Quantitative Evaluation of Cotton-Bound Glyoxal in the Presence of Glycols

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ABSTRACT: Cotton fabric is modified chemically to convey crease resistance to the cellulosic material by means of an appropriate crosslinking agent. For this purpose glyoxal was tested as a nonformaldehyde durable press agent. The cotton-bound glyoxal can be quantified by means of isocratic HPLC, whereby the glyoxal-treated fabric is hydrolyzed by a NaOH solution. During this pretreatment glyoxal is extracted from the cellulosic sample and converted into glycolate by an internal Cannizzaro reaction. The addition of glycols such as ethylene glycol or diethylene glycol into the formulation results in a remarkable decrease of the amount of glyoxal that is detected. This phenomenon can be explained by the fact that the glycol reacts with the glyoxal, thus hampering the internal Cannizzaro reaction. The acidic hydrolysis and the alkaline hydrolysis provide the same results, thus indicating that the alkaline treatment removes all the cotton-bound glyoxal. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1870–1875, 2003

Key words: cotton; durable press finishing; glyoxal; crosslinking; HPLC

INTRODUCTION

Cellulosic fabrics are chemically modified with durable press finishing agents to convey easy care properties. The most effective crosslinking agent, DMDHEU (dimethyloldihydroxyethyleneurea, Fig. 1), tends to release formaldehyde, a potential carcinogen substance.[1] As a consequence, polycarboxylic acids (PCAs), such as 1,2,3,4-butanetetracarboxylic acid (BTCA) or citric acid (CA), and dialdehydes such as glyoxal or glutardialdehyde have been intensively investigated with respect to replacing formaldehyde-emitting *N*-methylol compounds (Fig. 1). [2–10] The treatment of cellulosic material by means of crosslinking agents always effects an increase of strength loss and, in addition, yellowing effects are observed. Therefore, the incorporation of additives into the pad bath formulations were studied, in an attempt to reduce these negative phenomena. For this purpose, glycols proved to be very effective to prevent yellowing of glyoxal-treated cotton fabrics.[7]

The quantitative determination of cotton-bound glyoxal by means of isocratic HPLC was introduced in previous studies.[11,12] These investigations revealed that the alkaline attack of glyoxal-treated fabrics resulted in the formation of glycolic acid that could readily be identified and quantified using HPLC.

The present study deals with the quantification of glyoxal that has reacted with the cellulosic material. The influence of glycols such as ethylene glycol and diethylene glycol on the chromatographic determination is examined.

EXPERIMENTAL

Chemicals

Glyoxal [40% (w/w), >98%], applied during the entire investigation, aluminum sulfate hexadecahydrate [$Al_2(SO_4)_3 \cdot 16H_2O$, >98%], ethylene glycol (>99%), and diethylene glycol (>98%) were purchased from Merck GmbH (Darmstadt, Germany).

Fabric/fabric treatment

Desized, scoured, bleached 100% cotton fabric weighing 122 g m^{-2} was used throughout the investigations. The preweighed fabric was impregnated in a finish bath containing glyoxal, aluminum sulfate hexadecahydrate as curing catalyst, and ethylene glycol or diethylene glycol as additive. The amounts of the ingredients are specified in the text. No softener was applied. Subsequently, the sample (20 × 30 cm) was passed through a two-roll laboratory padder (HVL 500; W. Mathis AG, Niederhasli, Switzerland; air pressure 1 bar, fabric speed 3 m min^{-1}). This treatment was repeated to give a wet pickup of 95–100% based on the original weight of fabric. After drying (3 min,

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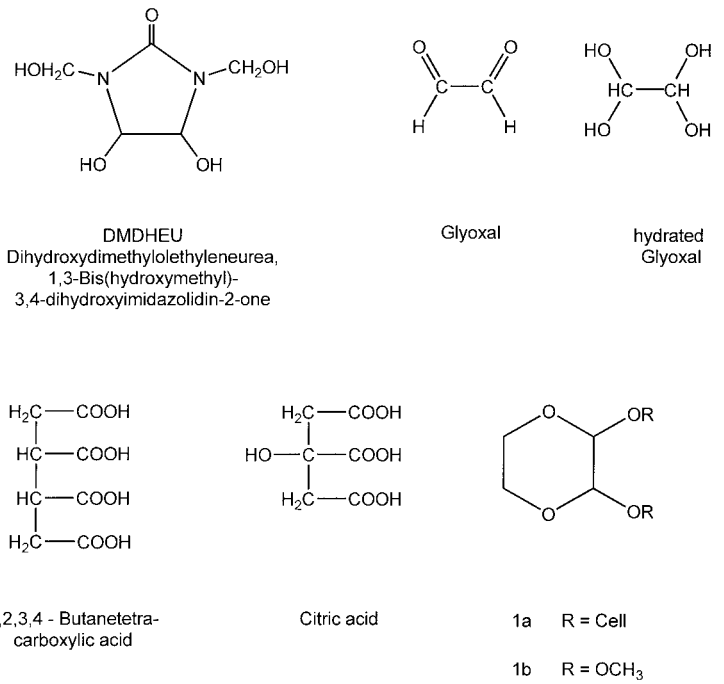


