PROCESS OF CREASE-PROOFING CELLULOSE FIBERS AND FABRICS BY APPLYING UREA-FORMALDEHYDE-GLYoxal REACTION PRODUCTS

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The present invention relates to new and useful improvements in the treatment of fibers and fabrics, particularly fibers and fabrics of native or regenerated cellulose, in order to impart crease-resistance thereto.

One of the principal objectives of the present invention is to substantially increase the resistance to creasing of fabrics or fibers while at the same time substantially improving the body and feel of the treated textiles as compared with those obtainable with the treatment methods heretofore customary.

A further object of the present invention is to provide a simple and effective method of treating fibers and fabrics of native or regenerated cellulose by which their resistance to creasing is increased, expressed by the angle of increase, increases 80 to 100% as compared with the value of the initial material.

A still further object of the invention comprises baths for the impregnation of fibers and fabrics of native or regenerated cellulose which make possible an increase of the crease-resistance of the order of magnitude indicated above, and also the method for the preparation of these baths.

A still further object of the invention is crease-proof fibers or fabrics of native or regenerated cellulose which have been treated in accordance with the invention.

These and still further objects will become evident from the following description:

It has been found that improved conditions for increasing the resistance to creasing can be obtained if the textile material which is to be treated is impregnated in aqueous solution which contain 1% to 35% and preferably 1% to 10%—of a derivative of tetrahydroimidazole, such as the type formed from urea and glyoxal or of urea, glyoxal and formaldehyde.

The impregnation of the textile material in such solutions containing tetrahydroimidazole compounds can be effected at a pH of between 3 and 8 and preferably between 3 and 5. Thereafter the impregnated textile material is freed from excess impregnation solution by squeezing, centrifuging or removal by suction and dried at temperatures of up to 100° C. or slightly above. In stead of using aqueous solutions of the said compounds, there can be also directly used the reaction mixtures, possibly after suitable dilution and adjustment of the proper pH, obtained upon the preparation of the said compounds from the starting materials. The reaction solutions thus obtained are well-suited for the impregnation without previous isolation of the reaction product, and preferably after the addition of a suitable catalyst and possibly a suitable softener, filler, finishing agent, etc., for the treatment of textiles of native or regenerated cellulose.

After the finishing, in accordance with the invention, the threads and fabrics have an excellent crease-resistance, while at the same time the finishing is reduced by about one-half. In this connection, the textiles impregnated with the new reaction solutions do not require any special heat treatment inasmuch as no after-condensation of the tetrahydroimidazole compounds on the fiber is necessary and a mere drying of the impregnated textile material after the excess impregnation solution has been removed, at temperatures up to 100° C. or slightly more, is sufficient.

In order to obtain the effect of the present invention, there can be used with excellent results for example an aqueous solution of dihydroimidazole which is obtained in the known manner by reacting ethylenediamine with urea, preferably using a slight excess of the ammine, by boiling under a reflux condenser. It is also possible to use other mono- or polynhydroxy, mono- or polynhydroxy, or mixed hydroxy, oxo derivatives of tetra-hydroimidazole for this purpose. As examples, there may be mentioned the 4,5-dihydroxytetrahydroimidazolone-1(2) known under the name Glyoxalmonouren, or the Hydanilin obtainable therefrom by the splitting off of water (4-oxotetrahydroimidazolone-1(2)) as well as parabanic acid (4,5-dioxotetrahydroimidazolone-1(2)).

In accordance with a preferred embodiment of the invention and with improved results, compounds which are produced by reaction of urea with glyoxal followed by reaction of the reaction product obtained thereby with formaldehyde or by reaction of urea with formaldehyde followed by reaction of the compound produced with glyoxal may be used. In both cases the best results with regard to the desired increase of the resistance to creasing is obtained with compounds for the preparation of which 1 or 1.5 mols formaldehyde are used per mol of urea and per mol of glyoxal.

In the preparation of the compounds or of the treatment baths containing them, it is of considerable importance on the one hand to maintain a given pH range during the reaction of urea with glyoxal or urea with formaldehyde and on the other hand during the subsequent reaction of the intermediate products with formaldehyde or glyoxal.

