FATTY GROUP CONTAINING METHYLOLATED, POLYOXYALKYLENE CARBAMATES AND TEXTILE MATERIALS SOFTENED BY TREATMENT THEREWITH

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Field of Search .......... 8/115.5, 115.6, 116.3, 8/127.6, 128 R, 115.7, 260/29.4 R, 404, 404.5, 482 B, 482 C

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1,970,578 8/1934 Schoeller et al. ............... 260/404
2,002,613 5/1935 Orthner et al. ................. 260/404
2,157,362 5/1939 Vairich et al. ................. 260/482 C
2,184,008 12/1939 Dickey et al. ................. 260/482 C
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2,218,939 10/1940 Steindorf ..................... 260/482 C
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2,585,826 2/1952 Olsen ........................ 260/482 B
2,598,445 8/1951 Stewart et al. ............... 260/482 C

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ABSTRACT

Carbamates are disclosed which are esters of carbamic acid, N-methyl carbamic acid, or N,N-dimethyl carbamic acid and an ethylene oxide adduct of a fatty acid, fatty alcohol, fatty acid ester of a polyol, fatty amine, or fatty acid amide. The carbamates contain at least one oxyethylene group, at least one fatty group, and at least one carbamate group. The carbamates are useful as textile treating agents or as intermediates for the preparation of textile treating agents. Process of treating textiles and textiles having improved properties are disclosed.

12 Claims, No Drawings
FATTY GROUP CONTAINING METHYLOLATED, POLYOXYALKYLENE CARBAMATES AND TEXTILE MATERIALS SOFTENED BY TREATMENT THEREWITH

This invention relates to novel carbamates. More particularly, this invention relates to novel carbamates which are useful as textile treating agents or as intermediates for the preparation of textile treating agents. This invention further relates to a process of treating textile material and to textile material having improved properties.

It is an object of this invention to provide novel carbamates.

It is another object of this invention to provide carbamates which are useful as intermediates for the preparation of textile treating agents.

It is another object of this invention to provide carbamates which are useful as textile treating agents.

It is another object of this invention to provide carbamates for application to textile materials to impart softness thereto, which will adhere to the textile materials through numerous subsequent laundering, drycleaning or similar operations and maintain a relatively high degree of softness in such materials without reapplication thereto.

It is another object of this invention to provide a process of treating textile materials.

It is another object of this invention to provide textile material having improved properties.

Other objects and advantages of this invention will be apparent from the following description and appended claims.

The novel carbamates of this invention are carbamates of an ethylene oxide adduct selected from the group consisting of:

1. an ethylene oxide adduct of a fatty acid containing from 12 to 28 carbon atoms, 2. an ethylene oxide adduct of a fatty alcohol containing from 12 to 28 carbon atoms, 3. an ethylene oxide adduct of a fatty amine containing from 12 to 28 carbon atoms, 4. an ethylene oxide adduct of an amide of a fatty acid containing from 12 to 28 carbon atoms, 5. an ethylene oxide adduct of a partial fatty acid ester of a polyhydric alcohol containing from 3 to 6 carbon atoms and from 2 to 6 hydroxyl groups, said fatty acid containing from 12 to 28 carbon atoms, and 6. a partial ester of a fatty acid containing from 12 to 28 carbon atoms and an adduct of ethylene oxide and a polyhydric alcohol containing from 3 to 6 carbon atoms and from 2 to 6 hydroxyl groups.

A preferred class of carbamates of this invention are carbamates of ethylene oxide adduct selected from the group consisting of (5) and (6).

The carbamates of this invention contain at least one oxoethylene group, at least one fatty group containing from 12 to 28 carbon atoms, and at least one

\[ \text{-O-} \text{C-} \text{N-} \text{R}_1 \text{C-} \text{NH}_2 \]

wherein \( \text{R}_1 \) and/or \( \text{R}_2 \) are hydrogen or methylol.