Figure 1 Formula of the chemical compounds of interest.

105°C) the fabric was cured for 3 min at 140°C in a lab dryer (LTE, W. Mathis AG), washed under occasional stirring (1 g L^{-1} Na_2CO_3, 10 min, 50°C, 1000 mL), and finally dried again (3 min, 80°C).

Chromatographic equipment

Pump: JASCO PU-1580 (Kyoto, Japan). Autosampler: Model Marathon, Spark BV (Emmen, Netherlands) and an 7010 Rheodyne (Cotati, CA) model 7010 sample injection valve with a 20-μL loop. Strong cationic exchange 300 $\times$ 7.8 mm column: Aminex HPX-87H (Bio-Rad Labs, Richmond, CA). Column oven compartment: Shimadzu CTO-2A (Kyoto, Japan). UV-detector: Shimadzu SPD-10 AVVP Data acquisition: chromatography software Borwin (JMBS Developpements, Le Fontanil, France). Chromatographic conditions were as follows: mobile phase: ($c_{1/2}$ H_2SO_4 = 0.01 mol L^{-1}), flow rate: 0.7 mL min^{-1}, column oven temperature: 80°C, UV-detector wavelength: 210 nm.

DCRA measurement

The measurements of the dry crease recovery angle (DCRA) were performed according to DIN 53 890 with a device from Karl Schröder (Weinheim, Germany).

The color measurements were taken three times with the Chroma Meter CR 210 (Minolta, Tokyo, Japan). The whiteness index (WI) was calculated according to ASTME 313.

Hydrolysis

Glyoxal-cured fabric (1–2 g) was cut into small pieces, accurately weighed, and transferred into the reaction vessel, to which 40 mL NaOH (c = 4 mol L^{-1}) was added. The reaction mixture was treated at 100°C for 20 min. After the hydrolysis the extraction solution and the wash solutions were transferred into a 50-mL volumetric flask and allowed to cool. Finally, the volumetric flask was adjusted to the mark with NaOH (c = 4 mol L^{-1}). Before the chromatographic analysis, the solution was filtered through a PTFE disposable filter unit.

Glyoxal [1000 mg 40% (w/w)] contained 402.5 $\pm$ 3.91 mg glyoxal (n = 6).[13]

RESULTS AND DISCUSSION

Glyoxal reacts with cellulose at 140°C, conveying durable press properties to the cotton material. The results of various investigations demonstrated that a crosslink structure is formed between the cellulose chains during this cure process.[3–5] To gain a better insight into the network of glyoxal-treated cotton, ^{13}C-NMR studies of the reaction of glyoxal with diols in solution were also conducted.[14,15] Because glyoxal is a difunctional aldehyde, the formation of bis acetals or bis semiacetals can be taken into consideration.[16] However, to date it is not possible to differentiate between this two possibilities.

