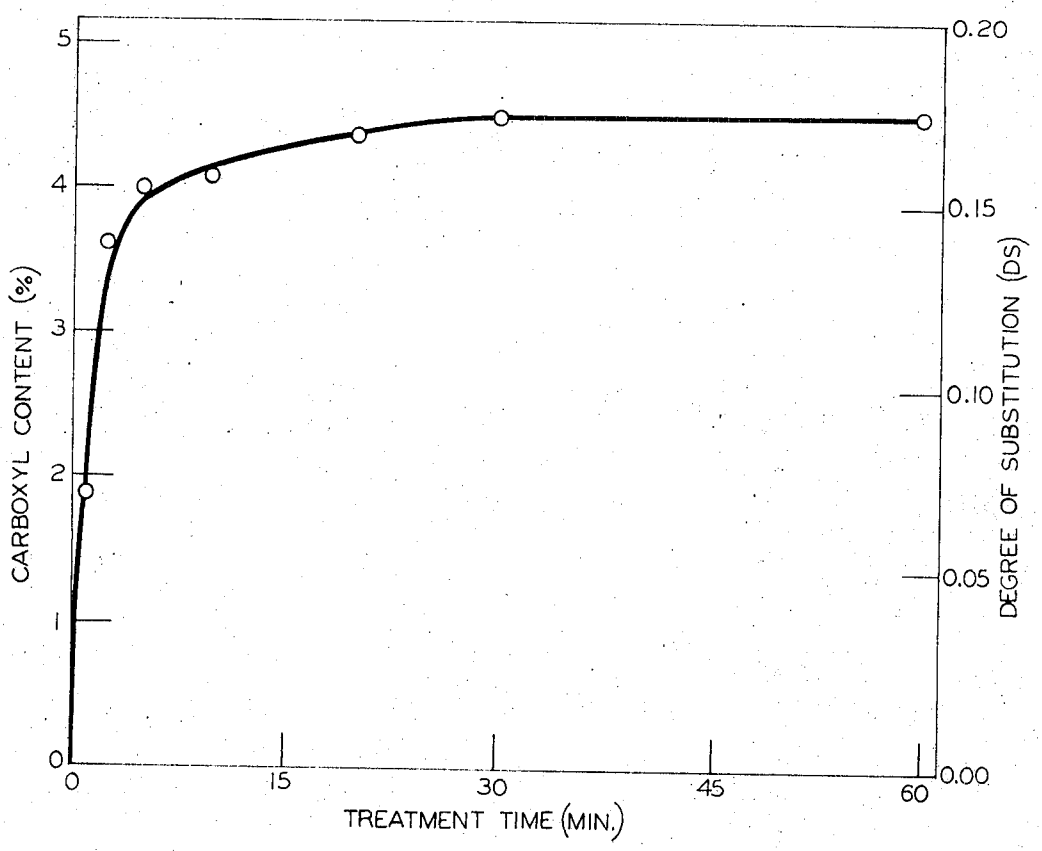
March 2, 1971 A. G. PIERCE, JR., ETAL 3,567,360

METHOD FOR INTRODUCING CARBOXYALKYL AND/OR CARBAMOYLALKYL GROUPS INTO CELLULOSIC TEXTILE MATERIALS AND PRODUCTS THUS PRODUCED

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METHOD FOR INTRODUCING CARBOXYALKYL AND/OR CARBAMOYLALKYL GROUPS INTO CELLULOSIC TEXTILE MATERIALS AND PRODUCTS THUS PRODUCED

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ABSTRACT OF THE DISCLOSURE

Cellulosic textile materials are etherified through treatment with a haloalkylamide or an N-substituted haloalkylamide. The carboxyl group content of the resulting material can be controlled by adjusting treatment conditions.

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 invention relates to the chemical modification of cellulosic textile materials. More specifically, it relates to a new and improved process for preparing carboxyalkylated fibrous cellulosic textile materials; and also to a new process for introducing carbamoylalkyl groups into fibrous cellulosic textile materials either exclusively, or concomitantly with the introduction of carboxyalkyl groups.

