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3,597,380

## MODIFIED METHYLOLATED ALIPHATIC CARBAMATE PERMANENT PRESS TEXTILE RESIN

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3 Claims

### ABSTRACT OF THE DISCLOSURE

Preparing a textile treating resin by reacting melamine with an aqueous solution of a methylolated aliphatic carbamate having free formaldehyde therein whereby reducing the free formaldehyde content. Suitable carbamates are methylolated alkyl, hydroxyalkyl and alkoxyalkyl carbamates. The pH ranges from 3.5 to 7.5 depending upon the specific carbamate used and the ratio of free formaldehyde to melamine is generally from about 6:1 to 9:1.

### BACKGROUND OF THE INVENTION

#### Field of the invention

This invention relates to the treating of cellulosic fibers such as cotton, rayon and blends of cellulosic fibers with synthetic textile fibers such as polyester/cotton, nylon/cotton and polyester/rayon to impart thereto wrinkle resistance and permanent press qualities. It particularly relates to an improved permanent press textile-treating resin for cellulosic textile fibers. The resins particularly involved are the methylolated aliphatic monocarbamate resins prepared through the reaction of an aliphatic monocarbamate with formaldehyde to form a resin finishing agent in an aqueous solution for use in a pad bath to impart a permanent press crease and wrinkle resistance to cellulosic textile fibers. After the cellulosic textile fabric is treated, the resin can be cured immediately or curing may be deferred until the material has been cut and fashioned into a garment.

#### Description of the prior art

The interest in wash and wear or permanent press garments is steadily increasing. In the attempts to find acceptable textile-treating resins for these fibers, many problems and considerations must be weighed. Of course, the products produced must be commercially acceptable and at a competitive price. Some of the technical problems involved in the production of a commercially acceptable garment relate directly to the choice of the permanent press treating agent involved. The prime consideration is that, of course, the crease must be permanent and not removed by continued washing. The cured finish should be chlorine resistant with no strength loss or yellowing due to continued laundering in the presence of a bleach. The finish should be unaffected by commercial laundering which includes the use of a souring agent. When the curing of the resin is deferred until the garment is produced, there should be no after wash required following the cure of the garment.

In the attempt to produce acceptable permanent press cellulosic textile garments which did not become wrinkled or mussed upon use and successive washing, many methylolated derivatives of organic nitrogen compounds which are formed by reacting the compound with formaldehyde in an aqueous solution have been tried as textile-treating resins. Many unsuccessful attempts are discussed in U.S. Pat. No. 3,144,299. Among the agents discussed is the methylol derivative of melamine. The disadvantages attributed to the textile-treating agents discussed in the patent are that they cannot be bleached by the usual hypochlorite bleaching agents during laundering without danger of suffering severe strength loss or discoloration.

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It has been found that the use of methylolated aliphatic carbamate resins do produce a garment with pleasing appearance in spite of continued laundering and exposure to bleaches and souring. Among these carbamates found to be acceptable are methylolated aliphatic carbamates such as the alkyl carbamates (methyl carbamate, ethyl carbamate, propyl carbamate and butyl carbamate, for example); the hydroxyalkyl carbamates (hydroxyethyl carbamate, hydroxypropyl carbamate, hydroxybutyl carbamate, and mixtures thereof, for example); and the alkoxyethyl carbamates (for example, methoxyethyl carbamate, ethoxyethyl carbamate and propoxyethyl carbamate, and mixtures thereof).

However, in spite of the fact that the appearance and permanent press qualities of garments treated with the above-mentioned methylolated carbamate treating resins are outstanding, the olfactory qualities which must be present in a garment are quite deficient since garments treated with the methylolated aliphatic carbamates are also impregnated with free formaldehyde which is present in the resin added to the textile fiber treating bath. Many attempts have been made to remove this free formaldehyde from the resin without sacrificing the appearance qualities necessary to produce a marketable permanent press garment. Thus far the attempts have met with failure. The resin solution cannot be distilled without decomposing the methylolated aliphatic carbamate itself. The addition of many treating agents which would otherwise react with the formaldehyde such as urea, dihydroxy ethylene urea, propylene urea and other compounds have been found to reduce the free formaldehyde content in the resin solution but are vastly deficient in producing an acceptable product as far as the wrinkle resistance, permanent crease, chlorine resistance and scorch resistance is concerned, both, as far as the consuming public is concerned, and standards postulated by the American Association of Textile Chemists and Colorists.

