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# Effect of Glycols and Catalysts on Cotton Fabrics Treated with Glyoxal

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**Abstract:** The optimum conditions for durable press treatment of cotton fabrics using glyoxal as a nonformaldehyde crosslinking agent were investigated. Crosslinking reaction was conducted in the presence of different catalysts such as aluminum sulfate, magnesium chloride, or magnesium chloride-citric acid mixture at various mole ratios of catalyst to glyoxal. Aluminum sulfate was proven the most effective one among those used. Glycol addition into a glyoxal padding bath increased the wrinkle recovery angle(WRA) and whiteness of treated fabrics. The optimum mole ratio of glycol to glyoxal was 1:1. Diethylene glycol addition produced better overall performance to the glyoxal-crosslinked fabric compared to ethylene glycol addition.

**Keywords:** Crosslinking, Glyoxal, Glycol, Aluminum sulfate, Curing, Wrinkle recovery angle, Whiteness

## Introduction

The reaction of crosslinking agent and a catalyst in the durable press finishing of cellulose fabrics should not deteriorate the whiteness of treated fabrics even under high curing temperatures. It is also important to retain its durable press performance throughout product life cycle [1-4].

Dimethyloldihydroxyethylene urea (DMDHEU), which forms an ether linkage with hydroxyl groups of cellulose, is most widely used as a crosslinking agent [5]. However, due to the formaldehyde release either from treated fabrics or during finishing processes, its use in textiles is expected to be replaced by other crosslinkers. Many investigations on nonformaldehyde crosslinking agents such as polycarboxylic acid, which forms an ester linkage with hydroxyl groups of cellulose, have been carried out [4,6-9]. 1,2,3,4-butanetetracarboxylic acid (BTCA) is known to be the most effective one among them, but the cost of the compound is too high, and sodium hypophosphite (SHP) [10], the most commonly used catalyst for BTCA, can cause a shade change of fabrics dyed with certain sulfur or reactive dyes.

Studies on crosslinking of cellulose with glyoxal began in 1960s. Gonzales and Guthrie [11] used magnesium chloride as a catalyst for glyoxal. Worth [12] treated cotton and cotton/polyester fabrics with glyoxal/reactive silicone under mixture catalysts of aluminum sulfate and magnesium sulfate. Welch *et al.* [13-15] found that aluminum salt is best for glyoxal, and when glycol was added durable press performance was improved and yellowing of treated fabrics could be prevented by changing crosslinking reactions and subsequent structure of crosslinkage.

In this study the influence of catalyst type on physical properties of treated fabrics and the optimum process conditions for catalyst and glycol addition were investigated when 100 % cotton fabrics were treated with glyoxal using a pad-dry-cure process.

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## Experimental

### Fabrics

Desized, scoured, bleached and mercerized 84 x 64 cotton cloth, weighing 118.9 g/m$^2$, was used.

### Chemicals

Glyoxal (Aldrich Chemical Co.), ethylene glycol (Aldrich Chemical Co.), and diethylene glycol (Duksan Pharmaceutical Co., first grade) were used for crosslinking agents. Aluminum sulfate (Shinyo Pure Chemical Co.), magnesium chloride (Aldrich Chemical Co.) and citric acid (Duksan Pharmaceutical Co., first grade) were used for catalysts. Triton X-100 (Shinyo Pure Chemical Co.) was used as a wetting agent.

### Treatment of Fabrics

Cotton fabrics were treated by a pad-dry-cure process. The aqueous padding solution consisted of crosslinking agent, catalyst, and wetting agent. Fabrics were padded with the 2 dip-2 nip method, and the wet pickup was 90 %. The dry temperature and time were 85 °C and 3 min, respectively. The cure temperature range was 140-190 °C, and the cure time was 1-5 min. Treated fabrics were thoroughly washed with frequent stirring in 50 °C water for 30 min, and then dried. All treated samples were conditioned under 20 °C, 65 % RH.

### Tests and Analysis

The wrinkle recovery angle was tested according to AATCC 66-1978. The tensile strength, tearing strength, and abrasion resistance were tested according to ASTM D 1682-64 (1-in. raveled strip), ASTM D 1424-83 (Elmendorf), and ASTM D 3883-80 (flex abrasion), respectively. Thermogravimetric analysis was carried out using Thermogravimeric Analyzer (Shimazu Co.) under a nitrogen gas atmosphere. The flow rate of nitrogen gas was 50 m*l*/min. The temperature range and heating rate were 30-450 °C and 10 °C/min, respectively. Whiteness index was measured by X-rite Spectrophotometer (X-rite Incorporated) using $D_{65}$ illuminant and 10 ° field.

## Results and Discussion

### Effect of Glyoxal Concentration

Formations of crosslinkage make the elasticity and resiliency of fibers increase, and consequently wrinkle resistance of fabrics increases. However, it may affect adversely the mechanical strength and whiteness of treated fabrics. Table 1 shows physical properties of fabrics treated with glyoxal and aluminum sulfate versus the glyoxal concentration. Wrinkle recovery angles increased linearly up to 5 % (owb) glyoxal concentration, but did not increase significantly beyond 5 %. The strength retention of treated fabrics was about 30 % at 3 % concentration of glyoxal, and from 3.5 % its decrease became very little. The whiteness of treated fabrics decreased as the glyoxal concentration increased. Figure 1 shows a thermogravimetric analysis of treated fabrics. The residual

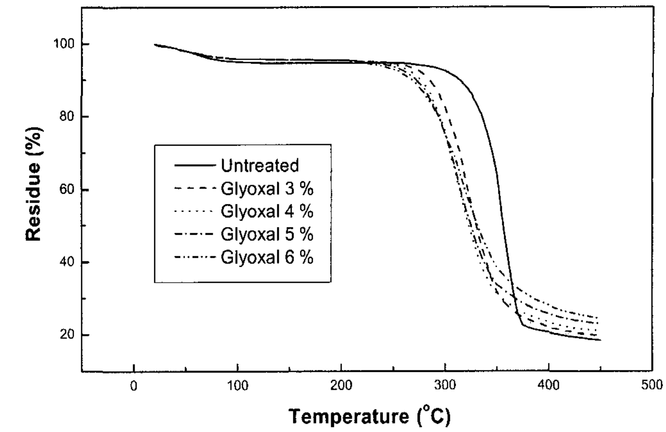


**Figure 1.** Thermogravimetric curves of fabrics treated with 3-6 % (owb) glyoxal.

**Table 1.** Effect of glyoxal concentration on physical properties of treated fabrics

| Run no. | Glyoxal conc. (%) | Wt. gain (%) | WRA (w + f)° | Breaking strength ret. (%) | Tearing strength ret. (%) | C.I.E whiteness index |
|---|---|---|---|---|---|---|
| Control | | | 196 | 100 | 100 | 82.31 |
| 1 | 3 | 2.7 | 252 | 30.6 | 28.4 | 52.63 |
| 2 | 3.5 | 2.9 | 261 | 26.6 | 26.7 | 48.46 |
| 3 | 4 | 3.2 | 277 | 26.3 | 23.8 | 42.17 |
| 4 | 4.5 | 3.4 | 281 | 25.9 | 21.4 | 36.96 |
| 5 | 5 | 3.8 | 288 | 24.1 | 18.5 | 34.25 |
| 6 | 5.5 | 4.33 | 289 | 25.6 | 18.4 | 34.18 |
| 7 | 6 | 4.5 | 289 | 24.7 | 17.9 | 33.69 |

Aluminum sulfate/gloxal mole ratio : 0.04; wet pick-up: 93 ± 2 %; dry : 85 °C, 3 min; curing : 150 °C, 3 min; washing : 50 °C, 30 min.

**Table 2.** Effect of catalyst for glyoxal on physical properties of treated fabrics

| Run no. | Catalyst | Mole ratio cat./glyoxal | Wt. gain (%) | WRA (w + f)° | Breaking strength ret. (%) | Tearing strength ret. (%) | C.I.E whiteness index |
|---|---|---|---|---|---|---|---|
| 1 | $Al_2(SO_4)_3 \cdot 16H_2O$ | 0.01 | 3.99 | 264 | 31 | 37.4 | 56.26 |
| 2 | | 0.02 | 4.06 | 272 | 27 | 25.2 | 50.11 |
| 3 | | 0.03 | 4.09 | 279 | 26 | 21.3 | 40.74 |
| 4 | | 0.04 | 4.33 | 288 | 24.1 | 18.5 | 34.25 |
| 5 | | 0.05 | 4.62 | 289 | 21 | 17.1 | 33.18 |
| 6 | $MgCl_2 \cdot 6H_2O$ | 0.1 | 5 | 190.5 | 70 | 64 | 72.04 |
| 7 | | 0.2 | 5.7 | 222.5 | 60.5 | 58 | 70.46 |
| 8 | | 0.3 | 6.6 | 228 | 53.7 | 53 | 69.03 |
| 9 | | 0.4 | 7.5 | 230 | 50.6 | 49.2 | 67.71 |
| 10 | | 0.5 | 8.7 | 238 | 48 | 46.8 | 67.23 |
| 11 | | 0.6 | 9.6 | 239 | 46 | 43.2 | 67.9 |
| 12 | CA[a]/$MgCl_2 \cdot 6H_2O$[b] | 0 | 5.7 | 222.5 | 60.5 | 57.8 | 70.46 |
| 13 | | 0.1 | 4.45 | 251 | 39.6 | 37.2 | 68.76 |
| 14 | | 0.2 | 4.4 | 273.5 | 36.2 | 34.7 | 58.94 |
| 15 | | 0.3 | 4.6 | 277.5 | 34.5 | 33.6 | 51.77 |
| 16 | | 0.4 | 4.6 | 282 | 31.5 | 30.7 | 47.08 |
| 17 | | 0.5 | 5.1 | 289 | 31.4 | 29.4 | 43.78 |

Treating solution: 5 % glyoxal and catalyst in water; wet pick-up: 93 ± 2 %; dry : 85 °C, 3 min; curing : 150 °C, 3 min; washing : 50 °C, 30 min; [a]: citric acid, [b]: mole ratio of $MgCl_2 \cdot 6H_2O$/glyoxal: 0.2.

char increased due to the increase of thermal stability [16,17] as the glyoxal concentration of treated fabrics increased.

**Effect of Catalyst**

Physical properties of treated fabrics versus catalysts and their concentrations were summarized in Table 2. As the mole ratio of a catalyst to glyoxal increased, the wrinkle recovery angle increased while the tensile strength and the whiteness decreased. Aluminum sulfate was superior to magnesium chloride in wrinkle recovery angles, but the former decreased the tensile strength and the whiteness of treated fabric more than the latter. In the mixed catalyst of magnesium chloride/citric acid where the concentration of magnesium chloride was fixed and that of citric acid was changed, as the amount of citric acid increased, wrinkle recovery angles of treated fabrics increased as much as aluminum sulfate. The tensile strength decreased as the amount of citric acid increased, but a little higher than that of aluminum sulfate. However, citric acid decreased the whiteness of treated fabrics significantly.

**Effect of Glycol**

Table 3 shows physical properties of treated fabrics according to glycol addition and their mole ratios to glyoxal in a padding bath. The glyoxal concentration was 5 % (owb). The mole ratio of aluminum sulfate to glyoxal was 0.04. Figure 2 shows the wrinkle recovery angles as a function of the glycol/glyoxal mole ratio. Wrinkle recovery angles increased and reached a maximum when the mole ratio of glycol to glyoxal reached 1.00. Diethylene glycol increased wrinkle recovery angles of treated fabrics more than ethylene glycol. Figure 3 and Figure 4 show effects of glycol on the tensile strength and the whiteness of treated fabrics. Addition of glycol improved whiteness significantly without influencing the tensile strength. It is considered that the yellowing of fabrics treated with glyoxal may be due to carbonyl groups of aldehyde, and ethylene glycol or diethylene glycol reacts with carbonyl group to form acetal linkage. The addition of ethylene glycol to glyoxal makes the hemiacetal form between glyoxal and cellulose during predrying step, and subsequently the hemiacetal reacts with ethylene glycol to form final crosslinkage in the curing stage [15]. However, diethylene glycol seems not to form cyclic adduct with

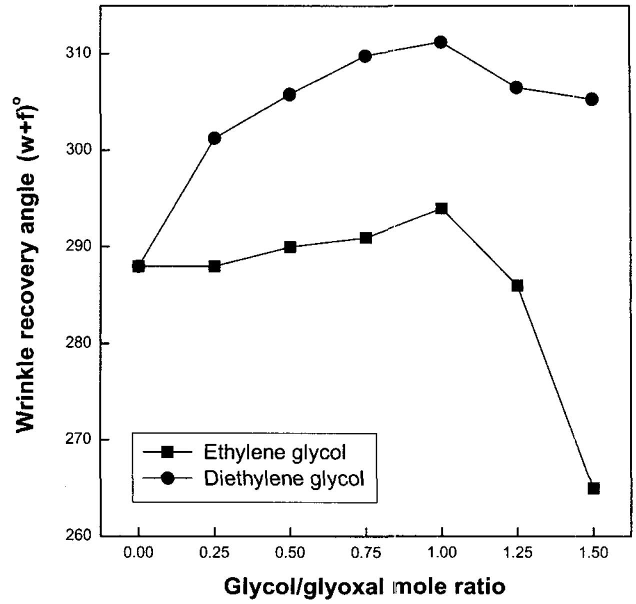


**Figure 2.** Effect of glycols on wrinkle recovery angle of treated fabric. $Al_2(SO_4)_3$/glyoxal mole ratio 0.04, curing 150 °C, 3 min.

**Table 3.** Effect of glycol on physical properties of glyoxal treated fabrics

| Run no. | Catalyst | Mole ratio cat./glyoxal | Wt. gain (%) | WRA (w + f)° | Breaking strength ret. (%) | Tearing strength ret. (%) | C.I.E whiteness index |
|---|---|---|---|---|---|---|---|
| 1 | Ethylene glycol | 0 | 3.8 | 288 | 24.1 | 18.5 | 34.25 |
| 2 | | 0.25 | 4.2 | 290 | 26.9 | 19.4 | 48.27 |
| 3 | | 0.5 | 5.45 | 291 | 28.2 | 19.8 | 52.32 |
| 4 | | 0.75 | 6.52 | 291 | 27.5 | 20.2 | 53.61 |
| 5 | | 1 | 7.17 | 294 | 27.5 | 19.9 | 56.73 |
| 6 | | 1.25 | 7.85 | 286 | 29.2 | 20 | 57.97 |
| 7 | | 1.5 | 8.41 | 269 | 27.5 | 20.8 | 59.23 |
| 8 | Diethylene glycol | 0.25 | 5.87 | 301 | 30.6 | 24.7 | 53.84 |
| 9 | | 0.5 | 7.43 | 305 | 30.7 | 24.8 | 54.04 |
| 10 | | 0.75 | 8.91 | 309 | 32.8 | 25.1 | 58.76 |
| 11 | | 1 | 10.3 | 311 | 33.4 | 25.3 | 58.98 |
| 12 | | 1.25 | 10.77 | 306 | 33.5 | 26 | 62.11 |
| 13 | | 1.5 | 10.11 | 305 | 33.7 | 26.8 | 67.66 |

Treating solution: 5 % glyoxal and catalyst in water; wet pick-up: 93 ± 2 %; dry : 85 °C, 3 min; curing : 150 °C, 3 min; washing : 50 °C, 30 min; mole ratio of $Al_2(SO_4)_3$/glyoxal : 0.04.

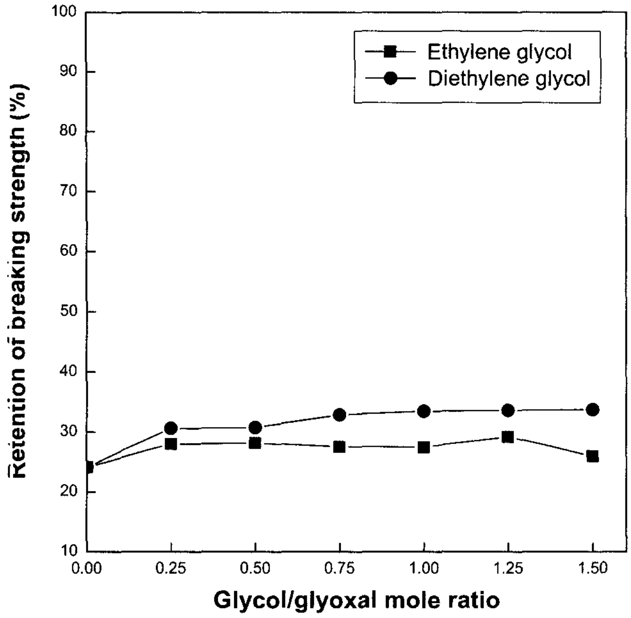


Figure 3. Effect of glycols on retention of breaking strength of treated fabric. $Al_2(SO_4)_3$/glyoxal mole ratio 0.04, curing 150 °C, 3 min.

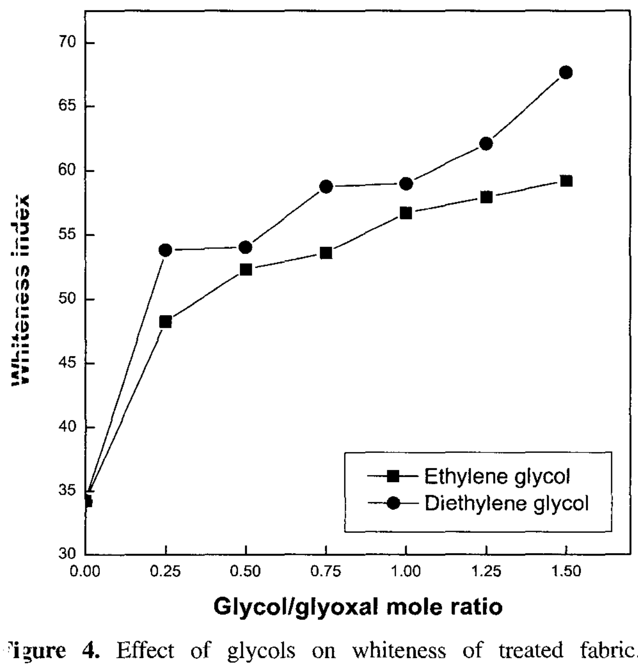


Figure 4. Effect of glycols on whiteness of treated fabric. $Al_2(SO_4)_3$/glyoxal mole ratio 0.04, curing 150 °C, 3 min.

glyoxal, but to form three dimensional network copolymers because the chain length between hydroxy groups is too long.

## Conclusions

The optimum processing conditions for durable pressing cotton fabrics with nonformaldehyde crosslinking agent, glyoxal, was 5 %(owb) of glyoxal, a 0.04 mole ratio of aluminum sulfate to glyoxal, and curing at 150 °C for 3 min. Aluminum sulfate was best for wrinkle recovery angles of treated fabrics, but mixed catalyst of magnesium chloride/citric acid was better in respect of both whiteness and strength retention. Both the whiteness and the wrinkle recovery angle improved significantly when either ethylene glycol or diethylene glycol was added to glyoxal solution, and diethylene glycol was better than glycol in this respect. The optimum mole ratio of either glycol or diethylene glycol to glyoxal was 1:1.

## Acknowledgement

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## References


1. B. H. Kim, J. H. Jang, and S. W. Ko, *Fiber Polym.*, **1**, 116 (2000).
2. J. H. Jang, K. C. Yoon, and S. W. Ko, *Fiber Polym.*, **2**, 184 (2001).
3. H. M. Choi and Y. M. Kim, *Fiber Polym.*, **2**, 190 (2001).
4. C. M. Welch, *Text. Res. J.*, **58**, 480 (1988).
5. C. M. Welch and B. A. Kottes-Andrews, *Am. Dyest. Rep.*, 15 (1985).
6. C. Q. Yang and B. A. Kottes-Andrews, *J. Appl. Polym. Sci.*, **43**, 1609 (1991).
7. H. M. Choi and C. M. Welch, *Am. Dyest. Rep.*, **83**(12), 48 (1994).
8. J. R. Park, E. S. Lee, and S. W. Ko, *J. Korean Fiber Soc.*, **33**, 429 (1996).
9. N. J. Lim, E. S. Lee, and S. W. Ko, *J. Korean Fiber Soc.*, **34**, 517 (1997).
10. B. A. Kotttes-Andrews and B. J. Trask-Morrell, *Am. Dyest. Rep.*, **80**(7), 26 (1991).
11. E. J. Gonzales and J. D. Guthrie, *Am. Dyest. Rep.*, **58**(3), 27 (1973).
12. D. L. Worth, *U. S. Patent*, 4269603 (1981).
13. C. M. Welch, *Text. Res. J.*, **53**, 181 (1983).
14. D. L. Worth and E. A. Freeman, *U. S. Patent*, 4269602 (1981).
15. C. M. Welch, *Text. Chem. Color.*, **16**, 265 (1984).
16. B. J. Trask-Morrell, W. E. Franklin, and R. H. Lui, *Text. Chem. Color.*, **20**(3), 21 (1988).
17. B. J. Trask-Morrell and B. A. Kottes Andrews, *Text. Res. J.*, **64**, 729 (1994).