 2.1% weight increase.

Example V

Example I was repeated but, instead of lauroyl-ethyl carbonic anhydride, phenylacetyl-ethyl carbonic anhydride was used and the reaction temperature was 80° C. instead of 90° C.

Such a treatment resulted in 3.0% weight increase.

Example VI

Samples of plain weave woolen fabric in the ready-to-dye state were conditioned and weighed as described in Example I. The weighed samples were padded with a 40% toluene solution of stearoyl-ethyl-carbonic anhydride, setting the rolls at such a pressure as to give 107-110% wet pickup. The samples so treated were dried at 60° C. and then cured in a forced draft laboratory oven or steamed in a laboratory steamer as specified below. The samples so treated were washed in toluene, DMF and finally in water, and then dried.

Sample	Reaction Conditions	Percent Weight Gain
C-2.....	Curing: 150° C. for 15 minutes.....	2.3
C-3.....	do.....	2.4
C-4.....	Steaming: 15 minutes.....	4.6

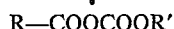
While solvents are employed in the examples, the presence of a swelling agent is not essential to the reaction.

The foregoing examples illustrate the present invention with respect to the treatment of woolen fabric. It is to be understood, however, that wool in any form or shape can be treated in accordance with the present invention and moreover, that wool mixed with other fibers to produce textile fabrics having blends of fibers therein may also be treated in accordance with the present invention.

What I claim is:

1. A method for the chemical modification of proteinaceous polymers which comprises reacting said polymers with a carboxylic-carbonic anhydride represented by the structural formula:

7



wherein R is selected from the group consisting of alkyl, aryl, aralkyl, R' is an alkyl group containing from 1 to 4 carbon atoms and wherein R+R' taken together may be a divalent cyclic organic group.

2. A method as defined in claim 1 wherein the proteinaceous polymer is wool.

3. A method as defined in claim 1 wherein the proteinaceous polymer is wool fiber.

4. A method as defined in claim 1 wherein the treatment is carried out in the presence of solvent.

5. A method for the chemical modification of a wool containing textile fabric with a solution in a solvent of carboxylic-carbonic anhydride represented by the structural formula:



wherein R is selected from the group consisting of alkyl, aryl and aralkyl groups, R' is an alkyl group containing from 1 to 4 carbon atoms and R+R' taken together may be a divalent cyclic organic group.

6. The method as defined in claim 5 wherein the reaction between the wool and said anhydride takes place in the presence of said solvent at a temperature below the boiling point of the solvent.

7. The method as defined in claim 5 wherein excess solution is removed from the fabric after impregnation and thereafter the fabric is heated to complete the reaction.

8. The method as defined in claim 5 wherein the reaction between the fabric and the anhydride takes place in the presence of steam.

9. The method as defined in claim 5 wherein the fabric is dried after impregnation and baked at an elevated temperature in the absence of moisture.

10. A method as defined in claim 5 wherein the fabric is washed and dried upon completion of the reaction.

11. The method as defined in claim 5 wherein the fabric

8

has deposited thereon sufficient reagent to obtain a weight increase of at least 10%.

12. The method as defined in claim 1 wherein the anhydride is lauroyl-ethyl carbonic anhydride.

13. The method as defined in claim 1 wherein the anhydride is benzoyl ethyl carbonic anhydride.

14. The method as defined in claim 1 wherein the anhydride is phenylacetyl ethyl carbonic anhydride.

15. The method as defined in claim 1 wherein the anhydride is stearoyl-ethyl-carbonic anhydride.

16. A method for imparting a durable configuration to wool containing textile materials comprising treating said textile material with a carboxylic-carbonic anhydride represented by the structural formula:



wherein R is selected from the group consisting of alkyl, aryl, aralkyl, R' is an alkyl group containing from 1 to 4 carbon atoms and wherein R+R' taken together may be a divalent cyclic organic group; and thereafter subjecting said textile material to elevated temperature while maintaining said material in the desired configuration to thereby set the configuration.

17. The method as defined in claim 16 wherein at least one crease is formed in a wool-containing fabric by heating while maintaining the crease in said fabric.

18. The product produced by the method as defined in claim 1.

References Cited

UNITED STATES PATENTS

2,986,445	5/1961	Koenig	8-128
3,079,215	2/1963	Koenig	2-128
3,097,052	7/1963	Koenig	8-128

J. TRAVIS BROWN, *Primary Examiner*.

J. CANNON, *Assistant Examiner*.

U.S. Cl. X.R.

8-128; 260-112