The residual formaldehyde also causes much irritation to the olfactory and respiratory senses of those workers who must handle, cut and sew the fabric in the manufacture of garments therefrom. This is especially true when the resin-treated cloth is to be post cured. That is, the fabric is treated, a garment is made and then the resin is cured to impart permanent press qualities to the material. The free formaldehyde vaporizes during storage and in the cutting and sewing rooms to cause a great deal of discomfort to workers who must handle the treated, but uncured cloth.

It is an object of this invention to provide an improved methylolated aliphatic monocarbamate permanent press textile-treating resin with a low formaldehyde content.

It is another object of this invention to provide an improved method for producing methylolated aliphatic monocarbamate permanent press textile-treating resins which will reduce the free formaldehyde content of the resin without sacrificing other desirable fabric treating characteristics.

It is an object of this invention to provide a methylolated aliphatic monocarbamate textile-treating resin which renders the cellulosic textile fiber resistant to wrinkling or mussing during use and is resistant to bleaching, souring and continued laundering but yet does not expose those cutting and forming garments from these textiles to the dangerous odors of free formaldehyde.

Other objectives and advantages to this invention will become apparent to those skilled in the art upon reading and understanding the following disclosure.

### SUMMARY OF THE INVENTION

The objects of this invention are accomplished through the addition to the methylolated aliphatic monocarbamate

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textile-treating resins of a quantity of melamine, of itself an unacceptable textile-treating resin, such that the resulting carbamate resin/melamine resin mixture has included therein 6 to about 9 mols free formaldehyde per mol of melamine added. Upon addition to the aqueous resin mixture, the melamine reacts to reduce the free formaldehyde content of the methylolated carbamate resin mixture and itself becomes a part of the textile-treating resin. We have surprisingly discovered that the melamine addition imparts none of the deleterious effects attributed to melamine used as a treating agent by itself and even more surprisingly forms a textile-treating resin which imparts improved appearance, permanent press, laundering, and other desired properties while substantially reducing the amount of free formaldehyde which is included in the pad bath and thus impregnated into the treated fabric, minimizing the formaldehyde odor of uncured and cured treated textiles.

We have discovered a finishing agent utilizing the methylolated aliphatic monocarbamates in aqueous solution which has a low formaldehyde content, 2 to about 4 wt. percent in a 50% solids resin solution, but yet shows no decrease to the desired crease retention or wrinkle-resistant properties in the cloth. Fabrics treated with the resin solution of our invention also have been found to be resistant to hypochlorite bleaching and acid souring during repeated launderings.

The low formaldehyde resin finishing agent of our invention is prepared by treating the reaction product of formaldehyde and the aliphatic monocarbamate with melamine at a critical initial pH depending upon the methylolated aliphatic carbamate involved. The amount of melamine added is determined by the amount of free formaldehyde in the aqueous solution of the reaction product. About one mol melamine is added per 6 to about 9 mols free formaldehyde present.

These resins, when incorporated into a pad bath for incorporation into the cloth produced from cellulosic fibers, have been found to give the cloth improved crease retention and wrinkle resistance along with resistance to damage due to the agents present in the laundering process.

#### DESCRIPTION OF THE INVENTION

This invention relates to an improved finishing agent for treating cellulosic textile fabrics to improve wrinkle-resistant and crease-retention properties among others to cellulosic textile fabrics. The cellulosic textile fabrics comprehended include cotton fabrics, linen fabrics, rayon and fabrics consisting of blends of cotton, linen or rayon, and fabrics consisting of blends of cellulosic fibers with noncellulosic fibers such as polyester/cotton blends and nylon/cotton blends. The term cellulosic textile fabric as used herein is intended to include fabrics, whether woven or knitted, and garments or other articles made from such fabrics and is intended to include both cellulosic fabrics including regenerated cellulosic fabrics and cellulose-containing fabrics.

It is known to treat cellulosic textile fabrics with finishing agents prepared by reacting formaldehyde with aliphatic monocarbamates to form methylolated aliphatic monocarbamates. Materials produced in this manner are highly effective in imparting wrinkle resistance and wash wear properties to the fabric and also provide excellent resistance to chlorine damage and durability under conditions promoting acid hydrolysis such as acid souring. It is, however detrimental to the use of these finishing agents that a high amount of free formaldehyde is left in the aqueous solution as a residual from the methylolation reaction. This free formaldehyde content sometimes varies between the ranges of 6 to about 10 wt. percent in a 50% solids solution. By 50% solids solution, as used herein, we mean an aqueous solution which is 50 wt. percent methylolated aliphatic monocarbamate.

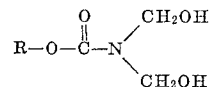
Carbamate finishing agents have been prepared in the past from alkyl carbamate such as methyl, ethyl, propyl

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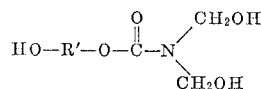
or butyl carbamate as is disclosed in U.S. Pat. No. 3,144,299, from hydroxyalkyl carbamates such as hydroxyethyl or hydroxypropyl carbamate, or mixtures thereof, as described in co-pending application Ser. No. 432,385, filed Feb. 12, 1965, now abandoned in the name of Leroy Whitaker and Floyd E. Bentley, or from alkoxyalkyl carbamates such as methoxyethyl carbamate, ethoxyethyl carbamate, etc.

The methylolated aliphatic carbamate finishing agent solutions to which this invention applies are produced by the reaction of formaldehyde with aliphatic monocarbamates. While the exact structure of this reaction product has not been established, it is believed that a mixture of monomethylol and dimethylol derivatives is produced. The conditions under which the methylolations are carried out are not narrowly critical with optimum conditions being determined primarily by the particular carbamate utilized. The reaction may be effected at temperatures of from about 20° C. to the reflux temperature of the reaction mixture with reaction times from several minutes to as much as 24 hours, and preferably from about 1 to about 5 hours. The formaldehyde is suitably reacted with the aliphatic monocarbamate in a ratio of from about 1.5 to about 3 mols of formaldehyde per mol of carbamate, the optimum amount depending on the particular carbamate employed. The initial pH of the reaction mixture may be in the range of about 4 to about 11, preferably from about 9 to about 11.

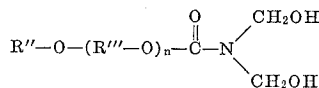
The useful methylolated aliphatic monocarbamates for the purpose of discussion in this invention are selected from the group consisting of methylolated alkyl carbamates of the general formula:



wherein R is an alkyl group of 1 to 4 carbon atoms such as methylolated methyl carbamate, methylolated ethyl carbamate, methylolated n-propyl carbamate, methylolated isobutyl carbamate, and the like; methylolated hydroxyalkyl carbamates of the general formula:



wherein R' is an alkylene radical of 2 to 4 carbon atoms, such as methylolated hydroxyethyl carbamate, methylolated hydroxypropyl carbamate and the like, and mixtures thereof; and alkoxyalkyl carbamates of the general formula:



wherein R'' is an alkyl group of 1 to 8 carbon atoms, R''' is an alkylene radical of 2 to 3 carbon atoms and n is an integer having a value of from 1 to 10 such as methylolated methoxyethyl carbamate, methylolated ethoxyethyl carbamate, methylolated n-butoxyethyl carbamate, methylolated iso-butoxyethyl carbamate, methylolated methoxyethoxyethyl carbamate, methylolated methoxyethoxyethoxyethyl carbamate, methylolated methoxyisopropyl carbamate, methylolated methoxypropoxypropyl carbamate, methylolated iso-butoxyethoxyethyl carbamate, and the like.