The reaction of glyoxal with urea in equi-molecular quantities to form glyoxalmonouren can be carried out in an acid to neutral reaction in which connection the pH should not be allowed to go below 3.5. The further reaction of the glyoxalmonouren with formaldehyde is effected adversely in neutral or weakly alkaline solution. At pH of 8, the imidazolone can rapidly react even at room temperature without the addition of heat, with 1 mol of formaldehyde. While at a pH of the solution of 6 the operation is preferably carried out at the boiling point. The new compound obtained after concentration in vacuum constitutes a colorless, viscous oil which is characterized by a pronounced sweet taste, evidently as a result of the hydroxyl groups contained therein. The compound obtained shows practically no free aldehyde in an aldehyde determination.

In the said reaction there is generally obtained an approximately 30% solution of the compound which can be used as such, without special isolation of the compound, for the impregnation of textile articles. The impregnation generally takes place best in the weakly acid range and therefore at a pH of from 3.5 to 4 at temperatures of up to 100° C.

It has been found that when using a reaction ratio of 0.5 mol formaldehyde to 1 mol glyoxalmonouren in acid solution there is produced a double ring compound in which 2 imidazolone carbonyl groups are connected with one another by a methylene bridge on nitrogen and therefore in the 1 position. If this compound, after completion of the reaction, is caused to react with another mol of formaldehyde per mol of monounre in neutral to weakly alkaline solution, there is obtained a compound which contains 1 hydroxymethyl group on each of the free nitrogen atoms and therefore in the 3-position of each ring, and therefore must be designated as methylene-1-bis-4,5-
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dihydroxydihydro-1 - hydroxymethyl-imidazolone - (2) or methylene - 1 - bis - 4,5 dihydroxy - 3 - hydroxymethyltetrahydroimidazol - methane - 1 - bis - 4,5 dihydroxytetrahydro-3-hydroxymethylimidazolone-2.

The same compound is obtained if 1 mol urea is first of all reacted with 1.5 mol formaldehyde in aqueous neutral to weakly alkaline solution forming a monoethyl urea and the latter after the reaction is caused to react in neutral or weakly alkaline medium with 1 mol of glyoxal, in which connection the methylol urea and the glyoxal react readily and completely even in the cold so that the reaction solution does not contain substantially any free aldehide. If however the reaction for instance of dimethylol urea with glyoxal does not take place in neutral or weakly alkaline solution but rather in acid solution, both free formaldehyde and free glyoxal can be detected in considerable quantities in the reaction solution even if the solution, in order to assist the reaction, is heated to 70° C. and over, and even after the reaction has proceeded for hours. In general not more than 35% of the starting materials used will react in acid solution. The fabrics treated with such a solution exhibit a relatively favorable resistance to scraping but however, have practically no resistance to creasing. Furthermore, the strength of fabrics which have been treated with such strongly acid impregnation solutions at elevated temperatures decreases substantially after a short time.

The successful results are only obtained in accordance with the invention if the reaction of the urea first of all terminates with an equimolecular quantity of glyoxal and this product is thereupon caused to react completely with formaldehyde.

As catalysts for the reaction of the textile material with the reaction products contained in the impregnation solution there are advantageously used boric acid, tartaric acid, aluminum chloride, organic aluminum salts and the like, either alone or in mixture.

Suitable softening agents which can be used for the treatment baths are for example, sulfonated oils such as sulfonated olive oil, a formic acid emulsion of trialkylammoniumestearate, the condensation product of 1 mol stearic acid and 6 mols ethylene-oxide, the products known under the name Soromin A and Soromin HSG and others.

Further details concerning the preparation of the products improving crease-resistance and the treatment baths containing them as well as concerning the impregnation of textiles with these baths can be noted from the following examples, which are given by way of illustration and not limitation.

The values for the crease angles of the untreated and treated textiles given in these examples were determined by folding the ends of a strip cut from the fabric to be tested over one another and holding the strip completely under a weight. After a given time of loading which was the same in all tests, the weight was lifted and the strip was laid on a smooth surface. Thereupon the strip sprang open to a certain crease angle which depended on its resistance to creasing. This angle was measured as the crease angle. The angle becomes greater with increasing resistance to creasing. In the ideal case, the crease angle is 180° under any load.

Example 1

300 grams of an approximately 30% solution obtained by the reaction of dihydroxydihydroimidazolone with formaldehyde were diluted to 1 liter and thereupon 2 grams of a non-ionicogen softener, as for example Soromin HSG, were added thereto. The pH of the solution was adjusted to 4 by the addition of a few drops of hydrochloric acid. A fabric, the warp and filler of which contained staple fiber, was immersed with this solution at room temperature, then squeezed out to 90% moisture and dried at temperatures of up to 100° C. The treated fabric exhibited a good body and softness and had a swelling value of 48.2% and a crease angle of 130° while the starting material had a swelling value of 95% and a crease angle of 70°.