A number of processes are known for the preparation of carboxymethylated cellulose. For example, a nontextile material, known as cellulose gum or CMC, is produced by impregnating cellulose pulp, usually wood pulp, with sodium hydroxide to form alkali cellulose and then causing the alkali cellulose to react with chloroacetic acid or sodium chloroacetate. The product, sodium carboxymethyl cellulose, as commercially produced, usually has a D.S. (degree of substitution, the average number of substituent groups per anhydroglucose unit of the cellulose) within the range of 0.50 to 0.85, but may vary from 0.4 to 1.5. The commercial product is readily soluble in water, insoluble in organic materials, resistant to oils and greases, physiologically inert, anionic in character, and is an efficient viscosity control agent. In 1959, about 41 million pounds of this material were produced in the United States for use in detergents and soaps, fabric sizes, warp sizes, paper sizes, adhesives, emulsions, latexes and dispersions, oil-well drilling fluids, ceramics, desensitizers for lithographic plates, core binders in foundry work, food, pharmaceuticals, and cosmetics.

Processes are known for the preparation of carboxymethylated cellulosic textile materials. Principal among these is the process by which cotton textile materials are impregnated with a solution of chloroacetic acid or sodium chloroacetate and then immersed in an excess of concentrated sodium hydroxide solution, in the cold or at a temperature below about 90° C., so as to yield carboxymethylated cottons. This carboxymethylation process has been the object of much research and development work and has been refined such that the effects of the variables of the process and limitations of the process are well known. A principal disadvantage of the process is the necessity for employing highly concentrated solutions of sodium hydroxide (40–50%) to obtain economic reaction efficiencies. The need for highly concentrated sodium hydroxide solution in the process makes continuous finishing in the plant difficult in that fortification of the sodium

hydroxide solution must be done with solid sodium hydroxide. This reagent which is highly deliquescent, is difficult to handle on a plant scale as a solid. Solutions of sodium hydroxide cannot be used for fortification since the concentrations needed are as close to the upper solubility limit of the reagent.

Other processess for carboxymethylating cellulosic textile materials include nonaqueous finishing processes, and two- or multi-phase finishing processes. In all the known processes for carboxymethylating cellulosic textile materials, however, the carboxymethylating agent employed is either a halogenated lower fatty acid or salt thereof, for example, chloroacetic acid or sodium chloroacetate.

Higher carboxyalkyl cellulose ethers are more difficult to prepare by use of halocarboxylic acids or their salts as the etherifying agent. As the distance of the halogen atom from the activating carboxyl group is increased, reactivity of the compound as an etherifying agent is greatly decreased. For example, beta-chloropropionic acid, in which the haloatom is separated from the carboxylic group by only two carbon atoms, is unsatisfactory for the preparation of carboxyethylated cotton.

Carbamoylalkylation of cellulose introduces into the cellulose molecule the nitrogenous, chemically reactive amide group which native cellulose does not possess. Processes are known for the introduction of carbamoylethyl groups into cellulosic textile materials. For example, Reeves and Guthrie (U.S. Pat. No. 2,824,779) have shown that carbamoylethyl groups may be introduced into cellulosic textile materials by causing them to react with acrylamide in the presence of certain alkaline catalysts in an appropriate solvent. Carbamoylalkylated cottons possess increased dye affinity, moisture affinity, insulating properties, chemical activity, and the like. Further, Gagliardi and Wehner (Textile Research Journal, 37, 118 (February 1967)) have shown that carbamoylalkylation prior to crosslinking gives wash-wear products with higher than normal tensile strength, elongation, overall toughness, flex and surface abrasion resistance.

We have found that carbamoylalkylation of cellulose can be achieved by treatment of the cellulosic material with a haloalkylamide in the presence of alkali. For example, carbamoylmethyl cellulose is obtained by treatment of cotton with 2-chloroacetamide in the presence of sodium hydroxide. The following equation illustrates the course of this reaction:

$$\text{Cell-OH} + \text{ClCH}_2\text{CONH}_2 \xrightarrow{\text{NaOH}} \text{Cell-O-CH}_2\text{CONH}_2 + \text{NaCl} + \text{H}_2\text{O}$$

Since the amide group is subject to hydrolysis to the corresponding carboxylic acid in certain alkaline media, the introduction of carbamoylmethyl groups into the cellulose substrate gives a product which is a potential source of carboxymethyl cellulose, viz:

$$\text{Cell-O-CH}_2\text{CONH}_2 \xrightarrow{\text{H}_2\text{O, NaOH}} \text{Cell-O-CH}_2\text{COONa} + \text{NH}_3$$

Indeed, we have found that, under certain operating conditions, it is possible to achieve a higher degree of carboxymethylation of cellulose with chloroacetamide than with chloroacetic acid itself. By altering the reaction conditions, one can achieve predominantly carbamoylmethyl cellulose or a product which contains both amide and carboxylic acid functions in various ratios.

We have also found that the corresponding N-methylol derivatives of haloalkylamides are suitable carbamoylalkylating agents for the process of this invention. In general, the N-methylol derivatives possess greater water

solubility than the corresponding unmethylolated amides and can be efficiently used in applications where a relatively high degree of substitution is needed. Processes employing N-methylol derivatives of haloalkylamides for the chemical modification of cellulosic materials are known. For example, Van Bochove and Huech (U.S. Pat. No. 2,938,815) describe a process for rendering cellulosic textile materials resistant to bacteria by treating the material with N-methylol-2-chloroacetamide at elevated temperature under the influence of an acidic catalyst. This type of reaction, however, involves attaching the amide to the cellulose substrate through the methylol group and leaves the chlorine moiety available to act as a bactericidal agent, viz:

$$\text{Cell-OH} + HOCH_2NHCOCH_2Cl \xrightarrow{\text{acid catalyst}} \text{Cell-O-}CH_2\text{-}NHCOCH_2Cl + H_2O$$

However, in the process of the present invention, the reaction with the cellulose substrate takes place in an alkaline medium through the halo atom forming a cellulose carbamoylalkyl ether with concomitant loss of halogen in the alkaline medium to form a metal halide salt (e.g. sodium chloride).

A primary object of this invention is to provide a process for chemically modifying cellulosic textile materials in order to produce textile materials that have substantially the same molecular arrangement but enhanced textile and chemical properties.

It is a further object of the present invention to provide a process by which fibrous cellulosic textile materials may be carbamoylalkylated and/or carboxylalkylated by impregnating them with a solution containing an appropriate alkali, padding or centrifuging to remove excess solution, followed by immersion of the impregnated material in a solution containing the carbamoylalkylating agent dissolved in an appropriate solvent, usually nonaqueous, and allowing the materials to react at a temperature of from about 0° C. to about 100° C. so as to yield fibrous textile products with valuable modified properties.

It is a further object of the present invention to provide a process by which fibrous cellulosic textile materials may be carbamoylalkylated and/or carboxyalkylated by impregnating them with a solution containing the carbamoylalkylating agent, padding or centrifuging to remove excess solution, followed by immersion of the impregnated material in a solution containing alkali dissolved in an appropriate solvent, usually aqueous, and allowing the materials to react at a temperature of from about 0° C. to about 100° C. so as to yield fibrous textile products with valuable modified properties.

It is a further object of the present invention to provide a process by which fibrous cellulosic textile materials may be carbamoyalkylated and/or carboxyalkylated by treating them with a single solution containing the carbamoylalkylating agent and alkali dissolved in an appropriate solvent, and allowing the materials to react at a temperature of from about 0° C. to about 100° C. so as to yield fibrous textile products with valuable modified properties.

It is a further object of the present invention to provide a process by which fibrous cellulosic textile materials may be carbamoylalkylated and/or carboxyalkylated by treating them in a high temperature, pad-bake process which comprises impregnating the material with a solution of the alkylating agent and alkali and then allowing the reaction to proceed on the material when it is essentially dry and at an elevated temperature in an oven.

It is a further object of the present invention that the process provide a method for carboxyalkylating cellulosic textile materials through the use of a relatively markedlyless concentrated solution of reactants than the solutions required in the conventional process for carboxyalkylation.