Accordingly, the carbamates of this invention may be described as esters of carboxylic acid, N-methylcarboxylic acid, or N,N-dimethylcarboxylic acid and the above defined ethylene oxide adducts. The carbamates wherein \( \text{R}_1 \) to \( \text{R}_4 \) are both hydrogen are useful as intermediates for the preparation of textile treating agents by reacting the carbamate with formaldehyde to introduce one or more methylol groups. The carbamates of this invention wherein \( \text{R}_1 \) and/or \( \text{R}_2 \) are methylol are useful as textile treating agents which impart a durable and permanent softness to textile materials when applied thereto.

The carbamates of this invention may be prepared by reacting one or more of the ethylene oxide adducts described herein with urea or with an alkyl carbamate such as ethyl or methyl carbamate. The reactions are illustrated by the following equations:

\[ \text{organic-} \text{OH} + \text{H}_2 \text{C-} \text{O-} \text{NH}_2 \rightarrow \text{H}_2 \text{COH} + \text{organic-} \text{O-} \text{C-} \text{NH}_2 \]

\[ \text{organic-} \text{OH} + \text{H}_2 \text{CNCNH}_2 \rightarrow \text{NH}_2 \text{+ organic-} \text{C-} \text{NH}_2 \]

These two well-known methods of forming carbamates are described in detail in the article by Adams et al. published in Chemical Reviews, Volume 65, pages 567-602, 1965. The disclosure of this article is hereby incorporated into this application by reference. Briefly, the reaction may be carried out by heating a mixture of urea or alkyl carbamate and an ethylene oxide adduct to a temperature in the range of from about 100°C to about 200°C. Catalysts, such as heavy metal salts of weak organic acids, zinc chloride, cobalt chloride, lead acetate, cupric acetate, boron trifluoride, aluminum isopropoxide, dicybutyl dilaurate, and dibutyltin oxide may be used to shorten the reaction time and increase the yield. The degree of carboxylation may be controlled by varying the amounts of ethylene oxide adduct and carboxymyating agent used. For example, the reaction of three moles of urea with one mole of an ethylene oxide adduct containing six hydroxyl groups will result in the formation of a carbamate containing an average of three carbamate groups. The carbamates of this invention may also be prepared by reacting an ethylene oxide adduct described herein with phosgene to form a chloroformic ester which then may be reacted with ammonia to give the carbamate. Other methods for preparing the carbamates of this invention will be readily apparent to one skilled in the art. The methylolated carbamates of this invention may be prepared by reacting the carbamate with formaldehyde, paraformaldehyde, or other convenient source of formaldehyde.

The ethylene oxide adducts which may be used to prepare the carbamates of this invention are known compounds. U.S. Pat. Nos. 1,559,930; 1,970,578; and 2,002,613, the disclosures of which are hereby incorporated hereinto by reference, disclose the preparation of ethylene oxide adducts which may be used to prepare the carbamates of this invention. Briefly, the ethylene oxide adducts may be prepared by reacting ethylene oxide with the appropriate fatty alcohol, fatty acid, fatty amine, fatty amide, or ester of fatty acid and a polyl or by reacting a fatty acid with an ethyl of ethylene oxide and a polyl.

Fatty alcohols which may be used to prepare the ethylene oxide adducts include saturated or unsaturated, straight or branched chain fatty alcohols having from...
A preferred group of fatty alcohols may be represented by the formula ROH wherein R is an alkyl group containing from 2 to 28 carbon atoms. Illustrative examples of such fatty alcohols include dodecanol, dodecenol, tetradecanol, tetradecene, hexadecanol, hexadecene, octadecanol, octadecene, eicosanol, eicosene, docosanol, docosenol, tetraicosanol, tetraicosene, hexacosanol, hexacosene, octacosanol, and octacosene.

Fatty acids which may be used to prepare the ethylene oxide adducts include saturated and unsaturated fatty acids having from 12 to 28 carbon atoms. A preferred group of fatty acids may be represented by the formula ROH wherein R is an alkyl group containing from 12 to 28 carbon atoms. Illustrative examples of such fatty acids include lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, oenadic acid, lauroieaid acid, myristoleic acid, palmitic acid, oleic acid, linolenic acid, ricinoleic acid, limic acid, eicosenoic acid, docosenoic acid, and tetracosenoic acid.

Fatty amines which may be used to prepare the ethylene oxide adducts include primary or secondary, saturated or unsaturated amines containing at least one fatty group having from 12 to 28 carbon atoms. A preferred group of fatty amines may be represented by the formula RNHR' wherein R is an alkyl or alkenyl group containing from 12 to 28 carbon atoms and R' is hydrogen or an alkyl or alkenyl group containing from 1 to 3 carbon atoms. Illustrative examples of such fatty amines include dodecylamine, hexadecylamine, octadecylamine, eicosylamine, pentacosylamine, dodecylamine, dodecylamine, N-ethyl octadecylamine, ARMEEEN TD, RMEEN SD cocoamine, oleylamine.

Fatty amides which may be used to prepare the ethylene oxide adducts include fatty amides having at least one fatty group containing from 12 to 28 carbon atoms. A preferred group of fatty amides may be represented by the formula RNR'H wherein R is an acyl group containing from 12 to 28 carbon atoms and R' is hydrogen or an alkyl or alkenyl group containing from 1 to 28 carbon atoms. Illustrative examples of such fatty amides include dodecanamide, hexadecanamide, octadecanamide, eicosanamide, pentacosanamide, N-methyl octadecanamide, N-stearyl dioxystearamide, dodecanamide, N-oleyl tetracetanamide, N-oleyl pentacetanamide, and N-aryl stearamide.

Polysols which may be used to prepare the ethylene oxide adducts include polysols having from 3 to 6 carbon atoms and from 2 to 6 hydroxyl groups. A preferred group of polysols may be represented by the formula ROHm wherein R is an aliphatic group having 3 to 6 carbon atoms and m is from 2 to 6. Illustrative examples of these polysols include propylene glycol, trimethylene glycol, butanediol, isosorbide, isomannide, glycerine, hexanetriol, pentaerythritol, erythritol, sorbitan, manitann, sorbitol, manritol, dulcitol, gueritol, inositol, and arabitol.

The novel carbamates of this invention may be characterized by a formula selected from the group consisting of the following generalized formulae wherein identical symbols have identical signification:

\[ R - O \left( \text{CH}_2 - \text{CH}_2 - O \right)_n R' \]

\[ \left( \text{CH}_3 - \text{CH}_2 - O \right)_n R' \]

\[ \left( \text{CH}_3 - \text{CH}_2 - O \right)_n R' \]

\[ \left( \text{CH}_3 - \text{CH}_2 - O \right)_n R' \]

wherein

\[ R \] is an alkyl group containing from 12 to 28 carbon atoms, an alkenyl group containing from 12 to 28 carbon atoms, an acyl group containing from 12 to 28 carbon atoms, or the group resulting from removing a hydroxyl group from lanolin,

\[ R' \] is hydrogen or \(-\text{CH}_2\text{OH}\), \(-\text{CH}_3\text{OH}\), \(-\text{CH}_2\text{OH}\), \(-\text{CH}_3\text{OH}\),

\[ n \] is an integer from 1 to 150,

\[ R_1 \] is the group remaining after removing all the hydroxyl groups from a saturated, aliphatic polyhydric alcohol having from 3 to 6 carbon atoms and from 2 to 6 hydroxyl groups,

\[ x \] is an integer from 2 to 6,

each A is independently selected from the group consisting of hydrogen, alkyl groups containing from 12 to 28 carbon atoms, alkenyl groups containing from 12 to 28 carbon atoms, acyl groups containing from 12 to 28 carbon atoms,
with the proviso that at least one \( \mathbf{R}_1 \) contains a

\[
\text{R}_{1} = \text{N} - \mathbf{R}_1
\]

group.

\( \text{R}_3 \) is \( \text{H} \) or

\[
\text{R}_{1} = \text{N} - \mathbf{R}_1
\]

with the proviso that at least one \( \mathbf{R}_5 \) is

\[
\text{R}_{5} = \text{H} - \mathbf{R}_5
\]

In order that those skilled in the art may better understand the nature and preparation of the carbamates of the present invention, the following examples are given. These examples are set forth solely for the purpose of illustration and any specific enumeration of details contained therein should not be interpreted as expressing limitations of this invention. All parts and percentages are by weight, unless otherwise stated.

The following procedure is employed in Example 1 to 25. The indicated amounts of urea and ethylene oxide adduct are charged to a three-necked flask and the contents of the flask heated to the indicated temperature for the indicated length of time. The reaction product is filtered to remove any unreacted urea. The filtrate is the carbamate of the starting ethylene oxide adduct. The recovered carbamate is then mixed with a 37% aqueous solution of formaldehyde and heated to about 50°C for 10 to 12 hours to form the methylolated carbamate.

<table>
<thead>
<tr>
<th>Example</th>
<th>Ethylene Oxide Adduct</th>
<th>Grams of Adduct</th>
<th>Grams of Urea</th>
<th>Temp. °C</th>
<th>Time-Hours Carbamate</th>
<th>Methylene Carbamate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyoxyethylene (4) lauryl alcohol</td>
<td>200</td>
<td>35.6</td>
<td>155</td>
<td>13.67</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>Dioleate of polyoxyethylene (20) sorbitol</td>
<td>60</td>
<td>5.8</td>
<td>150</td>
<td>9.62</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>Dioleate of polyoxyethylene (15) castor oil</td>
<td>500</td>
<td>5.8</td>
<td>160</td>
<td>6.66</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>Polyoxyethylene (20) tall oil</td>
<td>200</td>
<td>13.4</td>
<td>160</td>
<td>6.66</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>Dioleate of Polyoxyethylene (20) glycerol</td>
<td>106</td>
<td>5.3</td>
<td>150-160</td>
<td>5.6</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>Polyoxyethylene (20) ether of lanolin</td>
<td>200</td>
<td>7.8</td>
<td>160</td>
<td>7.27</td>
<td>1.2</td>
</tr>
<tr>
<td>7</td>
<td>Monopalmitate of Polyoxyethylene (20) glycerol</td>
<td>200</td>
<td>21.2</td>
<td>115-160</td>
<td>7.83</td>
<td>1.2</td>
</tr>
<tr>
<td>8</td>
<td>Polyoxyethylene (40)-N-decyl-12-hydroxystearamide</td>
<td>200</td>
<td>5.4</td>
<td>160</td>
<td>6.52</td>
<td>1.2</td>
</tr>
<tr>
<td>9</td>
<td>Polyoxyethylene (20) ether of sorbitol monooloate</td>
<td>200</td>
<td>17</td>
<td>155-160</td>
<td>6.64</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>Polyoxyethylene (30) stearic acid</td>
<td>200</td>
<td>10.4</td>
<td>160</td>
<td>4.65</td>
<td>1.2</td>
</tr>
<tr>
<td>11</td>
<td>Polyoxyethylene (5) ARMEEN SD</td>
<td>100</td>
<td>26</td>
<td>155-165</td>
<td>6.83</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>Polyoxyethylene (14) cocoamine</td>
<td>100</td>
<td>16.6</td>
<td>150</td>
<td>5.1</td>
<td>1.2</td>
</tr>
<tr>
<td>13</td>
<td>Polyoxyethylene (20) sorbitan monolaurate</td>
<td>100</td>
<td>33</td>
<td>150</td>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td>14</td>
<td>Polyoxyethylene (20) sorbitan monostearate</td>
<td>100</td>
<td>27.6</td>
<td>150</td>
<td>5.05</td>
<td>1.2</td>
</tr>
<tr>
<td>15</td>
<td>Dioleate of polyoxyethylene (20) sorbitol</td>
<td>100</td>
<td>15</td>
<td>150</td>
<td>7.08</td>
<td>1.2</td>
</tr>
<tr>
<td>16</td>
<td>Polyoxyethylene (5) octadecylamine</td>
<td>100</td>
<td>24</td>
<td>150-160</td>
<td>12.06</td>
<td>1.2</td>
</tr>
<tr>
<td>17</td>
<td>Polyoxyethylene (20) ARMEEN TD</td>
<td>100</td>
<td>19.8</td>
<td>155</td>
<td>6.6</td>
<td>1.2</td>
</tr>
<tr>
<td>18</td>
<td>Polyoxyethylene (25) hydrogenated castor oil</td>
<td>100</td>
<td>8.4</td>
<td>155</td>
<td>6.5</td>
<td>1.2</td>
</tr>
<tr>
<td>19</td>
<td>Polyoxyethylene (54) castor oil</td>
<td>100</td>
<td>6.6</td>
<td>155</td>
<td>7.88</td>
<td>1.2</td>
</tr>
<tr>
<td>20</td>
<td>Polyoxyethylene (81) castor oil</td>
<td>100</td>
<td>4.5</td>
<td>150-165</td>
<td>10.6</td>
<td>1.2</td>
</tr>
<tr>
<td>21</td>
<td>Polyoxyethylene (150) hydrogenated castor oil</td>
<td>100</td>
<td>3.2</td>
<td>155</td>
<td>6.75</td>
<td>1.2</td>
</tr>
<tr>
<td>22</td>
<td>Polyoxyethylene (50) octadecylamine</td>
<td>100</td>
<td>6</td>
<td>150</td>
<td>12.77</td>
<td>1.2</td>
</tr>
<tr>
<td>23</td>
<td>(3)</td>
<td>100</td>
<td>24</td>
<td>170-175</td>
<td>6.8</td>
<td>1.2</td>
</tr>
<tr>
<td>24</td>
<td>Polyoxyethylene (25) hydrogenated castor oil</td>
<td>100</td>
<td>5.6</td>
<td>155</td>
<td>7.53</td>
<td>1.7</td>
</tr>
<tr>
<td>25</td>
<td>Polyoxyethylene (25) hydrogenated castor oil</td>
<td>100</td>
<td>10.1</td>
<td>155</td>
<td>7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

(1) Number of carbamate groups introduced per hydroxy group in ethylene oxide adduct charged (by analysis for non-urea nitrogen).
(2) Number of N-methylol groups per carbamate group.
(3) Prepared by reacting ethylene oxide with an 85% aqueous sorbitol solution, and esterifying the reaction product with 2 mols of oleic acid per six equivalent of hydroxyl.

The procedure of Examples 1 to 25 is followed in Examples 26 to 29 except that the indicated amount of ethyl carbamate is used instead of urea and a toluene azetrop is used to remove the liberated ethanol. 100 grams of the indicated ethylene oxide adduct are employed in each example.

<table>
<thead>
<tr>
<th>Example</th>
<th>Ethylene Oxide Adduct</th>
<th>Grams of Ethyl Carbamate</th>
<th>Temperature °C</th>
<th>Time-Hours Carbamate</th>
<th>Methylene Carbamate</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Polyoxyethylene (5) octadecylamine</td>
<td>44.5</td>
<td>140</td>
<td>9.75</td>
<td>0.8</td>
</tr>
<tr>
<td>27</td>
<td>Polyoxyethylene (25) hydrogenated castor oil</td>
<td>13.3</td>
<td>130</td>
<td>6.9</td>
<td>0.9</td>
</tr>
<tr>
<td>28</td>
<td>Polyoxyethylene (20) sorbitan monolaurate</td>
<td>48.5</td>
<td>130</td>
<td>10%</td>
<td>1</td>
</tr>
<tr>
<td>29</td>
<td>Polyoxyethylene (5) octadecylamine</td>
<td>44.5</td>
<td>135</td>
<td>12%</td>
<td>0.8</td>
</tr>
</tbody>
</table>

(1) Number of carbamate groups introduced per hydroxy group in ethylene oxide adduct.
(2) Number of N-methylol groups per carbamate group.

droxy groups from an adduct of ethylene oxide and a partial fatty acid ester of a polyl having from 2 to 6 hydroxyl groups and from 3 to 6 carbon atoms, said fatty acid containing from 12 to 28 carbon atoms.

In accordance with the present invention, the carbamates containing at least one methylol group may be used to treat textile material to impart thereto improved physical characteristics such as softness. It has been found that if the methylolated carbamates of the
The present invention are applied to textile material along with a textile resin catalyst for the methylolated carbamate and the textile material heated to an elevated temperature, the methylolated carbamate will be attached to the fiber so that the softening properties imparted to the fabric will not be removed by subsequent washing or drycleaning. The methylolated carbamates of the present invention have been found to work well in cellulose fibers. Although this invention is in no way limited by theoretical considerations, the methylolated carbamates of the present invention are believed to react with the treated cellulose fibers during the curing operation by means of a condensation reaction between the methylo groups of the carbamate and the hydroxyl groups of the cellulose. Similarly, the methylolated carbamates are believed to react with the amino groups or the carbonyl groups present in wool, with the terminal amino or carboxyl groups in nylon or the amide groups therein having active hydrogen atoms, or with the end hydroxyl or carboxyl groups in polyester fibers.

The textile resin catalysts for the methylolated carbamate may be any of the catalysts known in the art for catalyzing the reaction of methylol groups with active hydrogen atoms of textile materials. A preferred class of catalyst is the acid or acid catalysts. By latent acid catalysts is meant substances which develop acidity during the curing step. Particularly suitable catalysts include metal salts of strong acids such as magnesium chloride, magnesium sulfate, zinc nitrate, and aluminum sulfate; ammonium salts such as ammonium chloride, ammonium dihydrogen phosphate, and ammonium thiocyanate; amine salts such as triethyamine hydrochloride, and triethanolamine hydrochloride. The amount of curing catalyst for the methylolated carbamate will depend on the nature of the carbinate, textile material, and catalyst and on the curing temperature and curing time. In general, satisfactory results may be obtained by using from about 0.05% to about 3%, preferably from about 3% to about 10%, by weight of catalyst based on the weight of methylolated carbamate.

Preferably, although not necessarily, the methylolated carbamates are applied to textile materials in the form of aqueous dispersions thereof by conventional methods. The curing catalyst may be applied to the textile material along with the carbamate or from a separate bath. The textile material may be treated with an aqueous dispersion of the carbamate by immersion therein or by spraying. In the immersion method of application, the textile material may either be run through padding machine wherein the textile material is first dipped into the aqueous dispersion or solution of the carbamate and then squeezed, or the textile materials may be dipped into the liquid and the excess liquid extracted by centrifugation. In the spraying method of application, the fabrics are simply sprayed with an aqueous solution or dispersion of the carbamate and then dried by any suitable means.

The amount of methylolated carbamate applied to the textile material may vary over a wide range and will depend, mainly, on the degree of softness desired. Preferably, the methylolated carbamates are applied to textile fabrics in amounts within the range of about 1% to about 5% by weight based on the dry weight of the fabric.

The heat cure of the textile fabric treated with the methylolated carbamates may be effective at temperatures from about 300°F. to 350°F. and in periods of time ranging from about 10 to about 15 minutes at the lower temperature to about 2 to 3 minutes at the higher temperatures. The reaction may take place at lower temperatures if the curing time is extended. Higher temperatures may also be employed.

The following examples are illustrative of the application of two preferred methylolated carbamates of the present invention to fabric materials. It is understood, of course, that other methylolated carbamates may be readily substituted for those employed in the following examples.

The following procedure is employed in Examples 30 and 31. Swatches of cotton poplin fabric are treated with the indicated treating solution at 80% pickup on the Butterworth Pad. The treated swatches contain 1% of the indicated methylolated carbamate and 0.1% of the zinc catalyst. The swatches are air dried at 200°F. for 5 minutes and then cured at 325°F. for 5 minutes. One half of the swatches are washed ten times in an automatic washing machine using 0.2% detergent (TIDE) solution at 60°C. The swatches are dried in a clothes dryer after each wash. The subjective hand rating and tear strength values are then determined using standard textile laboratory testing procedures.

<table>
<thead>
<tr>
<th>Example</th>
<th>Treating Solution</th>
<th>Subjective Hand Rating</th>
<th>Warpwise Elmendorf Tear Strength (lb.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Water</td>
<td>3.3</td>
<td>1.56</td>
</tr>
<tr>
<td>30</td>
<td>(3)</td>
<td>3.0</td>
<td>1.56</td>
</tr>
<tr>
<td>31</td>
<td>(4)</td>
<td>1.8</td>
<td>1.96</td>
</tr>
</tbody>
</table>

(1) The lower the numerical rating, the softer the fabric
(2) ASTM D1454-59
(3) 96.15% of water plus 0.12% of Zn(NH₄)₂H₂O₆ plus 3.75% of the methylolated carbamate of Example 2
(4) 97.98% of water plus 0.12% of Zn(NH₄)₂H₂O₆ plus 2.9% of the methylolated carbamate of Example 2.

Although this invention has been described with reference to specific reactant materials, including specific ethylene oxide adds, carbamate agents, and methylolating agents, it will be apparent that still other different and equivalent materials may be substituted for those described. Moreover, application processes and reaction steps thereof may be modified within the spirit and scope of this invention.

Having described the invention, what is desired is to be secured by Letters Patent is:

1. An ester of (1) carbamic acid, N-methyl carbamic acid, or N,N-dimethyl carbamic acid and (2) an ethylene oxide adduct of castor oil.

2. An ester of (1) carbamic acid, N-methyl carbamic acid, or N,N-dimethyl carbamic acid and (2)
an ethylene oxide adduct of hydrogenated castor oil.

3. An ester of (1) carbamic acid or N-methylol carbamic acid, and (2) polyoxymethylene(25) hydrogenated castor oil.

4. An ester of (1) carbamic acid, N-methylol carbamic acid, or N,N-dimethylol carbamic acid and (2) an ethylene oxide adduct of a secondary fatty amine containing from 12 to 28 carbon atoms.

5. A carbamate characterized by the formula

\[
R-O\left(CH_{2}-CH-O\right)_{x}C-N-R_{1}R_{2}
\]

wherein R is an acyl group containing from 12 to 28 carbon atoms or the group resulting from removing a hydroxyl group from lanolin, R is hydrogen or \(-CH_{2}OH\), R is \(-CH_{2}OH\), n is an integer from 1 to 150, R is the group remaining after removing all the hydroxy groups from a saturated, aliphatic polyhydric alcohol having from 3 to 6 carbon atoms and from 2 to 6 hydroxyl groups, x is an integer from 2 to 6, each A is independently selected from the group consisting of hydrogen, alkyl groups containing from 12 to 28 carbon atoms, alkenyl groups containing from 12 to 28 carbon atoms, acyl groups containing from 12 to 28 carbon atoms, and -(CH_{2}-CH-O)-Rio wherein R is hydrogen or

6. A carbamate of claim 5 having the formula

\[
R-O\left(CH_{2}-CH-O\right)_{x}C-N-R_{1}R_{2}
\]

wherein R is an acyl group containing from 12 to 28 carbon atoms, n is an integer from 1 to 150, R is hydrogen or methylol, and R is methylol.

7. A carbamate of claim 5 having the formula

\[
R_{a}-N-B
\]

with the proviso that at least one A contains an alkyl, alkenyl, or acyl group containing from 12 to 28 carbon atoms, or

8. A carbamate of claim 5 having the formula

\[
R_{a}-N-B
\]

wherein R is an alkyl group containing from 12 to 28 carbon atoms or an alkenyl group containing from 12 to 28 carbon atoms, each B is independently selected from the group consisting of alkyl groups containing from 1 to 28 carbon atoms, alkenyl groups containing from 1 to 28 carbon atoms, and -(CH_{2}-CH-O)-Rio wherein R is hydrogen or
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wherein \( R_1 \) is hydrogen or methylol, and wherein \( R_2 \)
is methylol.

8. A carbamate of claim 5 having the formula \((R_6)_2O-D\)
wherein \( R_3 \) is H or

\[
\begin{array}{c}
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

with the proviso that at least one \( R_3 \) is

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

\( y \) is a number from 1 to 5.

D is the group remaining after removing all the hy-
droxyl groups from an adduct of ethylene oxide
and a partial fatty acid ester of a polyol having from
2 to 6 hydroxyl groups and from 3 to 6 carbon
atoms, said fatty acid containing from 12 to 28 car-bon atoms, \( R_1 \) is hydrogen or methylol, and \( R_2 \)
is methylol.

9. A carbamate of claim 5 having the formula
\((R_6)(OA)_2\)
wherein

\( R_3 \) is the group remaining after removing all the hy-
droxyl groups from a saturated, aliphatic polyhy-
dric alcohol having from 3 to 6 carbon atoms and
from 2 to 6 hydroxyl groups,

\( x \) is an integer from 2 to 6,
each \( A \) is independently selected from the group con-sisting of hydrogen, alkyl groups containing from
12 to 28 carbon atoms, alkenyl groups containing 35
from 12 to 28 carbon atoms, acyl groups containing
from 12 to 28 carbon atoms,

\[
\begin{array}{c}
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

and \((\text{CH}_2=\text{CH}_2-O)_n\) \( R_8 \)
wherein \( R_8 \) is hydrogen, an acyl group containing
from 12 to 28 carbon atoms, or

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

12. An article of manufacture comprising textile ma-
terial treated in accordance with the process of claim

11.

with the proviso that at least one \( A \) contains an alkyl,
alkenyl, or acyl group containing from 12 to 28
carbon atoms, at least one \( A \) contains a \((\text{CH}_2=\text{CH}_2-O)_n\) \( R_8 \)
group, and at least one \( A \) contains a

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

\( R_1 \) is hydrogen or methylol, and \( R_2 \) is methylol.

10. A carbamate of claim 9 having the formula
\((R_6)(OA)_2\)
wherein

\( R_3 \) is the group remaining after removing all the hy-
droxyl groups from sorbitol.

\( A \) is independently selected from the group consist-
ing of hydrogen,

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

or \((\text{CH}_2=\text{CH}_2-O)_n\) \( R_8 \)
wherein \( R_8 \) is hydrogen, an acyl group containing
from 12 to 28 carbon atoms, or

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

with the proviso that at least one \( A \) contains an acyl
group containing from 12 to 28 carbon atoms, at
least one \( A \) contains a \((\text{CH}_2=\text{CH}_2-O)_n\) \( R_8 \)
group, and at least one \( A \) contains a

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N} \\
\text{R}_1 \\
\text{R}_4 \\
\end{array}
\]

11. A process of treating textile material containing
cotton and nylon which comprises depositing a carba-
mate of claim 5 and an acidic textile resin catalyst on
the surface of the textile material and thereafter curing
by heating the textile material to an elevated tempera-
ture.

12. An article of manufacture comprising textile ma-
terial treated in accordance with the process of claim

11.

* * * * *
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,925,009
DATED : December 9, 1975
INVENTOR(S) : Thomas F. Rutledge and John D. Zech

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 4, "R₁ to R₂" should read -- R₁ and R₂ --.

Column 3, line 60, "guercitol" should read -- quercitol --.

Column 6, lines 22 & 56,"Carbamate(1)" should read--Carbamate(1)/-. Hydroxy Hydroxy

Column 6, lines 22 & 56,"Methylole(2)" should read--Methylole(2)/-. Carbamate Carbamate

Column 10, line 65, "\(\text{CH}_2\text{-CH}_2\text{-O-nC-N}^\text{R}_1\text{R}_2\)" should read --

\(\text{CH}_2\text{-CH}_2\text{-O-nC-N}^\text{R}_1\text{R}_2\) group,

Signed and Sealed this Twenty-seventh Day of September 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks