United States Patent Office 3,226,428
Patented Dec. 28, 1965

3,226,428

BISCARBAMATE-FORMALDEHYDE ADDUCTS

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No Drawing. Original application July 19, 1962, Ser. No. 211,141, now Patent No. 3,160,469, dated Dec. 8, 1964. Divided and this application July 15, 1963, Ser. No. 338,542

1 Claim. (Cl. 260—482)
(Granted under Title 35, U.S. Code (1952), sec. 266)

A non-exclusive irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a division of Serial No. 211,141, filed July 19, 1962, now Patent No. 3,160,469.

This invention relates to the treatment of cellulosic textile materials to produce textiles having improved properties. More specifically, the present invention relates to new textile treating agents and a method of treating cellulosic textile fabrics with these agents whereby the fabrics are rendered resistant to wrinkling, have improved resiliency, and possess wash-and-wear properties. Moreover, the finishes produced from the new textile treating agents of this invention were found to be extremely durable. These finishes were found to effectively resist hydrolytic removal under conditions that remove the finishes based on the commonly used N-methylol treating agents.

In general, the production of wrinkle resistant and wash-and-wear fabrics has been accomplished by the use of di- and polyfunctional N-methylol finishing agents. These agents are generally formed by the addition of formaldehyde to ureas (cyclic or straight chain), melamine, and other similar type compounds. However, it is well known that finishes produced from the agents are fairly easily removed by repeated washing procedures which employ moderately strong acidic solutions, that is, the "souring" step used in most commercial launderings. After such treatments, it is often found that the treated fabric has generally lost the finish and the desired wrinkle resistance and wash-and-wear properties. Consequently, these treating agents can not be used to produce acceptable wash-and-wear cellulosic fabrics which are to be subjected to these, or similar, hydrolytic conditions. In general, alkaline hydrolysis is somewhat less detrimental than acidic hydrolysis under the normal conditions encountered in use.

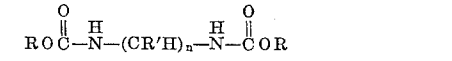
It has been suggested that bisformamide-formaldehyde adducts be used as crease-proofing agents. Although these materials produce wrinkle-resistant and wash-and-wear fabrics of high resistance to harsh conditions of acidic hydrolysis, the treated fabrics are susceptible to damage from hypochlorite bleaching agents. Consequently, these creaseproofing agents cannot be used on all fabrics. Ethyl carbamate-formaldehyde adducts have been shown previously [American Dyestuff Reporter, 50, p. 849 (1961)] to be an effective agent for producing treated cotton fabrics which are wrinkle-resistant. Also, it was noted in this work that some carbamate finishes retained chlorine after hypochlorite bleaching, but that these finished fabrics were not susceptible to chlorine damage. It was considered that the N-methylol derivatives of biscarbamates would form new finishes on cellulosic fabrics which would prove to be more highly resistant to acid hydrolysis than those finishes based on ethyl carbamate. Also, it was considered that many of the advantages, such as resistance to chlorine damage,

of the finishes based on ethyl carbamate would be retained by these new finishing agents.

A primary object of the present invention is to provide N-methylol derivatives of biscarbamates which have outstanding characteristics as treating agents for cellulosic textiles.

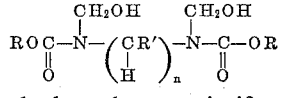
Another object of the invention is to provide a process for the treatment of textile fabrics, composed mainly of cellulose, with a new type of N-methylol biscarbamate treating agent, whereby the finished fabric acquires the properties of increased resiliency and wrinkle resistance. It is furthermore an object of this invention to provide such a treatment whereby the finish produced is resistant to harsh conditions of acidic hydrolysis. Also the treated fabric may be laundered repeatedly by ordinary procedures, which procedures may include the use of hypochlorite bleaching agents, without suffering discoloration or significant loss in strength in the laundering procedure or subsequent treatment.

In general, these and other objects of the invention are accomplished by treating the cellulosic textile with an aqueous solution containing the N-methylol derivatives of biscarbmates having the following structure:



wherein n is an integer of one to four, R is a member of the group consisting of an alkyl group of one to four carbon atoms, and R′ is a member of the group consisting of H or an alkyl group of one to four carbon atoms.

The biscarbamate-formaldehyde adducts used for the treatment of the cellulosic textile in the process of this invention can be obtained by the reaction of a biscarbamate of the above-described structure and formaldehyde in aqueous media under alkaline conditions. It is preferred to use an excess of formaldehyde in this reaction, the excess being about one to two molar equivalent of "free" formaldehyde based on the presumption that all amido >NH groups will methylolate to form N-methylol groups. Thus, although two molar equivalents of formaldehyde would theoretically fully methylolate the biscarbamates of the above-described structure to produce reaction products having the structure



where R, R′, and n have the same significance as above, it is preferable to have about three to four molar equivalents of formaldehyde for the reaction with the biscarbamates. The chemical effect of the excess formaldehyde is not definitely known. However, in general, it appears that some formaldehyde reacts with the cellulose to form methylene ether crosslinks in addition to the crosslinking through the nitrogenous agent. An amount of formaldehyde significantly in excess of the four to one ratio can also be employed, but it is inefficient and uneconomical to use such a large excess. The other conditions of this reaction are well-known in the trade. Generally, heating the alkaline, aqueous solution of the biscarbamate and formaldehyde at 60° C. for 30 minutes or allowing the solution to stand at room temperature (20–25° C.) for 18–24 hours is sufficient to achieve formation of the N-methylol derivatives. The reaction products thus produced are water soluble. The solution can be used as is or can be diluted with water for treatment of the cellulosic material.