The objects of the present invention may be achieved by treating a cellulosic textile material with a carbamoylalkylating agent of the general structure:

$$X—CH_2—(CH_2)_n—\underset{\underset{O}{\|}}{C}—\underset{\underset{R}{|}}{N}—H$$

such that X represents Cl, Br, or I; n is an integer value either zero or one, and R represents either H or $—CH_2OH$. The carbamoylalkylating agent is generally dissolved in a solvent such as water, alcohol, dimethylformamide, or the like. If the treatment involves impregnation of the cellulosic material with the carbamoylalkylating agent followed by immersion in the alkali solution, the nature of the solvent for the carbamoylalkylating agent is generally of little significance as long as the solvent is miscible with the solvent used to dissolve the alkali. However, if the treatment involves impregnation with alkali followed by immersion in a solution of the carbamoylalkylating agent, the nature of the solvent is important. Generally, higher degrees of substitution are achieved with solvents lower dielectric constant such as iso-propyl alcohol, methyl alcohol, dioxane, and the like, than with solvents of higher dielectric constant, such as dimethylformamide or water. The alkali generally employed in the process of this invention is sodium hydroxide; however, other strong alkalis, such as potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, and the like are suitable.

Because amide groups are susceptible to hydrolysis in alkaline media to the corresponding carboxylic acid salt, the treated cellulosic textile material may thus bear ether groups of the type:

$$—CH_2—(CH_2)_n—\underset{\underset{O}{\|}}{C}—\underset{\underset{R}{|}}{N}—H$$

or

$$—CH_2—(CH_2)_n—\underset{\underset{O}{\|}}{C}—OM$$

or both, substituted for the H of primary or secondary alcohol groups of the anhydroglucose units which make up the repeating polymer units of cellulosic textile materials. In the above general structures, n is an integer value of 0 or 1, R is either H or CH_2OH, and M represents the cation of the particular alkali used in the process. The degree of substitution (D.S.), or average number of substituent groups per anhydroglucose unit, of the carbamoylalkylated and/or carboxyalkylated cellulosic material depends upon the variables of the conditions used in the process. By adjusting these variables, which are principally: the nature of the cellulosic textile material, the nature and concentration of the carbamoylalkylating agent, the nature and concentration of the alkali used, the amount of solution retained by the textile material after padding or centrifugation, the time and temperature of treatment, and the dielectric constant of the solvent used, an almost infinite number of treatments are possible which permit the preparation of carbamoylalkylated and/or carboxyalkylated cellulosic textile materials of a wide range of ratios and degrees of substitution.

The cellulosic textile material employed may be composed of natural fibers, such as cotton, linen, ramie, and the like, or of man-made fibers, such as rayon, and the like. It must be fibrous but may be in the form of fiber, yarn, fabric, or the like. It may be in the natural state, but better treatment is effected if the cellulosic material has been prepared by conventional procedures to remove natural waxes and other noncellulosic impurities. If desired, the textile material may be mercerized.

The degrees of substitution of the products of the process of this invention were determined from chemical analyses for the carboxyl and nitrogen contents of the modified celluloses. For the determination of the carboxyl content, samples of the carboxyalkylated cellulosic textile materials were acidified by soaking in a 2% aqueous solution of hydrochloric acid for four hours, washed free of mineral acid and dried. Weighed portions of the acidi-

fied material were placed in flasks with 100 ml. of distilled water and an aliquot of standardized 0.1 N sodium hydroxide solution added. The flasks were stoppered and allowed to stand at room temperature for two hours with occasional shaking. The residual sodium hydroxide was then back-titrated with standardized 0.1 N hydrochloric acid to the phenolphthalein end-point. From this, the carboxyl content was calculated and the D.S. estimated from the following equation:

$$D.S.=\frac{(162)\ (\text{percent COOH})}{4500-(E)\ (\text{percent COOH})}$$

where E is the molecular weight of the substituent group minus one, e.g. 58 for carboxymethylated cellulose, 72 for carboxyethylated cellulose, etc. The nitrogen content of the treated cellulosic materials was determined by the Kjeldahl method, and the D.S. estimated from the following equation:

$$D.S.=\frac{(162)\ (\text{percent N})}{1400-(E)\ (\text{percent N})}$$

where, again, E represents the molecular weight of the substitutent group minus one, e.g. 57 for carbamoylmethylated cellulose, 71 for carbamoylethylated cellulose, etc.

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 processes of this invention or for the production of an acceptable finished textile material. 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 parts and percentages are by weight and temperatures are in degrees centigrade unless noted otherwise.

EXAMPLE 1

Skeins of mercerized 7/2 cotton yarn weighing approximately 8 grams (0.05 mole) were impregnated with aqueous 25% sodium hydroxide solution and centrifuged to approximately 180% wet pickup. Each skein was then placed in a flask containing 4.68 grams of 2-chloroacetamide (0.05 mole) dissolved in 80 ml. of isopropyl alcohol. The solutions were maintained at 60° in a water bath and were agitated continuously during the reaction period. After various amounts of time, the skeins were removed, rinsed several times with dilute (2%) hydrochloric acid, then with distilled water, and dried. Nitrogen contents of the samples were less than 0.05%, even for short time treatments. A plot of carboxyl content versus reaction time for this treatment is shown in the figure. The data indicate that the carboxymethylation reaction has essentially reached completion after approximately 20 min. at this temperature.

EXAMPLE 2

The effect of sodium hydroxide concentration on the extent of reaction in this process is illustrated by the following example. Skeins of mercerized 7/2 cotton yarn weighing approximately 8 grams (0.05 mole) were impregnated with aqueous solutions of sodium hydroxide of various concentrations (cf. table below) and centrifuged to approximately 180% wet pickup. Each skein was then placed in a flask containing 4.68 grams of 2-chloroacetamide (0.05) dissolved in 80 ml. of iso-propyl alcohol. The solutions were maintained at 60° in a water bath and were agitated continuously during the reaction period. The reactions were run for 10 min., after which, the skeins were removed, rinsed several times with dilute (2%) hydrochloric acid, then with distilled water, and dried. For comparison, similar treatments were conducted with an equimolar quantity of chloroacetic acid substituted for the chloroacetamide. Data from these treatments are shown in Table 1. The data indicate an increase in extent of reaction with increasing caustic concentration with an optimum concentration being reached somewhere between 25 and 50 percent. The sample treated with 5% sodium hydroxide and chloroacetamide contained 0.18% bound nitrogen. All others had less than 0.05% nitrogen content.

TABLE 1

Etherifying agent	Concentration of NaOH applied (percent)	Carboxyl content (percent)	D.S. carboxymethyl
Chloroacetamide	5	0.80	0.03
Do	15	4.81	0.19
Do	25	8.42	0.34
Do	50	6.22	0.24
Chloroacetic acid	5	0.04	<0.01
Do	15	4.50	0.17
Do	25	5.40	0.21
Do	50	5.43	0.21

The data also indicate that chloroacetamide is a more effective carboxymethylating agent than chloroacetic acid. Since sodium hydroxide concentration does influence the extent of reaction, and since the wet pickup in the centrifugation step is difficult to control precisely, the magnitude of carboxyl content is subject to some variability in duplicate treatments. However, in all duplicate treatments performed under these same conditions, the same rank order was obtained in spite of this variability (i.e., chloroacetamide treatment produced higher carboxyl contents than chloroacetic acid).

EXAMPLE 3

The effects of both temperature and certain solvent effects are demonstrated by the treatments illustrated in this example. Skeins of 7/2 mercerized cotton yarn weighing approximately 8 grams (0.05 mole) were impregnated with aqueous 25% sodium hydroxide solution and centrifuged to approximately 180% wet pickup. Each skein was then placed in a flask containing 4.68 grams of 2-chloroacetamide dissolved in 80 ml. of solvent (cf. Table 2 below). The solutions were maintained at controlled temperatures in a water bath for the duration of the treatment, and were continuously agitated. The treatments were run for 30 min. after which the skeins were removed, washed several times with dilute (2%) hydrochloric acid, then with distilled water, and dried. Data from these treatments are shown in Table 2.

TABLE 2

Solvent	Reaction temp.	Carboxyl content (percent)	D.S. carboxymethyl
Isopropanol	40	4.08	0.15
Do	60	7.65	0.31
Do	80	8.98	0.37
Dimethylformamide	40	0.94	0.04
Do	60	1.06	0.04
Do	80	1.55	0.06
Do	100	2.03	0.08
Water	60	0.16	<0.01
Water-acetone Mixture [1]	60	1.34	0.05

[1] 60 ml. acetone and 30 ml. of water.

EXAMPLE 4

Two skeins of 7/2 mercerized cotton yarn were impregnated with an aqueous 5% sodium hydroxide solution and centrifuged to approximately 180% wet pickup. Each skein was then placed in a flask containing 23.4 grams of 2-chloroacetamide dissolved in 80 ml. of N,N-dimethylformamide. The solution had been cooled to 4° C. prior to the addition of the impregnated skeins. The flasks were maintained at 4° C. for 4 hrs. and 24 hrs. respectively, after which times the skeins were removed, rinsed, and dried as described in the previous examples. The skein treated for 4 hrs. contained 0.14% carboxyl (D.S. <0.01) and 0.41% bound nitrogen (D.S. carbamoylmethyl 0.05). The skein treated for 24 hrs. contained 0.14% carboxyl and 0.68% bound nitrogen (D.S. carbamoylmethyl 0.08). Since a carboxyl content equivalent to a D.S. of less than 0.01 is often found in textile materials as a result of oxidation which occurs in yarn

and fabric preparation (desizing, scouring, bleaching, etc.), it is obvious that the low temperature treatment described in this example introduces only carbamoylmethyl ether substituents.

Infrared spectra of these treated yarns exhibited a band at 1670 $cm.^{-1}$ which is characteristic of the amidic carbonyl.

EXAMPLE 5

Two skeins of mercerized, 7/2 cotton yarn were impregnated with aqueous 25% sodium hydroxide solution and centrifuged to approximately 180% wet pickup. One skein was placed in a flask containing 9.3 grams of 2-iodoacetamide dissolved in 80 ml. of isopropanol. For comparison, the other skein was placed in a flask containing 9.3 grams of 2-iodoacetic acid dissolved in 80 ml. of isopropanol. The flasks were maintained at 60° in a water bath and were agitated continuously during the duration of the reaction period. The treatment was run for 30 min., after which the skeins were removed, rinsed and dried as above.

The skein treated with 2-iodoacetamide contained 6.32% carboxyl (D.S. carboxymethyl 0.25) and 0.27% bound nitrogen (D.S. carbamoylmethyl 0.03). The skein treated under similar conditions with the corresponding acid and contained 4.52% carboxy (D.S. carboxymethyl 0.17). Here, again, the haloalkylamide provide to be a better carboxymethylating agent than the corresponding carboxylic acid.

EXAMPLE 6

Two skeins of 7/2, mercerized cotton yarn were impregnated with aqueous 25% sodium hydroxide solution and centrifuged to approximately 180% wet pickup. One skein was then placed in a flask containing 5 grams of 3-chloropropionamide dissolved in 80 ml. of isopropanol. The other skein was placed in a flask containing 5 grams of 3-chloropropionic acid dissolved in 80 ml. of isopropanol. The flasks were maintained at 80° in a water bath for 30 min., after which the skeins were removed, rinsed, and dried as in the previous examples. The skein treated with 3-chloropropionamide contained 3.04% carboxyl (D.S. carboxyethyl 0.11) and 0.13% bound nitrogen (D.S. carbamoylethyl 0.02). The skein treated with 3-chloropropionic acid contained 0.55% carboxyl (D.S. carboxyethyl 0.02). Here, again, the amide proved to be a better carboxyalkylating agent than the corresponding carboxylic acid.

EXAMPLE 7

A skein of 7/2 mercerized cotton yarn weighing approximately 8 grams was impregnated with aqueous 23% sodium hydroxide solution, and centrifuged to approximately 200% wet pickup. The skein was then placed in a flask containing 6.2 grams of N-methylol-2-chloroacetamide dissolved in 150 ml. of isopropyl alcohol. The flask was maintained at 60° in a water bath for 30 min., after which the skein was removed, rinsed several times with dilute (2%) hydrochloric acid, and then with distilled water, and dried. Chemical analysis showed the skein to contain 6.00% carboxyl and 0.04% nitrogen.