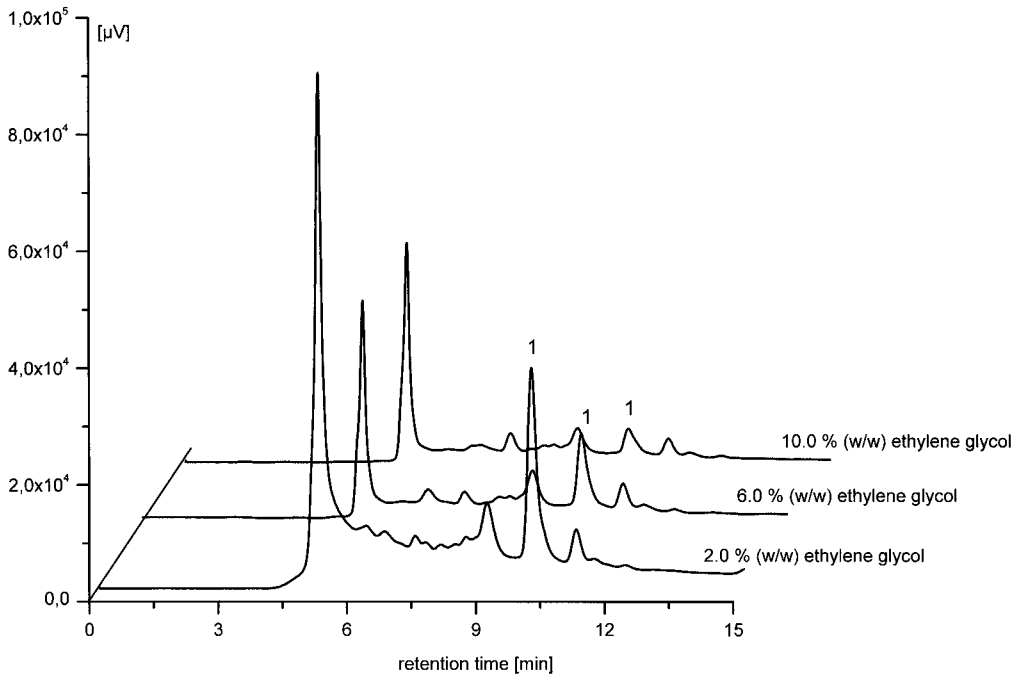


Figure 2 Chromatograms of the hydrolysis solutions (NaOH, c = 4 mol L^{-1}, 100°C, 20 min) of cotton fabrics that had been treated with formulations containing glyoxal and various amounts of ethylene glycol. 1 = glycolic acid, $c_{1/2}$ (H_2SO_4) = 0.01 mol L^{-1}; BioRad Aminex HPX-87H, flow rate: 0.7 mL min^{-1}; column oven temperature: 80°C; UV-detector wavelength: 210 nm.

A previous study gave evidence that cotton-bound glyoxal undergoes an internal Cannizzaro reaction, when the sample is subjected to an alkaline treatment.[10] In the course of this reaction glyoxal disproportionates to glycolate. As a consequence, glyoxal is released from the cellulosic material. The glycolate, thus formed, was measured by means of isocratic HPLC.

Chromatographic data

To quantify sodium glycolate by means of HPLC, five standard solutions were prepared in concentration ranges 200–1000 mg L^{-1} glycolic acid, respectively, using NaOH (c = 4 mol L^{-1}) as solvent. The regression analysis showed good linear correlations ($y = 518.0x - 272.1$, $r = 0.9998$). The detection limit was 1.87 mg L^{-1} (S/N = 3).

To compare the results of the experiments the peak area were normalized to 1 g of fabric weight and 100% wet pickup as described in a previous study.[10]

Glycol

Various investigations demonstrated that the incorporation of ethylene glycol into the pad bath formulation gives rise to a significant improvement of the WI index. In addition, it was found that the application of glycols results in an increase of the add-on. These findings were explained by the fact that ethylene glycol forms a six-membered 1,4-dioxane ring [Fig. 1(a)].[7]

To investigate the impact of the addition of ethylene glycol on the quantification of glyoxal finishing formulations were prepared containing 14.5% (w/w) glyoxal solution, and 4.5% (w/w) aluminum sulfate hexadecahydrate. Various amounts of ethylene glycol [0, 2, 4, 6, 8, and 10% (w/w)] were added. The cotton samples were impregnated, dried, and cured at 140°C for 3 min and analyzed as described in the Experimental section. Figure 2 shows the chromatograms of the hydrolysis liquors that were obtained, when a cotton fabric was treated with 14.5% (w/w) glyoxal, 4.5% (w/w) $Al_2(SO_4)_3 \cdot 16H_2O$ and 2.0, 6.0, and 10.0% (w/w) ethylene glycol, cured at 140°C, and washed as described in the Experimental section. Peak 1 was assigned to glycolic acid. A comparison of the peaks demonstrates that the peak area decreases as the weight fraction of ethylene glycol increases.