As hereinbefore mentioned these methylolated aliphatic monocarbamates are in aqueous solutions containing from about 6 to about 10 wt. percent of free formaldehyde resulting from the excess formaldehyde added in the methylolation reaction. Even though the free formaldehyde content may be less than the range stated, it is desired to reduce this free formaldehyde content. We have surprisingly discovered that the addition of melamine after the methylolation reaction to produce the methylolated ali-

phatic carbamate accomplishes this reduction to about 2 to about 4 wt. percent free formaldehyde without causing a resulting deterioration in the desired properties of the treated textile fabric.

The addition of melamine forms a melamine formaldehyde reaction product which remains in the textile-treating resin and becomes a part of it when applied to the cloth. Though heretofore these melamine-formaldehyde reaction products have been poor textile-treating agents because of the loss in tensile strength of the cloth and discoloring resulting from their presence, we have discovered that surprisingly their presence in the practice of producing the resins of our invention does not cause a deterioration of properties in the resulting textile-treating resin.

In the practice of our invention two factors are important to the successful commercial operation of our improved low free-formaldehyde textile-treating resins. These factors are the initial pH at which the melamine is added and which varies according to the methylolated aliphatic carbamate being treated. The other factor is the ratio of the melamine to the free formaldehyde present in the resin when the melamine is added. The importance of these two factors is brought about by the necessity of not only reducing the free formaldehyde content of the resin, but also producing a resin which forms a stable pad bath for the treatment of the textiles as hereinafter discussed and also the effect that these conditions have upon the final treated cellulosic fabric.

The particular pH chosen will be that appropriate to the particular class of aliphatic carbamates being modified and will fall within the general range of 3.5 to about 7.5. From the following discussion it will be clear as to which pH range is appropriate for a particular methylolated aliphatic monocarbamate.

In treating methylolated alkyl carbamates as described above, melamine is added such that the molar ratio of free formaldehyde to the amount of melamine added is from about 7:1 to about 9:1, and preferably 8 mols of free formaldehyde in the resin to be modified to one mol of melamine added. The pH of the methylolated alkyl carbamate at the time the melamine is added is from about 5.5 to about 7.5 and preferably about 6.0. We have discovered that this pH range at the time the melamine is added gives the desired stable pad bath a lower free-formaldehyde content and desirable properties to the treated cloth.

When a methylolated hydroxylalkyl carbamate as hereinbefore described is to be treated, the molar ratio of free formaldehyde in the methylolated carbamate solution to the melamine added is from about 6:1 to about 9:1, and the pH at which the melamine is added in range of 3.5 to about 5, and preferably the pH is about 4.0 and the molar ratio of free formaldehyde to the melamine is about 8:1.

When the carbamate resin to be modified by adding melamine is a methylolated alkoxyalkyl carbamate, as hereinbefore described, it is preferable to add the melamine at a pH of about 3.5 to about 6.0 with the preferred pH being about 5.0. The melamine is added so that the molar ratio of free formaldehyde to melamine is from about 7.5:1 to about 8.5:1, with the preferable molar ratio being about 8:1.

During the reaction between the melamine and the formaldehyde, the pH changes but the important factor in the practice of our invention is the pH of the methylolated aliphatic carbamate solution when the melamine modifying agent is added.

The reaction of the melamine with the free formaldehyde in the aqueous solution occurs at substantially the same time and temperature conditions which the initial methylolation in reaction is carried out. That is to say, for several minutes or as high as 24 hours but preferably from about 1 to about 5 hours at a temperature of from about 20° C. to about the reflux temperature of the re-

action mixture. It must be stated, however, that very high temperatures should be avoided, since the methylolated aliphatic monocarbamates are subject to decompose at high temperatures. We have found that it is preferable to allow the formaldehyde and melamine to react at a temperature of about 45° to about 70° C. for about 1 to about 2 hours.

The melamine modified methylolated aliphatic carbamate finishing agents of our invention are ordinarily applied to the cellulosic textile fabric from aqueous solution utilizing conventional dipping or padding techniques. Following application to the fabric, curing is required to promote reaction with the fibers of the fabric and thereby impart the desired properties such as wrinkle resistance and wash/wear characteristics. Use of a catalyst to promote curing is necessary and the catalysts which are known to the art to be most effective are acidic catalysts or acid reacting salts. Such salts generally are salts of weak bases and strong acid. The catalysts which are known to be most effective are hydrated magnesium chloride, zinc chloride, zinc nitrate, magnesium nitrate, magnesium fluoborate and amine salts of strong mineral acids. Hydrochloric acid may also be used as the catalyst.