EXAMPLE 8

A skein of 7/2 mercerized cotton yarn weighing approximately 8 grams was impregnated with aqueous 50% potassium hydroxide solution and centrifuged to approximately 200% wet pickup. The skein was then placed in a flask containing 4.8 grams of 2-chloroacetamide dissolved in 80 ml. of isopropyl alcohol. The flask was maintained at 80° in a water bath for 30 min., after which time the skein was removed, rinsed as above, and dried. The product contained 6.40% carboxyl (D.S. carboxymethyl 0.25) and 0.17% bound nitrogen (D.S. carbamoylmethyl 0.02).

EXAMPLE 9

A piece of 80 x 80 cotton printcloth was padded with a saturated solution of 2-chloroacetamide in water at 23° C. The wet pickup was approximately 80%. The padded fabric was then immersed for 30 min. in aqueous 50% sodium hydroxide solution also at 23° C. The fabric was removed, rinsed in dilute acetic acid, then in running tap water and dried. Fabric contained 1.57% carboxyl (D.S. carboxymethyl 0.06) and 0.66% nitrogen (D.S. carbamoylmethyl 0.08).

EXAMPLE 10

A piece of cotton printcloth was padded to approximately 80% wet pickup with a solution containing 15% N-methylol-2-chloroacetamide dissolved in water. The fabric was then immersed in aqueous 50% sodium hydroxide solution for 30 min. at room temperature. The fabric was then removed, rinsed in acetic acid solution and then water, and dried. This fabric contained 1.52% carboxyl (D.S. carboxymethyl 0.06) and 0.13% nitrogen (D.S. carbamoylmethyl 0.02). A second piece of printcloth was treated in a similar manner except that it was dried for 7 min. at 60° C. after the initial padding and prior to immersion into the sodium hydroxide solution. This fabric contained 2.53% carboxyl (D.S. carboxymethyl 0.09) and 0.21% nitrogen (D.S. carbamoylmethyl 0.04).

EXAMPLE 11

A skein of mercerized, 7/2 cotton yarn was placed in a solution containing 4.8 grams of 2-chloroacetamide, 8 grams of sodium hydroxide, 80 ml. of isopropyl alcohol, 40 ml. of methyl alcohol, and 20 ml. of water. The solution was maintained at 80° C. for 30 min. after which time the skein was removed, rinsed in dilute acetic acid, then rinsed in water, and dried. Carboxyl content of the treated yarn was 4.42% (D.S. carboxymethyl 0.17) and nitrogen content was 0.17% (D.S. carbamoylmethyl 0.03).

EXAMPLE 12

A skein of viscose rayon yarn weighing approximately 8 grams was placed in a flask containing 70 ml. isopropyl alcohol, 35 ml. of methyl alcohol, 17.5 ml. water, 7 grams of sodium hydroxide, and 4.2 grams of 2-chloroacetamide. The solution was maintained at 80° C. for 30 min., after which time the skein was removed, rinsed in dilute acetic acid, then water, and dried. Carboxyl content of the yarn was 8.49% (D.S. carboxymethyl 0.34).

EXAMPLE 13

Pieces of cotton printcloth were padded to a wet pickup of about 80% with aqueous solutions containing a carbamoylalkylating agent and alkali, and then baked in an oven at 140° C. for 5 min., removed, washed free of unreacted agents and byproducts and dried. Data from these treatments are shown in Table 3.

TABLE 3

Carbamoylalkylating agent	Alkali	COOH, percent	D.S. Carboxymethyl	N, percent	D.S. Carbamoylmethyl
8% 2-chloroacetamide	2% NaOH	0.57	0.02	0.13	0.02
Do	10% Na_2CO_3	0.16	0.01	0.15	0.02
5% 2-chlarsacetamide	5% NaoH	0.85	9.03	0.17	0.02
8% N-methylol-2-chloracetamice	2% NaOH	0.20	0.01	0.28	0.03
Do	10% Na_2CO_3	0.18	0.01	0.23	0.03
5% N-methylol-2-chloroaceoamide	5% NaOH	0.62	0.02	0.19	0.02

The figure depicts the relationship between the duration of reaction and the degree of substitution effected.

We claim:

1. A process of etherifying a cellulosic textile material to a D.S. within the range of from 0.01 to 0.4 comprising:
   (a) impregnating the cellulosic textile material to a wet pickup of from about 100 to 250% by weight with an aqueous solution of from about 5 to 50% by weight of an alkali selected from the group consisting of sodium hydroxide and potassium hydroxide,
   (b) treating the alkali impregnated material from step (a) with a solution of from about 2 to 25% by weight of a haloalkylamide selected from the group consisting of 2-chloroacetamide, 2-iodoacetamide, 3-chloropropionamide, and N-methylol-2-chloroacetamide, in a solvent selected from the group consisting of water, dimethylformamide, acetone, isopropyl alcohol, methyl alcohol and mixtures of the aforementioned solvents, at a temperature of from about 0 to 100° C. and for a period of time of from about 5 minutes to 24 hours,
   (c) neutralizing the residual alkali,
   (d) washing the material free of excess reagents and byproducts and drying.

2. The process of claim 1 wherein the alkali is sodium hydroxide.

3. The process of claim 1 wherein the alkali is potassium hydroxide.

4. The process of claim 1 wherein the haloalkylamide is 2-chloroacetamide.

5. The process of claim 1 wherein the haloalkylamide is 2-iodoacetamide.

6. The process of claim 1 wherein the haloalkylamide is 3-chloropropionamide.

7. The process of claim 1 wherein the haloalkylamide is N-methylol-2-chloroacetamide.

8. The process of claim 1 wherein the solvent is water.

9. The process of claim 1 wherein the solvent is dimethylformamide.

10. The process of claim 1 wherein the solvent is acetone.

11. The process of claim 1 wherein the solvent is isopropyl alcohol.

12. The process of claim 1 wherein the solvent is methyl alcohol.

13. The process of claim 1 wherein the solvent is a mixture of the aforementioned solvents.

14. A process of etherifying a cellulosic textile material to a D.S. within the range of from 0.01 to 0.09 comprising:
   (a) impregnating the cellulosic textile material to a wet pickup of from about 70–80% by weight with an aqueous solution of from about 15% by weight to saturation of a haloalkylamide selected from the group consisting of 2-chloroacetamide and N-methylol-2-chloroacetamide in a solvent selected from a group consisting of water and methanol,
   (b) immersing the haloalkylamide-impregnated material from step (a) in an aqueous solution of about 50% by weight of sodium hydroxide,
   (c) neutralizing the residual alkali,

   (d) washing the material free of excess reagents and byproducts and drying.

15. The process of claim 14 wherein the haloalklamide is 2-chloroacetamide.

16. The process of claim 14 wherein the haloalkylamide is N-methylol-2-chloroacetamide.

17. A process of etherifying a cellulosic textile material to a D.S. within the range of from 0.05 to 0.08 comprising:
   (a) impregnating the cellulosic textile material to a wet pickup of about 180% with an aqueous solution of about 5% sodium hydroxide,
   (b) immersing the alkali impregnated material from step (a) in a precooled, saturated solution of 2-chloroacetamide in N,N-dimethylformamide and maintaining at a temperature of about 4° C for a reaction period of from about 4 hours to about 24 hours,
   (c) neutralizing the excess alkali,
   (d) washing the material free of excess reagents and byproducts and drying.

18. A process of etherifying a cellulosic textile material to a D.S. within the range of from 0.01 to 0.03 comprising:
   (a) impregnating the cellulosic material to a wet pickup of about 80% with a solution of from about 5 to 8% by weight of a carbamoylalkylating agent selected from the group consisting of 2-chloroacetamide and N-methylol - 2-chloroacetamide and about 2 to 10% by weight of an alkali selected from the group consisting of sodium hydroxide and sodium carbonate dissolved in water,
   (b) baking the impregnated material in an oven for a period of about 5 minutes at a temperature of about 140° C.

19. The process of claim 18 wherein the carbamoylalkylating agent is 2-chloroacetamide.

20. The process of claim 18 wherein the carbamoylalkylating agent is N-methylol-2-chloroacetamide.

21. The process of claim 18 wherein the alkali is sodium hydroxide.

22. The process of claim 18 wherein the alkali is sodium carbonate.

23. The product produced by the process of claim 17.

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