Prior to application of the agent to fabric, an acidic substance or a substance producing acidity at elevated temperatures is added to the diluted solution to serve as a catalyst. The concentration of the reactants, i.e., the

biscarbamate-formaldehyde adduct plus the excess or unreacted formaldehyde, can be varied depending on the particular textile processing conditions used, the type of textile being treated, and the properties desired in the finished textile. Generally, it is preferred to use from about 5% to 20% by weight of the reactants in the diluted treating solution. The catalysts which may be used are well known in the trade. Magnesium chloride, zinc fluoborate, and zinc nitrate are examples of particularly suitable catalysts. From about 0.5% to about 5% by weight of the acidic catalyst is generally preferred.

Treatment of the cellulosic textile material is carried out by standard procedures. The textile is thoroughly wetted with the above-described treating solution; the excess liquid is mechanically removed, and the wetted textile is dried and cured. Following the curing operation, it is preferable but not absolutely necessary, to afterwash the treated textile in a slightly alkaline, aqueous solution to remove any unreacted materials.

The processes of this invention can be used to treat substantially any hydrophilic fibrous cellulosic material such as cotton, rayon, ramie, jute, and the like which can be impregnated with a liquid, dried, and cured.

The following examples are given by way of illustration and not by way of limitation of the invention. The detailed procedures given below in the examples are illustrative, and are not the only or specific conditions for the production of an acceptable finished textile. Many variations or additions within these procedures can be made, as will be readily apparent to those skilled in the art. In the examples, all percentages are by weight. The fabrics were tested by the following methods: wrinkle recovery angle, Monsanto method, American Society for Testing Materials (ASTM) test D 1295–53T; breaking strength, ASTM test D 39–49; damage caused by retained chlorine, American Association of Textile Chemists and Colorists tentative test method 92–1958T.

Example 1

A weighed portion of the biscarbamate was dissolved in an alkaline, aqueous solution of formaldehyde such that the molar ratio of formaldehyde to the biscarbamate was 3:1. The pH of the solution was checked and, if necessary, aqueous sodium hydroxide was added to adjust the pH to a value of from 8 to 11. The solution was heated at about 60° C. for 30–60 minutes, cooled, and the pH adjusted to about 7 with dilute hydrochloric acid. Then, a weighed portion of magnesium chloride hexahydrate was added such that its final concentration in the padding solution was about 4%. Concentration of the biscarbamate (prior to methylolation) in the padding solution was about 5%. Using this general procedure, with variations noted where appropriate, the following carbamates were used to produce various padding solutions:

Solution A. Methylenebis(ethyl carbamate)
Solution B. Methylenebis(ethyl carbamate), with a catalyst of 1% zinc fluoborate
Solution C. Ethylenebis(ethyl carbamate)
Solution D. Ethylidenebis(ethyl carbamate)
Solution E. Methylenebis(methyl carbamate), with a catalyst concentration of 2%, the catalyst composed of 60% citric acid and 40% magnesium chloride hexahydrate.
Solution F. A 12% dimethylol ethyl carbamate solution was prepared using the general procedure outlined above except the solution was allowed to stand at 20–25° C. for a period of about 20 hours.

Example 2

A sample of 80 x 80 cotton print fabric was dipped in the treating solution and padded to give about 70–80% increase in weight of the fabric. The wet fabric was dried seven minutes at 60° C. and cured three minutes at 160° C., except for the fabric dipped in Solution E, Example 1. This fabric was cured for one minute at 140° C. The cured fabrics were washed in warm alkaline water, with a nonionic detergent added, and then dried. The properties of the fabrics produced by this process are shown in Table I.

TABLE I.—PROPERTIES OF TREATED FABRICS

Fabrics From Solution	Wrinkle Recovery Angle (warp only), degrees	Breaking Strength Retained After Scorch Test, percent
A	126	99
B	133	99
C	139	92
D	125	91
E	130	95
F	125	
Untreated Fabric	85	95

Example 3

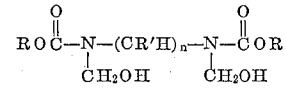
The durability of some of the finishes to acidic hydrolysis was tested by treating the fabrics for thirty minutes at 80° C. in a solution containing 1.5% phosphoric acid and 5% urea. The results of this hydrolysis on properties of the treated fabrics are given in Table II.

TABLE II.—ACID HYDROLYSIS OF CARBAMATE FINISHES

Fabrics From Solution	Percent of Original Nitrogen Retained After Hydrolysis	Wrinkle Recovery Angle (warp only), degrees
A	56	120
C	44	131
D	33	121
E	60	120
F	31	97

We claim:

A compound having the formula:



wherein *n* is an integer of one to four, R is an alkyl group of from 1 to 4 carbon atoms, and R′ is a member of the group consisting of H and an alkyl group of from 1 to 4 carbon atoms.

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