The findings of the analytical evaluation are presented in Table I. The data clearly make evident that an increase of the weight fraction of ethylene glycol results in a remarkable decrease of glyoxal being bound to the fabric. In contrast, the values of the DCRA remain at the same level, indicating that the extent of the crosslinkage is not influenced by the weight fraction of ethylene glycol in the formulation. The decrease of cotton-bound glyoxal that is quantified by means of HPLC can be explained by the fact

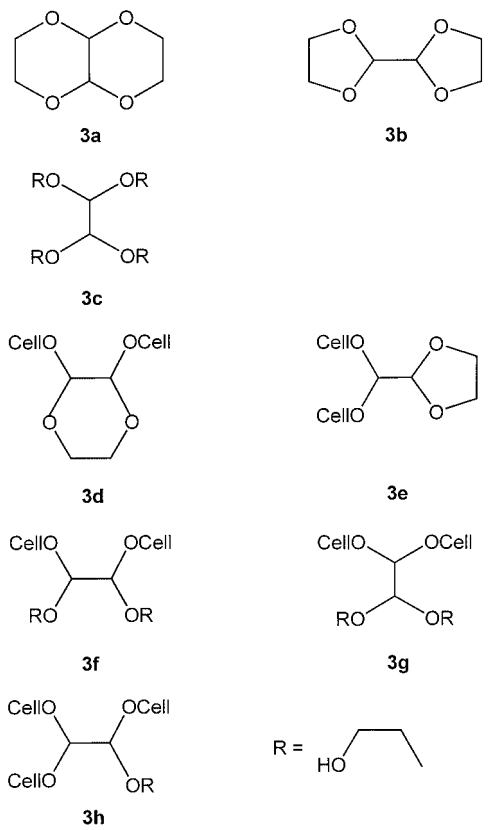


Figure 3 Possible compounds of the reaction between hydrated glyoxal and ethylene glycol at elevated temperatures.

that glyoxal reacts with ethylene glycol during the cure process, thus forming a six-membered 1,4-dioxane ring. As a consequence, glyoxal is not converted to glycolate by means of an alkaline attack and therefore cannot be determined using HPLC.

In an attempt to verify this phenomenon, 2,3-dimethoxy-1,4-dioxane [Fig. 1(b)] was applied as a model for the glyoxal-crosslinked cellulose. A suspension of this compound was treated with an alkaline solution at 100°C for 60 min. The chromatographic analysis of the alkaline solution did not indicate the formation of glycolate. Hence, it can be concluded that glyoxal reacts with ethylene glycol to the corresponding diacetal. As a consequence, that portion of glyoxal that is incorporated in an 1,4-dioxane ring cannot be converted to glycolate by an alkaline attack. In addition, these findings also give evidence that the crosslinkage of glyoxal is not preferably effected by means of four ether linkages, since in this case the amount of glyoxal that is accessible to a quantification applying HPLC should be much lower.

TABLE I
Amount of HPLC-Determined Glyoxal as a Function of the Weight Fraction of Ethylene Glycol and Diethylene Glycol in the Pad Bath Formulation

	Ethylene glycol		Diethylene glycol	
Formulation glycol [% (w/w)]	Glyoxal analyzed[a] (mg)	DCRA (w + f) (°)	Glyoxal analyzed[a] (mg)	DCRA (w + f) (°)
0	21.5 ± 0.08	289	21.8 ± 0.01	296
2	18.7 ± 0.03	299	22.6 ± 0.06	309
4	15.9 ± 0.07	298	17.9 ± 0.12	304
6	11.0 ± 0.13	294	14.7 ± 0.12	299
8	6.9 ± 0.20	292	13.6 ± 0.01	298
10	6.5 ± 0.04	292	8.9 ± 0.07	295

[a] Related to 1 g fabric and 100% wet pickup.

TABLE II
Amount of HPLC-Determined Glyoxal as a Function of the Molar Ratio Between Glyoxal and Ethylene Glycol and Diethylene Glycol in the Pad Bath Formulation

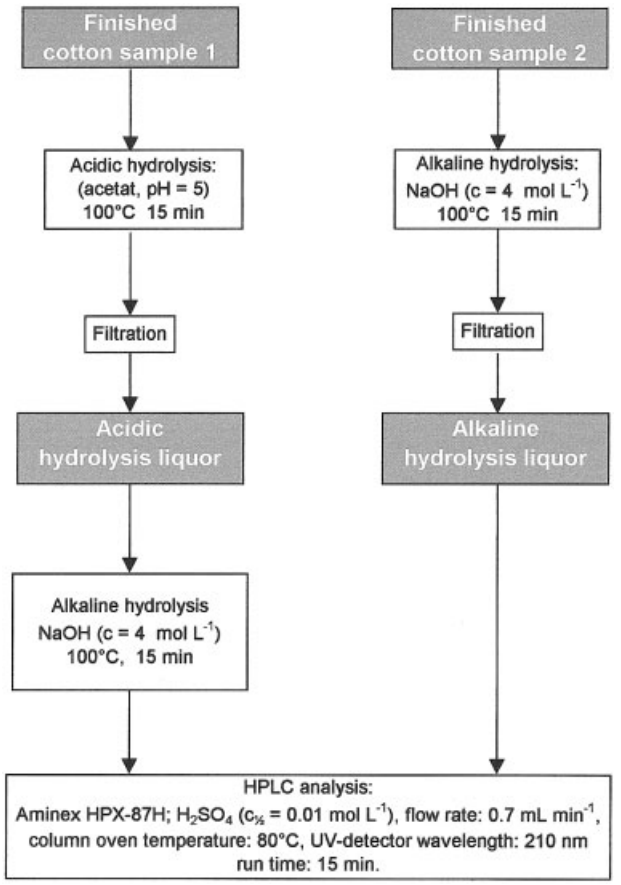
	Ethylene glycol		Diethylene glycol	
Ratio glyoxal/glycole in formulation	Glyoxal analyzed[a] (mg)	DCRA (w + f) (°)	Glyoxal analyzed[a] (mg)	DCRA (w + f) (°)
1 : 0.00	19.5 ± 0.37	272	22.9 ± 0.98	293
1 : 0.10	19.7 ± 0.03	283	23.4 ± 0.43	296
1 : 0.20	20.2 ± 0.07	288	20.1 ± 0.03	289
1 : 0.30	17.7 ± 0.13	286	18.6 ± 0.23	295
1 : 0.40	17.8 ± 0.20	283	18.5 ± 0.46	298
1 : 0.50	16.9 ± 0.04	278	15.4 ± 1.51	298
1 : 0.60	16.4 ± 0.28	287	15.0 ± 0.49	294
1 : 0.70	14.0 ± 0.02	293	10.6 ± 0.30	296
1 : 0.80	13.1 ± 1.21	287	12.3 ± 0.07	294
1 : 0.90	10.3 ± 0.24	281	12.1 ± 0.06	300
1 : 1.00	8.4 ± 0.11	280	9.3 ± 0.02	298
1 : 1.25	6.4 ± 0.06	279	7.4 ± 0.12	294
1 : 1.50	4.9 ± 0.46	273	6.4 ± 0.64	299
1 : 1.75	3.6 ± 0.03	274	4.7 ± 0.13	301
1 : 2.00	3.4 ± 0.10	267	3.6 ± 0.34	302
1 : 2.50	3.5 ± 0.04	270	3.3 ± 0.42	301
1 : 3.00	3.6 ± 0.01	280	3.0 ± 0.11	302

[a] Related to 1 g fabric and 100% wet pickup.

Identical experimental runs were performed with various concentrations of diethylene glycol in the formulation. The results listed in Table I reveal that the amount of glyoxal determined by means of HPLC also decreases. However, the extent of the reduction is somewhat lower compared to the value obtained when ethylene glycol was added to the formulation. In addition, an improvement of the DCRA value can be observed.

Glycol/glyoxal molar ratio

In a second approach, formulations were prepared that consisted of glyoxal and ethylene glycol or diethylene glycol in various molar ratios (Table II). The cotton samples were treated as described in the Experimental section. The results of the chromatographic measurements are summarized in Table II. As expected, the increase of ethylene glycol in the formulation results in the decrease of the amount of glyoxal being detected. When the molar ratio of glyoxal/eth-



Scheme 1 Acidic and alkaline pretreatment of a glyoxal-treated fabric.

ylene glycol is 1 : 1.00 the amount of glyoxal being detected is 8.4 mg/g fabric. Compared to the value obtained when no ethylene glycol was added, a remarkable reduction can be noted, indicating that the major portion of glyoxal has reacted with ethylene glycol. The duplication of the moles of ethylene glycol results in an additional reduction of cotton-bound glyoxal that is accessible to quantification.

These results can be explained on the basis of the fact that an excess of ethylene glycol is necessary to achieve a nearly complete reaction of glyoxal to the 1,4-dioxane ring. The application of diethylene glycol does not result in such a high reduction of the glyoxal detected.

Two-step impregnation

To investigate the reaction of glyoxal-bound cotton fabric with ethylene glycol a cotton fabric was impregnated with a formulation containing 14.5% (w/w) glyoxal and 4.5% (w/w) aluminum sulfate hexadecahydrate. The fabric was cured and washed under the conditions usually applied. Subsequently, the sample was divided into part A and part B. Part B was impregnated with a solution containing 100 g L^{-1} ethylene glycol, and cured again at 140°C for 3 min. The amount of detectable glyoxal was analyzed chromatographically. Part B provided a value of 16.4 g glyoxal/g fabric; that with ethylene glycol, 4.0 g/g fabric. These findings demonstrate that ethylene glycol reacts with the crosslinked glyoxal. As a consequence, it can be concluded that the crosslinkage is not only effected by means of bis acetalization of glyoxal.

Acidic hydrolysis

In the presence of alcohols, aldehydes are transformed by the hemiacetal stage to acetals. The latter are not attacked by many basic reagents. In contrast, they readily revert to aldehydes in excess acidic water. As a consequence, the acidic hydrolysis of glyoxal-bound cotton must result in the liberation of the entire crosslinking agent, independent of whether the crosslinkage is achieved by means of a diacetal or bis hemiacetal structure.

To investigate the acidic hydrolysis, cotton samples were finished with 14.5% (w/w) glyoxal and 4.5% (w/w) aluminum sulfate hexadecahydrate and treated as described in the Experimental section. The sample treatment was conducted according to **Scheme 1**. The findings in Table III indicated that the optimum hydrolysis period for the acidic treatment is 20 min. When the cotton sample was subjected to an acidic hydrolysis, then 22.3 ± 2.09 mg glyoxal/g fabric was obtained. The alkaline treatment resulted in the detection of 21.8 ± 0.03 mg glyoxal/g fabric. These results clearly reveal that the alkaline hydrolysis removes the entire amount of glyoxal being bound to the cellulosic material.

CONCLUSIONS

The findings demonstrate that the incorporation of glycols into a glyoxal-containing pad bath formulation results in a remarkable decrease of the amount of cotton-bound glyoxal being detected by means of HPLC. This phenomenon can be explained by the fact that the glycol reacts with the glyoxal, thus hampering the conversion of cotton-bound glyoxal to glycolate.

TABLE III
Amount of Glyoxal Determined After an Acidic Hydrolysis of the Glyoxal-Treated Cotton Fabric as a Function of the Treatment Period

Hydrolysis time (min)	Glyoxal analyzed[a] (mg)
5	12.3 ± 1.68
10	18.4 ± 0.53
15	20.4 ± 1.22
20	22.3 ± 2.08

[a] Related to 1 g fabric and 100% wet pickup.

In addition, the two-step experiments demonstrated that glyoxal, which had already reacted with the cotton material, still has the possibility to react with ethylene glycol.

The cotton fabrics were treated with a formulation containing both glyoxal and ethylene glycol. Subsequently, the samples were subjected to a cure process at 180°C. As a consequence, the following reaction mechanisms have to be considered.

First, glyoxal reacts with ethylene glycol during the cure process, thus forming the cyclic compounds 3a and/or 3b or the acyclic compound 3c. As a consequence, glyoxal cannot be converted into glycolic acid and therefore the amount of glyoxal being detected by HPLC decreases as the weight portion of ethylene glycols increases. In this case, however, glyoxal would not be able to react with the cellulosic material, given that the hydroxyl groups of glyoxal already have reacted to the corresponding bis acetals. Consequently, the degree of crosslinking should be reduced. This phenomenon, however, cannot be observed because the value of the DCRA remains nearly at the same level (Table II), although the portion of ethylene glycol in the formulation is increasing.

Second, glyoxal reacts with the hydroxyl groups of the cellulosic material, thus affecting the crosslinkage. Subsequently, the residual hydroxyl groups of the cotton-bound glyoxal react with ethylene glycol. These reactions could result in the generation of the cyclic compounds 3d, 3e, and/or the acyclic compounds 3f, 3g, and 3h. These assumptions are supported by the fact that the DCRA values are not changed (Table II). Additionally, the two-step impregnation procedure also gives rise to a remarkable decrease of the amount of glyoxal, indicating that cotton-bound glyoxal does not preferably crosslink with the cellulose chains by four ether linkages. The acidic hydrolysis and the alkaline hydrolysis provide the same results, thus indicating that the latter treatment removes all the cotton-bound glyoxal.

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