If desired, the aqueous treating solution may contain in addition to the modified carbamate finishing agent other materials employed in textile finishing such as plasticizers, softening agents, hand builders and the like.

The concentration of the melamine modified methylolated aliphatic carbamate finishing agent in the solution will usually be between about 5 and about 35 wt. percent, and the catalyst will usually comprise from about 0.5 to about 8 wt. percent of the solution.

The amount of finishing agent which is applied to the fabric will depend upon the type of fabric and its intended application, but will ordinarily be from about 1% to about 30% by weight based upon the weight of the textile fabric; i.e., a weight pick up of about 1% to about 30%. Preferably the amount of finishing agent will be at least 4% by weight. The increase is, of course, determined by the concentration of the finishing agent in the treating solution and the weight of the solution which the textile fabric will retain. In practice, the wet pickup will be in the range of from about 50% to about 120%, and the treating solution applied to the textile fabric may contain as little as about 5% to as much as about 35% or more of the modified methylolated aliphatic carbamate finishing agent.

Following the application of the melamine modified finishing agent to the textile fabric, curing is required to promote reaction with the fibers of the fabric and thereby impart the desired crease resistance and wash-wear characteristics. Typically the fabric is first dried; i.e., subjected to low temperature heating, about 100° C., to remove the water, and then cured by the application of further heat. This curing step is generally at a temperature from about 130° to 200° C., and the cure is complete from about 1 to about 5 minutes and preferably in the range of 1½ to about 3 minutes. Curing may be deferred, as hereinbefore mentioned, until after the fabric has been fashioned into a garment.

Evaluation of the properties of textile fabrics treated in the manner herein described utilizing the melamine modified low formaldehyde methylolated aliphatic monocarbamates of our invention was in accordance with test procedures as may be found in the technical manual of the American Association of Textile Chemists and Colorists (AATCC), volume 39, 1963.

The advantages of the present invention will be further illustrated by the following examples which are offered for purposes of illustration only and not to be considered as limitations upon our invention.

#### Example I

This example is to illustrate that the treatment of our invention, with melamine, is effective to lower the free

formaldehyde content of the resins while not causing a deterioration of an important property in the treated cloth, the strength loss due to retained chlorine. This is not so when the resin is treated with other known compounds used for textile-treating resins. Methylolated hydroxyethyl carbamate is used for the purpose of comparison.

Pad baths were made using the following formulation: 20 parts by weight modified hydroxyethyl carbamate (50% solids), 4 parts by weight  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 2 parts by weight polyethylene softener, and 74 parts by weight water. The bath was adjusted to pH 4.5 and padded onto 136 x 64 all cotton broadcloth. The fabrics were cured at 170° C. for 90 seconds. After curing, the fabrics were washed and then acid scoured in an aqueous solution at pH 2.0 and a temperature of 40° C. for 30 minutes. The fabric samples were then subjected to the Standard Test Method, AATCC 92-1962, for damage due to retained chlorine. The results in the table below show that of all the modifying agent used only melamine modified hydroxyethyl carbamate resin does not result in excessive loss of tensile strength to the treated fabric.

TABLE I

| Resin No. | Modifying agent             | Free formaldehyde after treatment, percent | Tensile strength loss due to chlorine damage (percent of original) |
|-----------|-----------------------------|--------------------------------------------|--------------------------------------------------------------------|
| 1.....    | None.....                   | 8.35                                       | 4.8                                                                |
| 2.....    | Propylene urea.....         | 2.43                                       | 51.1                                                               |
| 3.....    | Dihydroxyethylene urea..... | 2.27                                       | 54.5                                                               |
| 4.....    | Melamine.....               | 3.40                                       | 1.8                                                                |

#### (A) METHYLOLATED ALKYL CARBAMATES

##### Example II

Seventy-five grams methyl carbamate (1 mol), 141 grams 44% formalin (2.07 mols) and 10 grams 20% NaOH are reacted at 50° C. At the end of one hour the solution contained 4.56% (0.34 mol) by weight free formaldehyde. The pH of the solution was adjusted to 4.0 and 5.1 grams melamine (0.04 mol) added, resulting in a formaldehyde/melamine molar ratio of 8.5/1. After heating at 60° C. for one hour, the formaldehyde content was reduced to 2.62%. This illustrates the effectiveness of the melamine treatment to lower the free formaldehyde content of the resin.

##### Examples III-IV

The experiment in Example II was repeated using melamine in the amounts shown in Table II. The results in Table II show the importance of the amounts of melamine used for the modification to establish a stable, usable pad bath.

TABLE II

| Example  | Original free formaldehyde, percent | Formaldehyde to melamine (molar ratio) | Final free formaldehyde, percent | Appearance                       |
|----------|-------------------------------------|----------------------------------------|----------------------------------|----------------------------------|
| III..... | 7.82                                | 6/1                                    | 2.11                             | Clear liquid became a white gel. |
| IV.....  | 4.56                                | 8/1                                    | 2.62                             | Clear liquid.                    |

##### Examples V-X

The experiment in Example II was repeated using the 8/1 excess formaldehyde to melamine molar ratio at the pH values listed in Table III. The results in Table III show the importance of the initial pH at which the reaction is carried out between the melamine and the free formaldehyde.

TABLE III

| Example   | Original free formaldehyde, percent | pH   | Final free formaldehyde, percent | Appearance and results                       |
|-----------|-------------------------------------|------|----------------------------------|----------------------------------------------|
| V.....    | 4.54                                | 1.5  | 2.49                             | Clear liquid. Pad bath unstable immediately. |
| VI.....   | 4.56                                | 4.0  | 2.62                             | Do.                                          |
| VII.....  | 4.54                                | 5.0  | 2.31                             | Clear liquid. Pad bath stable 3 hours.       |
| VIII..... | 4.54                                | 6.0  | 2.63                             | Clear liquid. Pad bath stable 5 hours.       |
| IX.....   | 4.54                                | 8.0  | 4.00                             | Clear liquid with a white precipitate.       |
| X.....    | 4.54                                | 10.0 | 3.85                             | White emulsion that became a white gel.      |

#### Examples XI-XII

Of the melamine-modified resins prepared, the resin made by the reaction of 8 mols excess formaldehyde to 1 mol melamine at pH 6.0 was found to be the most stable resin that made a stable pad bath.

A pad bath was made using the following formulation: 20 parts by weight modified methyl carbamate (50% solids), 4 parts by weight  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 2 parts by weight polyethylene softener, and 74 parts by weight water. The bath was adjusted to pH 4.5 and padded onto a 100% cotton fabric. The results in Table IV show the excellent wash and wear properties of the cured fabric. The 350° F. cure particularly shows the excellent resistance to chlorine damage following an acid sour and bleach.

TABLE IV

| Example.....               | XI   | XII   |
|----------------------------|------|-------|
| Cure temperature, ° F..... | 350  | 330   |
| Crease recovery angle..... | 277  | 266   |
| Tear strength.....         | 880  | 1,048 |
| Tensile strength:          |      |       |
| Before scorch.....         | 38.6 | 40.9  |
| After scorch.....          | 35.3 | 31.4  |
| Percent retained.....      | 91.4 | 77.1  |

#### (B) METHYLOLATED HYDROXYALKYL CARBAMATES

##### Example XIII

For example, a mixture of 1575 grams hydroxyethyl carbamate (15 mols) and 2565 grams 44% formalin (37.5 mols HCHO) was treated with 175 grams 20% sodium hydroxide solution at a pH of 10.5. The mixture was heated at 50° C. for one hour, cooled and the pH was adjusted to 7.0. The free formaldehyde content at this point was 7.78% (11.4 mols HCHO).

The pH was then adjusted to 4.0 with concentrated hydrochloric acid and 240 grams melamine (1.9 mols) was added. The mixture was heated to 50° C. and held at that temperature for one hour after the melamine had dissolved (total reaction time 1 1/4 hours). The solution was cooled to ambient room temperature and the pH was adjusted to 7.0 (from 5.4) with 18 grams 20% sodium hydroxide solution. Water was added to bring the resin solids (HEC+melamine+combined formaldehyde) to 50% by weight.

The final product was a clear, colorless liquid with 2.42% free formaldehyde.

##### Examples XIV-XVII

Following the procedure of Example XIII, the following tests were run to determine the molar ratio of free formaldehyde to melamine which would give a stable usable solution. The results are shown in Table V.

TABLE V

| Example   | Original free formaldehyde, percent | Formaldehyde to melamine (molar ratio) | Final free formaldehyde, percent | Appearance and results                                         |
|-----------|-------------------------------------|----------------------------------------|----------------------------------|----------------------------------------------------------------|
| XIV.....  | 8.52                                | 3/1                                    | -----                            | White solid.                                                   |
| XV.....   | *8.50                               | 4/1                                    | 2.76                             | Clear liquid but damaged the fabric after treatment.           |
| XVI.....  | 8.52                                | 6/1                                    | 3.40                             | Clear liquid. Gives a good finished fabric.                    |
| XVII..... | 5.00                                | 8.5/1                                  | 2.73                             | Clear liquid. Good finish on fabric. Pad bath stable 20 hours. |

\*Approximately.

## Examples XVIII-XXIII

The procedure of Example XIII was repeated using the 6 to 1 excess formaldehyde to melamine molar ratio at the pH values listed in Table VI. The results shown in Table VI show the importance of the pH at which the reaction is carried out.

TABLE VI

| Example   | Original free formaldehyde, percent | pH   | Final free formaldehyde, percent | Appearance and results                 |
|-----------|-------------------------------------|------|----------------------------------|----------------------------------------|
| XVIII.... | 8.52                                | 1.5  | 3.18                             | Clear liquid that became a gel.        |
| XIX.....  | 8.52                                | 3.0  | 3.42                             | Clear liquid.                          |
| XX.....   | 8.52                                | 4.0  | 3.40                             | Do.                                    |
| XXI.....  | 8.52                                | 5.0  | 3.52                             | Do.                                    |
| XXII....  | *8.00                               | 8.0  | 4.27                             | Clear liquid with a white precipitate. |
| XXIII...  | 8.52                                | 10.6 | 4.08                             | White gel.                             |

\*Approximately.

## Examples XXIV-XXV

A pad bath was made using the following formulation: 20 parts by weight of the melamine modified hydroxyethyl carbamate of Example XX (50% solids), 4 parts by weight  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 2 parts by weight polyethylene softener, and 74 parts by weight water. The bath was adjusted to pH 4.0 and padded onto a 100% cotton fabric. The results in Table VII show the excellent wash and wear properties of the cured fabric and in particular the excellent resistance to chlorine damage after bleach and scorch as indicated by the high percentage of the tensile strength retain for both the 350° F. cure and the 330° F. cure.

TABLE VII

| Example.....               | XXIV | XXV  |
|----------------------------|------|------|
| Cure temperature, °F.....  | 350  | 330  |
| Crease recovery angle..... | 297  | 282  |
| Tear strength.....         | 712  | 949  |
| Tensile strength:          |      |      |
| Before scorch.....         | 40.3 | 48.2 |
| After scorch.....          | 37.2 | 45.6 |
| Percent retained.....      | 92.2 | 94.5 |

## (C) METHYLOLATED ALKOXYALKYL CARBAMATES

## Examples XXVI-XXVII

One hundred nineteen grams methoxyethyl carbamate (1 mol), 137 grams 44% Formalin (2 mols) and 10 grams 20% NaOH are reacted at 50° C. At the end of one hour the solution contained 3.73% (0.35 mol) by weight excess formaldehyde. The pH of the solution was adjusted to 4.0 and 5.5 grams (0.044 mol) melamine added. After heating 60° C. for one hour, the formaldehyde content was reduced to 1.99%.

This experiment was repeated using an amount of melamine to result in a molar ratio with the free formaldehyde present of 6/1. The results in Table VIII show the importance of the amount of melamine used.

TABLE VIII

| Example  | Original free formaldehyde, percent | Formaldehyde to melamine (molar ratio) | Final free formaldehyde, percent | Appearance                            |
|----------|-------------------------------------|----------------------------------------|----------------------------------|---------------------------------------|
| XXVII... | 6.56                                | 6/1                                    | 2.95                             | Clear liquid that became a white gel. |
| XXVI.... | 3.73                                | 8/1                                    | 1.99                             | Clear liquid.                         |

## Examples XXVII-XXXIII

The procedure of Example XXVI was repeated using the 8/1 excess formaldehyde to melamine molar ratio at the pH values listed in Table IX. The results in Table IX show the importance of the pH at which the reaction is carried out.

TABLE IX

| Example   | Original free formaldehyde, percent | pH   | Final free formaldehyde, percent | Appearance and results                                                         |
|-----------|-------------------------------------|------|----------------------------------|--------------------------------------------------------------------------------|
| XXVIII... | 3.59                                | 1.5  | 2.13                             | Clear liquid. Pad bath unstable immediately.                                   |
| XXIX..... | 3.73                                | 4.0  | 1.99                             | Do.                                                                            |
| XXX.....  | 3.59                                | 5.0  | 2.07                             | Clear liquid. Pad bath stable for greater than 9 hours but less than 20 hours. |
| XXXI....  | 3.59                                | 6.0  | 2.19                             | Clear liquid. Pad bath stable for 5½ hours.                                    |
| XXXII.... | 3.59                                | 8.0  | 3.29                             | White precipitate in the resin.                                                |
| XXXIII... | 3.59                                | 11.0 | 2.60                             | Do.                                                                            |

## Examples XXXIV-XXXV

Of the melamine-modified resins prepared, the resin made by the reaction of 8 mols excess formaldehyde to 1 mol melamine at pH 5.0 was found to be the most stable resin that made a suitably stable pad bath.

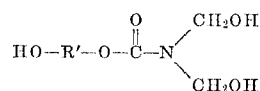
A pad bath was made using the following formulation: 70 parts by weight of the modified methoxyethyl carbamate of Example XXX (50% solids), 4 parts by weight  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 2 parts by weight polyethylene softener and 74 parts by weight water. The bath was adjusted to pH 4.5 and padded onto a 100% cotton fabric. Results in Table X show the excellent wash and wear of the cured fabric and, in particular, the excellent resistance to chlorine damage after an acid sour and bleach as indicated by the high percentage of the tensile strength retained for both the 350° F. and 330° F. cure.

TABLE X

| Example.....               | XXXIV | XXXV |
|----------------------------|-------|------|
| Cure temperature, °F.....  | 350   | 330  |
| Crease recovery angle..... | 282   | 279  |
| Tear strength.....         | 856   | 931  |
| Tensile strength:          |       |      |
| Before scorch.....         | 33.1  | 37.8 |
| After scorch.....          | 34.3  | 35.9 |
| Percent retained.....      | >100  | 94.6 |

We claim:

1. In a process for producing a methylolated hydroxyalkyl carbamate textile treating resin from formaldehyde and a hydroxyalkyl carbamate represented by the formula:



wherein R' is an alkylene radical of 2 to 4 carbon atoms the improvement comprising treating an aqueous solution

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of the reaction product of said formaldehyde and said hydroxyalkyl carbamate with melamine at an initial pH from about 3.5 to 5.0, wherein melamine is employed in an amount to provide about one mol melamine per about 6 to 9 mols of free formaldehyde in said solution, and wherein said treating is conducted at a temperature from about 20° C. to about the reflux temperature of the reaction mixture for about 1 to 5 hours. 5

2. The process according to claim 1 wherein the free formaldehyde content of the treated aqueous solution is from about 2 to about 4 wt. percent when said aqueous solution contains 50% solids. 10

3. The process according to claim 2 wherein said treating is conducted at a pH of about 4.0 and wherein about

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1 mol melamine per about 8 mols of free formaldehyde in said solution is employed.

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