The example was repeated using instead of the compound described, a solution of hydroxymethylbenzaldimine and good results were obtained.

Example 2

A fabric, the warp and filling of which consisted of viscose rayon 100/40, was treated as follows: 10. 280 grams of approximately 30% solution of a product which was produced by reaction of dihydroxydihydroimidazolone with formaldehyde, were diluted to 1 liter whereupon 3 grams of a cation-active softener i.e. Soromin A, were added. The pH of the solution was adjusted to 4 by the addition of phosphoric acid. The fabric was impregnated, squeezed out and dried in the manner indicated in Example 1. It exhibited a swelling value of 47.2% and a crease angle of 118°, while the swelling value of the initial material was 105% and the crease angle 47°. The impregnated fabric did not show any trace of yellowing and could therefore be dyed excellently even in light, sensitive shades.

Example 3

30 kilograms of urea were added to a vessel provided with an agitator and thereupon dissolved with 50 kilograms technical 30% glyoxal, the pH of which had previously been adjusted to 3.5 by the use of NaOH with thorough mixing. As soon as the reaction temperature had risen to 30° C., small portions of technical glyoxal solution were added until a total quantity of 50 kilograms had been added, to the reaction mass. The termination of the reaction was ascertained by aldehyde determination. As a rule, there are obtained aldehyde values of 0.5 to 0.8% corresponding to a reaction of 98.5%. There was then added sufficient 10% caustic solution to increase the pH to 8. and thereupon there were immediately added 37.5 kilograms 40% formaldehyde solution. Reaction took place with a slight generation of heat, it being possible to note the progress of the reaction by the determination of the untreated aldehyde. After about 2 hours, the residual aldehyde decreased to 0.8% and there was thereupon added a quantity of HCl corresponding to the sodium acetate (produced upon the neutralization of the acetic acid in the technical glyoxal with NaOH). The solution in this way was imparted a pH of 3.5 which will not alter, in this form, when stored.

20 kilograms of the above described solution were dissolved in 80 liters H₂O of about 30° C. whereupon there was added, in addition to 1 kilogram boric acid, 0.5 kilogram of a cation-active softener, such as a formic acid emulsion of trialkylammoniumestearate. A fabric, the warp of which consisted of viscose rayon and the filling of staple fiber, was then treated with the solution and squeezed out to 90% moisture and finally dried at 100° C. in a conventional drying apparatus. The treated fabric had an entirely pleasant feel. The swelling value of the goods was 46% as compared with 87% for the starting material. The crease angle was improved from 84° to 150°. The effect is resistant to dry-cleaning.

Example 4

15 kilograms hydrolyzed starch as filler were mixed with 50 kilograms H₂O and dissolved by the addition of 50 kilograms 18% caustic solution forming a clear liquid. Thereupon, 120 kilograms urea were introduced into the above mass and 200 kilograms technical glyoxal (30%) added and dissolved by stirring. After 1 hour there were again added 200 kilograms technical glyoxal while stirring until the free aldehye had dropped to 0.3%. 200 kilograms 20% formaldehyde were then added with sufficient 18% caustic solution to bring the pH to 7.5. After the reaction had terminated, 35 kilograms
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AlCl₃·3H₂O were added and the pH was brought to 3.5. 18 kilograms of the above solution were dissolved with 82 liters of H₂O. To the dilute solution there was furthermore added 0.3 kilogram of a non-ionic softener (condensation product of 1 mol stearic acid and 6 mol ethylene oxide) and a staple fiber poplin was treated therein and then pressed out to 80% moisture and dried without tension at 100°C. Thereupon the goods are straightened and finished in the customary manner. The fabric had good body and excellent crease-resistant properties.

Example 5

30 kilograms of urea were placed in a vessel having an agitator and thereupon dissolved by thorough mixing with 50 kilograms technical 30% glyoxal, the pH of which had previously been brought to 3.5 by means of NaOH. Small portions of glyoxal solution were added to the reaction mass in a total quantity of 50 kilograms as soon as the reaction temperature had risen to 30°C. The end of the reaction could be ascertained by aldehyde determination. As a rule, there were obtained aldehyde values of 0.5 to 0.8% corresponding to a 98.5% conversion. The solution which was thus obtained could be used directly for the treatment of cellulose yarns or fabrics without isolation of the solid substance.

25 kilograms of the reaction mass were dissolved in 75 liters H₂O. The sodium acetate produced during the preparation, i.e. upon the buffering with NaOH, was first of all decomposed by the addition of an equimolecular quantity of HCl. Thereupon, 15 grams of glycolic acid were added. The pH of the solution was 3.0-3.2. A fabric of viscose rayon was then impregnated in this solution and thereupon squeezed out and dried in circulating air at 100°C. The finished goods, in addition to a decreased swelling value (51%), showed an excellent improvement in the resistance to creasing (increase from 90° to 145°).

Example 6

6 mols urea were mixed with 6 mols glyoxal contained in a 30% solution, the pH of which had been adjusted to 4 by means of caustic soda solution prior to use. The reaction temperature rose without the addition of heat to 52°C. After the temperature had dropped again, 3 mols of formaldehyde were added and the mixture was allowed to react for one hour. After the end of this reaction period, it was ascertained that the reaction was complete by the determination of the free aldehyde. The free aldehyde should not be higher than 1%. The reaction mass was then brought to a pH of 8 by the addition of caustic solution and 6 mols of formaldehyde were added. After about 3 hours, the reaction had come to completion without the addition of heat. The reaction mass contained about 1/5% free residual aldehyde; in this connection a compound methylene-1-bis-4,5-dihydroxydihydro-3-hydroxymethylimidazolone-(2) or methylene-1-bis-4,5-dihydroxy-3-hydroxymethyltetrahydroimidazole-one (2) of the following formula had been formed:

Thereupon, 30 cc. of a 10% hydroxylaminohydroxyhydrate solution was added, followed by boiling for 30 minutes under a reflux condenser, titrating with

\[
\frac{1}{2} \text{NaOH}
\]

after cooling

\[
(1 \text{ cc} \frac{1}{2} \text{NaOH} = 0.029 \text{ gram CHO})
\]

After adding further addition agents such as fillers, finishers, particularly tylose or water-repellent finish, the pH of the solution was finally adjusted to 3.0 by means of HCl.

In this bath, a dress material consisting of 100% viscose staple fiber was impregnated and thereupon squeezed out to 100% moisture followed by drying at 100°C without tension. After the drying, the material was straightened out and cutted. The examination of the material treated in this manner gave the following values as compared with the untreated material:

| Crease angle | degrees | 145 | 70 |
| Resistance to scraping with an initial load of 400 grams | percent | 52 | 100 |
| Swelling value | percent | 1,040 | 1,300 |

Swelling value and crease angle were not changed even by repeated laundering.

Example 7

The product described in Example 1 was used in the same concentration but 10 grams of an organic aluminum salt, as for example aluminum formate, were added to the treating bath. After the addition of this salt, the pH again was corrected and set at 3.0.

A dress material of 100% viscose rayon which had been previously dyed with 2% sirius light green BTL was treated in this bath and finished in the manner set forth in Example 1. The crease angles of the treated material were 150° and are not substantially reduced even upon repeated laundering.

Example 8

2 mols hydantoin were boiled under a reflux condenser with 1 mol formaldehyde for 30 minutes at a pH of 5.5. The complete reaction of the aldehyde was verified by analysis. Thereupon the pH of the solution was set at 8 by means of caustic solution and 2 mols of formaldehyde were again added and the solution was boiled for a short time under a reflux condenser and set aside to cool. From the product thus produced which has the formula:

\[
\text{(methylen-1-bis-3-hydroxy-4-oxy-tetrahydromidazole-}
\text{ol-121)}
\]

300 grams were diluted with 700 grams H₂O. The pH of the bath was set at 3.0 by the addition of HCl whereupon there was also added 2 grams tylose (methylcellulose) and the bath was brought to a temperature of 30°C.

A dress material of 100% viscose staple fiber was soaked therein, the excess bath was squeezed out to 90% moisture and thereupon dried without tension at 100°C. After the drying, the goods were straightened out and brought to the desired width and thereupon cutted and rolled. The dress material treated in this manner had a crease angle of 150° while the untreated dress
material had a crease angle of 70°. The swelling value was reduced by 40% as compared with the initial goods.

Example 9

From 170 grams of the substance obtained in accordance with Example 6, there was prepared an impregnating bath by dissolving the same in 830 cc. H₂O with additions of 8 grams AlCl₃, crystalline plus 10 grams boric acid. 2 grams per liter of Soramin A were further added to the bath. In this solution, there was impregnated a dress material, the warp and filling of which consisted of 100% viscose rayon, whereupon the material was squeezed out and then reconditioned at 115°C. The material had a crease angle of 140° which even after being washed three times with soap still amounted to 130°.

Example 10

60 grams urea were boiled under a reflux condenser for 5 minutes with 150 grams 40% formaldehyde and 2.5 grams K₂CO₃ and then impregnated cooled to 30°C. Thereupon, 200 grams technical glyoxal containing 30% glyoxal and having an acid number of 70 were added, the pH thereof having previously been brought to 7.5–8.0 by means of NaOH. After the reaction, which took place without the addition of heat, had terminated, the mixture was diluted to 2 liters with H₂O whereupon 23 grams AlCl₃.H₂O+20 grams boric acid were added. In this solution there was impregnated a twill comprising of 100% viscose staple fiber, which was then squeezed out to 100% moisture and thereupon dried at 100 to 110°C. There was obtained a full-bodied soft fabric which had the following values as compared with the untreated fabric.

<table>
<thead>
<tr>
<th></th>
<th>Crease Angle, degrees</th>
<th>Swelling Value, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Warp</td>
<td>Filling</td>
</tr>
<tr>
<td>Treated</td>
<td>146</td>
<td>147</td>
</tr>
<tr>
<td>Untreated</td>
<td>81</td>
<td>78</td>
</tr>
</tbody>
</table>

The scraping value of the treated goods was 70% that of the untreated goods.

Example 11

1200 grams urea were left to stand for 3 hours mixed with 3000 grams 30% formaldehyde and 15 grams NaOH. After the temperature had dropped, 4000 grams technical glyoxal (as in Example 10) were added and the pH was immediately adjusted to 8.5 by means of NaOH. After 24 hours, there was obtained, without the addition of heat, a product which contains less than 2% free aldehyde.

250 grams of the above product were mixed with 750 cc. of H₂O at a temperature of 30°. Thereupon the pH was adjusted by means of HCl to a value of 3.0 and 5 grams tartaric acid were added. The stable bath served for the crease-proofing and swelling-proofing of fabrics. Softeners, water-repelling agents and finishers could be added to the bath.

Example 12

A bath which contained 200 grams per liter of the product obtained in accordance with Example 11 was prepared. This corresponded to about 65 grams per liter active solid substance. Thereupon, there were added 10 grams crystalline AlCl₃ and 5 grams boric acid, the bath was brought to 40°C and a dress material, the warp and filling of which consisted of 100% viscose staple fiber, was impregnated therein; the excess liquid was squeezed out and the fabric was then reconditioned at 100°C. A material, after being treated in this manner, had a crease angle of 150° in the warp and filling and scraping resistance of 1200 turns with an initial load of 400 grams. The original material as compared with this showed a crease angle of 70° and a scrape resistance of 1300 turns with an initial load of 400 grams.

Example 13

80 grams of the compound obtained in accordance with Example 11 were dissolved in 1 liter of water of 40°C. Thereupon, there were added 12 grams aluminum chloride and 19 grams sodium acetate, crystalline, and a staple fiber fabric consisting in the warp and filling of simple No. 34 yarn (metric number) was impregnated therein; the excess liquid was then squeezed out to a moisture content of 90% and the material was dried under slight tension at 95°C. The goods, which before treatment had a swelling value of 95% and a crease angle of 80°, had a swelling angle of 50% and a crease angle of 145°. The scraping resistance of the original goods was 1250 turns at 400 grams load; the treated goods had a scraping resistance of 1150 turns.

Example 14

A bath was prepared in accordance with Example 13, whereupon there were added 10 grams per liter boric acid and the same material as described in Example 13 was treated therein in the same manner. Upon examination, the material showed the same values as in the case of Example 13. After washing twice with 2 grams per liter of soap at 70°C, the goods still had a crease angle of 130° and a swelling value of 48%.

Example 15

90 grams of the compound obtained in accordance with Example 11 were dissolved in 1 liter of water, whereupon there were added 12 grams aluminum chloride and 19 grams sodium acetate crystalline and furthermore 10 grams per liter boric acid as well as 5 grams per liter soluble starch which was previously dissolved in boiling water. This mixture was used to treat a staple fiber poplin, the excess liquid being then 80% pressed out, followed by drying at 90°C. After the first drying, a final drying at 120°C was effected. The length thereof was limited to 3 minutes. The resultant material showed a swelling value of 40% and a crease angle of 150°. After a washing with soap as described in Example 14, the crease angle and swelling value did not change. The scrape resistance of the finished material was 85% that of the untreated material. The shrink values of the finished poplin were less than 2% both in the warp and in the filling and were not changed even by repeated washings.

Example 16

70 grams of the compound obtained in accordance with Example 11 were dissolved in 1 liter water and thereupon thereupon added 12 grams aluminum chloride and 19 grams sodium acetate. There was further added 40 grams of a commercial alumina paraffin emulsion and a man's suit material made of cupric staple fiber was impregnated with it. It was then dried with a slight tension at 105°C, there being obtained a crease-proof, water-repellent material which, in view of its high resistance to scraping, wears excellently.

Example 17

15 grams of the compound obtained in accordance with Example 11 were dissolved in 200 cc. water whereupon 5 grams sulfonated olive oil in emulsion were added. There was furthermore added 5 grams boric acid whereupon the temperature of the mixture was brought to 40°C. In this solution, there was impregnated viscose, centrifugal rayon. The moisture was then centrifuged out followed by drying for 48 hours at 60°C. The
2,876,082 rayon had a swelling value of 70% and the following textile data:

<table>
<thead>
<tr>
<th>Strength</th>
<th>Elongation, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>200 grams per 100 denier</td>
<td>90 grams per 100 denier</td>
</tr>
<tr>
<td>22</td>
<td>25</td>
</tr>
</tbody>
</table>

The rayon could be worked without difficulty and had excellent dyeing properties. The untreated rayon had a swelling value of 104% and the following textile data:

<table>
<thead>
<tr>
<th>Strength</th>
<th>Elongation, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>140 grams per 100 denier</td>
<td>90 grams per 100 denier</td>
</tr>
<tr>
<td>25</td>
<td>31</td>
</tr>
</tbody>
</table>

Example 18

Staple fiber flock, which was still wet and which was spun in accordance with the viscose process, was treated after the acidification and removal of sulfur, with a bath which was prepared in the manner indicated in Example 13, but which contained 20 grams per liter, rather than 10 grams per liter, of reactive substance. Thereupon it was treated in a centrifuge and dried for 23% hours at 100° C. There was obtained a staple fiber of 65% water swelling having excellent working properties.

All kinds of cellulose fibers and fabrics can be treated in a process according to the invention, especially such of native cellulose like cotton, or regenerated cellulose like viscose or copper oxide ammonia cellulose solutions, be it in the form of staple fibers or of endless filaments, be it in the form of woven or knitted materials, be it as underwear, stockings, clothing etc.

The various catalysts as for instance boric acid, oxalic acid, aluminum salts etc. can be present in the solution in quantities of from 0.5 to 5.0%, preferably in quantities of from 1.0 to 3.50%.

As aluminum salts according to the invention inorganic aluminum salts like aluminum chloride, aluminum bromide, aluminum nitrate, acid aluminum sulfate or aluminum double salts like aluminum potassium sulfate can be applied, or else organic aluminum salts, like aluminum acetate, aluminum formiate, aluminum oxalate etc.

The temperature of the treating bath for the textile material is of no great concern for the process according to the invention. Generally the bath will have room temperature or will be heated slightly to approximately 30 to 50° C. In principal the temperature of the treating bath can be kept at between 0 to 100° C.

As filling and finishing agents all those compounds can be used which have hitherto been known for this purpose, for instance carboxylate like soluble starch, dextrine or soluble cellulose compounds, especially cellulose ether, like methyl cellulose, cellulose glycolic acid, furthermore fat and oil emulsions for instance an emulsion of paraffin which has been stabilized with aluminum oxide, or sulfonated fats and oils, for instance sulfonated olive oil. These agents will preferably be applied in quantities of from 0.1 to 1.0% calculated on the treating solution, although still bigger quantities of the filling agents of 5% and more according to the intended result can be used.

The compound “Soromin HSG” mentioned in Example 1 is a fatty acid polyethylene glycolic compound whilst “Soromin A” mentioned in Example 2 is a triethanolmonoamine stearate.

The term “scratching value” means the abrasion resistance of the material. This scratching value is defined by the number of movements of two cumbered abrasion surfaces between which is placed the material to be investigated. The experiment is continued until the material to be investigated has got a hole. In this case the upper abrasion surface is always loaded with a weight of 400 grams.

As tetrahydropyrimidazol derivatives according to the invention primarily the imidazolone derivatives must be mentioned and amongst these especially such which bear at least one more hydroxy- or oxogroup at one or more carbon atoms of the imidazone ring.

The compound results from the reaction of equimolecular quanties of urea, glyoxal and formaldehyde has apparently the following formula:

\[
\begin{align*}
\text{H} & \text{N} \\
\text{O} & \text{O} \\
\text{H} & \text{N} \text{C} \text{O} \\
\text{O} & \text{O} \\
\text{H} & \text{H}
\end{align*}
\]

and has therefore to be denominated as 1-hydroxymethyl-4,5-dihydroxy-tetrahydropyrimidazol-one-2. A viscous, colourless, clear liquid of decidedly sweet taste results from the vacuum distillation thereof.

We claim:

1. Method for grease-proofing a cellulose material selected from the group consisting of cellulose fibers and cellulose fabrics which comprises impregnating said group member with an aqueous solution having a pH of from 3-5 containing from 1-35% of a reaction product selected from the group of products produced by (1) the reaction between urea and formaldehyde in an acid to neutral solution having a pH above about 3.5, thereafter reacting the urea-formaldehyde reaction product with glyoxal in a neutral to weakly alkaline solution, the molar proportions of said reactants being respectively urea-1:formaldehyde-1 to 1.3:glyoxal-1, and (2) the reaction between urea and glyoxal in neutral to not below pH 3.5 solution and then reacting the reaction product formed thereby with formaldehyde in a neutral to weakly alkaline solution, the molar proportions of said reactants being respectively urea-1:glyoxal-1:formaldehyde-1 to 1.5, thereafter removing the excess impregnating solution and drying said cellulose group member.

2. Method according to claim 1, in which said drying is effected at a temperature not substantially in excess of about 100° C.

3. Method according to claim 1, in which said reaction product is produced by the reaction between urea and formaldehyde in an acid to neutral solution having a pH above about 3.5, thereafter reacting the urea-formaldehyde reaction product with glyoxal in a neutral to weakly alkaline solution, the molar proportions of said reactants being respectively urea-1:formaldehyde-1 to 1.5:glyoxal-1.

4. Method according to claim 3, in which the molar proportions of said reactants is respectively urea-1:formaldehyde-1:5:glyoxal-1.

5. Method according to claim 1, in which said reaction product is produced by the reaction between urea and glyoxal in neutral to not below pH 3.5 solution and then reacting the reaction product formed thereby further with formaldehyde in a neutral to weakly alkaline solution, the molar proportions of said reactants being respectively urea-1:glyoxal-1:formaldehyde-1 to 1.5.

6. Method according to claim 3, in which the molar proportions of said reactants is respectively urea-1:glyoxal-1:formaldehyde-1:5.

7. Method according to claim 1, in which said aqueous solution additionally contains a catalyst selected from the group consisting of boric acid, tartaric acid, glycolic acid, oxalic acid, aluminum chloride, aluminum nitrate, aluminum nitrate, aluminum bromide, acid aluminum sulfate, aluminum potassium sulfate, aluminum formiate, and aluminum oxide.

8. Method according to claim 1, in which said aqueous
solution additionally contains boric acid and aluminum chloride as a catalyst.

9. Method for crease-proofing cellulose materials from the group consisting of cellulose fibers and cellulose fabrics, which comprises impregnating said group member from with an aqueous solution having a pH of 3–5, containing from 1–10% of methylene-1,4-bis-4,5-dihydroxytetrahydro-3-hydroxymethyl-imidazolone-2, and additionally containing boric acid and aluminum chloride as a catalyst, thereafter removing the excess impregnating solution, and drying said group member.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,876,062

November 3, 1959

Erich Torke et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 46, for "solution" read -- solutions --; column 2, line 37, for "aldehye" read -- aldehyde --; column 3, line 72, for "stable" read -- staple --; column 7, line 71, for "100%" read -- 100% --; column 10, line 10, for "imidazone" read -- imidazole --; lines 72 and 73, strike out "aluminum nitrat," --; column 11, line 6, before "with" strike out "from".

Signed and sealed this 30th day of June 1959.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents