Bonding in Cotton Fiber from Formaldehyde-Free Crosslinks

J. G. FRICK, JR., *Southern Regional Research Center,* New Orleans, Louisiana 70179*

Synopsis

Cotton fabric was crosslinked with five agents, three of which were prepared form formaldehyde and two of which were formaldehyde-free. The formaldehyde-free agents produced less bonding between layers in the laminated microstructure of the cotton fiber. One agent, 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone, gave no evidence of any interlayer bonding. All five agents gave the same relationship between wrinkle recovery angle and molar substitution on the cotton up to moderate recovery angles, but only agents based on formaldehyde gave higher wrinkle recovery angles with additional reaction. Intralayer crosslinking did not reduce absorptivity, as shown by moisture regain and dye receptivity, but did restrict swelling in cupriethylenediamine hydroxide to the same extent as combined interlayer and intralayer crosslinking. The decrease in extensibility of treated fabric with increasing wrinkle recovery angle was the same with all agents. These results indicate the regions of the fiber that are important for each of these properties.

INTRODUCTION

In some of our investigations noticeable differences in performance appeared among cotton fabrics treated with conventional crosslinking agents prepared from formaldehyde and those treated with formaldehyde-free crosslinking agents.[1] To provide data that could explain these differences a comparison was made of properties imparted by several agents at various levels of crosslinking. The agents selected were: (1) dimethyloldihydroxyethyleneurea (DMDHEU) or 4,5-dihydroxy-1,3-bis(hydroxymethyl)-2-imidazolidinone, a potentially tetrafunctional agent that is the most common crosslinking agent in commercial use at present; (2) dimethylolethyleneurea (DMEU) or 1,3-bis(hydroxymethyl)-2-imidazolidinone, a difunctional agent that has been in common use; (3) formaldehyde (CHO), a simple reactive aldehyde; (4) 4,5-dihydroxy-1,3- dimethyl-2-imidazolidinone (DHDMI), a formaldehyde-free agent prepared from glyoxal and *N,N'*-dimethylurea; and (5) 1,1,4,4-tetramethoxybutane (TMB), the most effective of acetal crosslinking agents.[2] All agents were applied in the conventional pad-dry-cure procedure from aqueous solution with magnesium chloride catalyst. It was recognized, however, that magnesium chloride will not have the same acidity with nitrogenous and nonnitrogenous agents.[3]

MATERIALS AND METHODS

Formaldehyde, in a 37% solution stabilized with methanol, and magnesium chloride hexahydrate were obtained as reagent grade chemicals from

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a supplier of laboratory chemicals. Other agents for treating the cotton fabric were prepared in the laboratory.

Dimethyloldihydroxyethyleneurea, or 4,5-dihydroxy-1,3-bis(hydroxymethyl)-2-imidazolidinone, was prepared as follows. Urea, 75 g, was dissolved in 145 g neutralized 40% glyoxal. The solution was adjusted to pH 8 with sodium carbonate, allowed to stand 3 days, and then chilled. 4,5-Dihydroxy-2-imidazolidinone, 45 g, mp 129–132°C, was removed by filtration. A 26.0 g portion of the dihydroxyimidazolidinone was mixed with 30 g water, and 35.7 g neutralized 37% formaldehyde were added. The mixture was adjusted to pH 8 with sodium hydroxide solution and brought to 98.0 g with water. The mixture was allowed to stand 24–48 hours, with occasional shaking until dissolution was complete, to give a 40% solution of dimethyloldihydroxyethyleneurea.

Dimethylolethyleneurea, or 1,3-bis(hydroxymethyl)-2-imidazolidinone, was prepared as follows. 2-Imidazolidinone obtained from a chemical supplier was recrystallized from 2-butanone. The recrystallized imidazolidinone, 22.4 g, was mixed with 25 g water, and 42.2 g neutralized 37% formaldehyde were added. The mixture was adjusted to pH 8 with sodium hydroxide solution and brought to 95.0 g with water. The mixture allowed to stand 24–48 h, with occasional shaking until dissolution was complete, to give a 40% solution of dimethylolethyleneurea.

4,5-Dihydroxy-1,3-dimethyl-2-imidazolidinone was prepared as follows. N,N′-Dimethylurea, 88 g, was dissolved in 131 g neutralized 40% glyoxal. The mixture was adjusted to pH 8 with sodium carbonate, allowed to stand 4 days, and then chilled. The solid product was removed by filtration and recrystallized from ethanol to give 30 g dihydroxydimethylimidazolidinone, mp 139–142°C.

1,1,4,4-Tetramethoxybutane was prepared by the method of Frick and Harper.[2]

Fabric treatments were performed on scoured and bleached cotton printcloth. Agents were diluted or dissolved in water to give the desired concentration, and the solution was adjusted to pH 5 with hydrochloric acid. Magnesium chloride hexahydrate was added to make the amount in solution equal to 10% of agent weight plus 0.6% of solution weight. Fabric samples were padded with the solutions using a nip pressure that gave 95% wet add-on with application of water. Padded samples were dried 7 min at 70°C and cured 3 min at 160°C in mechanical convection ovens. Before testing samples were washed by procedure IIB in the determination of durable press rating.

Wrinkle recovery angle on the fabric samples was determined by the AATCC recovery angle method[4] with conditioning at 21°C and 65% RH and is presented as the sum of values determined in the warp and filling directions. Durable press rating was determined by the AATCC method for "Appearance of Durable Press Fabric after Repeated Home Launderings" using one wash only by procedure IIB.[4] Breaking strength and elongation at break were determined on an Instron tester using warpwise strips of fabric that were raveled to 80 threads—about 1 in.—and a 3-in. gauge length.

Moisture regain was water content as percent of dry cotton weight determined from weight loss on drying fabric samples at 105–110°C for 4 h after conditioning 24 h at 21°C and 65% RH from a slightly dried state. Dye receptivity was the depth of color, judged visually in side to side comparisons, that was imparted to fabric by the direct dyeing procedure of Goldthwait[5] but using the direct red 81 dye (CI no. 28160) only. All samples compared were dyed in the same dyebath.

Nitrogen content was determined on dried fabric by the Kjeldahl method. Formaldehyde content was determined by the method of Roff.[6]

Data were statistically analyzed with correlation and analysis of covariance techniques. One data point with a wrinkle recovery angle below 190° was discarded due to lack of confidence in its accuracy. Covariance models all had R^2 values greater than 0.9, indicating a good fit to the data. Comparison of the treatments were made at mean values of the independent variables as usual.

RESULTS AND DISCUSSION

Analyses of the treated cotton printcloths are in Table I. Molar substitution of the nitrogenous crosslinking agents was calculated from the nitrogen contents of the washed fabrics corrected for a 0.07 average blank value. Molar substitution of formaldehyde was calculated from the uncorrected formaldehyde contents of the washed fabrics. No data for tetramethoxybutane are in Table I because no good method was found for determining the extent of reaction. The percent efficiency of the reaction between agents and cellulose was calculated from the amount of bound agent and the amount of applied agent assuming a constant 95% wet add-on in the application of agent solutions. Values for efficiency with lowest levels of applied agent are unreliable because of the high percent error in the low analytical values.

The efficiency of reaction with the three nitrogenous agents decreased with increasing concentration of the applied agent as a general trend. Dihydroxydimethylimidazolidinone, the formaldehyde-free nitrogenous agent, gave only about half the efficiency of the other nitrogenous agents at all levels of application. Formaldehyde gave a very low efficiency that remained nearly constant as the level of application increased. With formaldehyde the low efficiency was from volatilization of agent before reaction with cellulose.[7] With dihydroxydimethylimidazolidinone, however, volatilization was not the cause of low efficiency; nitrogen analysis before washing showed that 85–95% of applied agent was retained through curing.

Two measures of desired performance in crosslinked cotton fabric are the increases in durable press ratings and wrinkle recovery angle. For this investigation, wrinkle recovery angle was selected as the measure of performance from crosslinking. Figure 1 shows that the relationship between the two properties was linear and nearly the same with all agents used in this investigation; only formaldehyde gave significantly lower durable press ratings. Wrinkle recovery angle, however, gave better definition because of the greater number of units and ease of replication.

Figure 2 shows a plot of molar substitution of crosslinking agent and wrinkle recovery angle with four of the agents. The relationship fell into two groups, one involving the three agents based on formaldehyde—dimethyloldihydroxyethyleneurea, dimethylolethyleneurea, and formalde-

TABLE I
Reaction of Crosslinking Agents with Cotton Printcloth

Concentration of agent applied (mol/10,000 g solution)	Fabric analyses		Molar substitution (mol agent bound/10,000 g cellulose)	Efficiency (% of applied agent bound to cellulose)
	Nitrogen (%)	Formaldehyde (%)		
Dimethyloldihydroxyethyleneurea				
0.6	0.26	—	0.69	121
1.1	0.34	—	0.98	94
1.7	0.42	—	1.28	79
2.8	0.71	—	2.38	90
3.9	0.88	—	3.05	82
5.1	1.05	—	3.73	77
6.7	1.32	—	4.85	76
Dimethylolethyleneurea				
0.7	0.27	—	0.72	108
1.4	0.43	—	1.31	99
2.1	0.60	—	1.95	98
3.4	0.79	—	2.67	83
4.8	1.06	—	3.73	82
6.2	1.31	—	4.73	80
8.2	1.42	—	5.18	67
Formaldehyde				
3.3	—	0.10	0.33	11
6.7	0.07	0.30	1.00	16
13.3	0.07	0.75	2.51	20
20.0	0.09	1.02	3.41	18
26.6	0.05	1.39	4.66	18
33.3	0.05	1.66	5.57	18
40.0	0.05	2.09	7.02	18
Dihydroxydimethylimidazolidinone				
0.7	0.11	0.02	0.14	21
1.4	0.25	0.00	0.65	49
2.7	0.47	0.01	1.46	57
4.1	0.56	0.00	1.80	46
5.5	0.77	0.01	2.59	50
6.8	0.81	0.00	2.75	43
8.2	0.93	0.00	3.21	41
10.9	1.15	—	4.37	42
13.7	1.21	—	4.61	35

hyde, itself—and another with dihydroxydimethylimidazolidinone. Both groups gave similar wrinkle recovery angles up to a substitution near 2.0 mol/10,000 g cellulose, where maximum wrinkle recovery angles were obtained with dihydroxydimethylimidazolidinone. The other three agents generated higher wrinkle recovery angles until a substitution near 3.5 mol/10,000 g cellulose was reached. The relationships for all the formaldehyde-based agents are so close that the number of crosslinks from a mole of agent must not vary appreciably.

With tetramethoxybutane as crosslinking agent, the relationship between wrinkle recovery angle and molar substitution appeared similar to that with dihydroxydimethylimidazolidinone. Table II shows that tetramethoxybutane gave about the same maximum wrinkle recovery angle as dihydroxydimethylimidazolidinone. However, the lack of a good method for de-

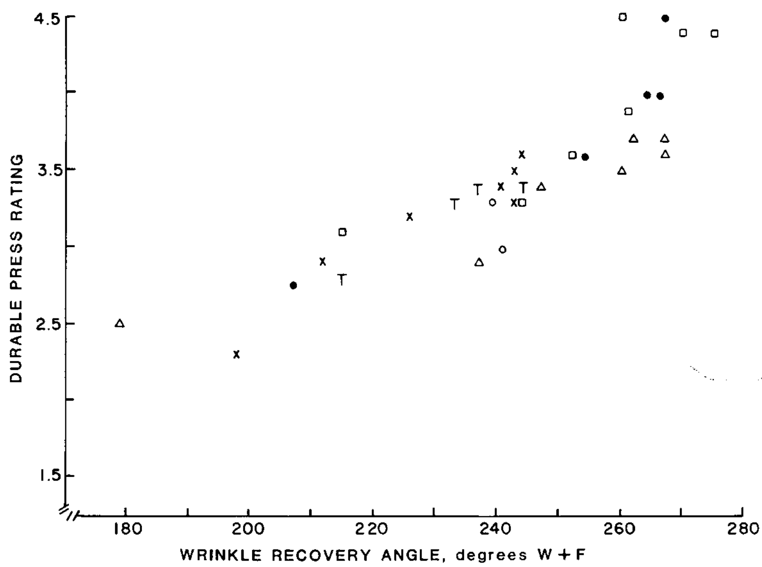

Fig. 1. Relationship of durable press rating to conditioned wrinkle recovery angle for treatments with the following crosslinking agents: (·) DMDHEU; (□) DMEU; (△) CHO; (×) DHDMI; (T) TMB.

termining molar substitution of tetramethoxybutane prevented a certain classification with dihydroxydimethylimidazolidinone.

The lower maximum wrinkle recovery angle with the two formaldehyde-free agents here is not a property of all formaldehyde-free crosslinking agents. There are at least three examples in the literature of formaldehyde-free agents that gave wrinkle recovery angles approaching the maximum

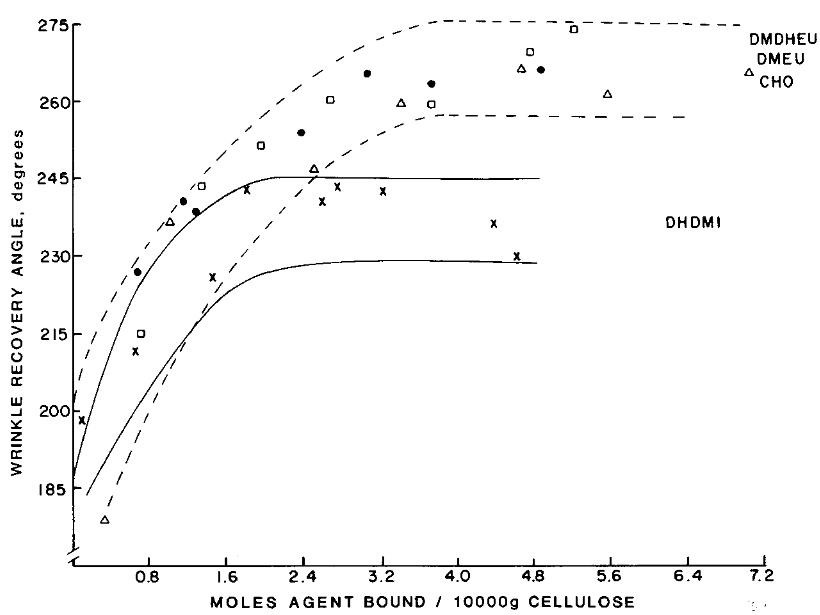

Fig. 2. Relationship of wrinkle recovery angle to molar substitution for crosslinked cottons. Crosslinking agents were: (·) DMDHEU; (□) DMEU; (△) CHO; (×) DHDMI.

TABLE II
Wrinkle Recovery from 1,1,4,4-Tetramethoxybutane

Concentration of tetramethoxybutane applied (mol/10,000 g solution)	Wrinkle recovery angle (degrees, $w + f$)
1.1	215
2.8	233
5.6	237
8.4	247
11.2	244

from formaldehyde-based agents, namely glyoxal,[8] glutaraldehyde,[9] and polyepoxides.[10]

The absorptivity of the crosslinked cottons is shown by the moisture regain and dye receptivity values in Table III. Dye receptivity was compared on a relative scale where 5 indicated dyeing to the darkest shade and 1 to the lightest. With dimethyloldihydroxyethyleneurea and dimethylolethyleneurea as crosslinking agents, moisture regain and dye receptivity decreased as substitution and wrinkle recovery angle increased. A similar but less pronounced trend occurred with formaldehyde treatments. Correlation coefficients between wrinkle recovery angle and moisture regain or dye receptivity were -0.89–-0.99 with these three agents. The smaller effect with formaldehyde is because formaldehyde reacts with cellulose to form a cellulose ether—hydroxymethylcellulose—before crosslinking,[11] and the crosslinking reaction occurs on a cellulose ether. Crosslinking of etherified cottons gives a product with more swelling ability than crosslinking of unmodified cotton because the ether substituent tends to prevent collapse of the fiber during drying before crosslinking.[12] In contrast to these results, response to finishing with the formaldehyde-free agents was quite different. With dihydroxydimethylimidazolidinone as crosslinking agent, there was no decrease in absorptivity with the increase in wrinkle recovery angle. With tetramethoxybutane as crosslinking agent, the decrease in absorptivity with increasing wrinkle recovery angle was small, less than occurred with the formaldehyde-based agents at similar recovery angles.

Cotton fibers crosslinked with the series of agents showed different responses in the methacrylate "expansion" technique.[13] In this microscopical examination, cotton is swollen in a boiling solution of alcohol and water, embedded in methacrylate, and examined by electron microscopy to observe separation of layers in the laminated microstructure of the cotton fiber. The formaldehyde-based agents can restrict layer separation completely. However, at the highest levels of application used in this work, tetramethoxybutane gave only partial restriction, and dihydroxydimethylimidazolidinone provided no restriction beyond that in untreated cotton. As shown by representative photomicrographs in Figure 3, at similar levels of performance—wrinkle recovery angles of 237–244°—there was extensive restriction of layer separation with dimethyloldihydroxyethyleneurea, moderate restriction with formaldehyde and dimethylolethyleneurea, little restriction with tetramethoxybutane, and no restriction with dihydroxy-

TABLE III
Absorption and Swelling in Crosslinked Cottons

Molar substitution (mol agent bound/10,000 g cellulose)	Wrinkle recovery angle (degrees, $w + f$)	Moisture regain (%)	Dye receptivity	Distention index
Dimethyloldihydroxyethyleneurea				
0.69	227	6.2	5.0	17
0.98	241	6.1	3.5	14
1.28	239	5.8	2.5	14
2.38	254	5.4	2.0	14
3.05	266	5.2	2.0	12
3.73	264	5.1	1.0	11
4.85	267	4.9	1.0	13
Dimethylolethyleneurea				
0.72	215	6.3	5.0	21
1.31	244	6.2	4.5	17
1.95	252	5.9	3.5	15
2.67	261	5.5	2.5	14
3.73	260	5.2	2.0	13
4.73	270	5.1	2.0	13
5.18	275	4.8	1.5	10
Formaldehyde				
0.33	179	6.5	5.0	17
1.00	237	6.5	4.5	17
2.51	247	6.3	3.5	16
3.41	260	6.1	3.0	16
4.66	267	6.0	3.0	15
5.57	262	6.0	2.5	13
7.02	267	5.9	2.5	13
Dihydroxydimethylimidazolidinone				
0.14	198	6.6	5.0	16
0.65	212	6.5	5.0	—
1.46	226	6.6	5.0	20
1.80	243	6.6	5.0	18
2.59	241	6.6	5.0	16
2.75	244	6.6	5.0	18
3.21	243	6.7	5.0	15
Tetramethoxybutane				
—	215	6.4	5.0	17
—	233	6.4	5.0	17
—	237	6.6	4.0	—
—	247	6.4	4.0	14
—	244	6.4	4.0	—
Untreated				
—	171	6.6	5.0	—

dimethylimidazolidinone. These results show that these formaldehyde-free crosslinking agents form fewer crosslinks that bind together the layers of the cotton fiber.

With the less extensive interlayer bonding, the formaldehyde-free agents would be expected to be even less effective for increasing wrinkle recovery angles than they are. Previous work correlated the increase in wrinkle recovery angle of dry or conditioned fabric directly with interlayer or interlamella bonding.[14] On a fabric that gave a 286° wrinkle recovery angle

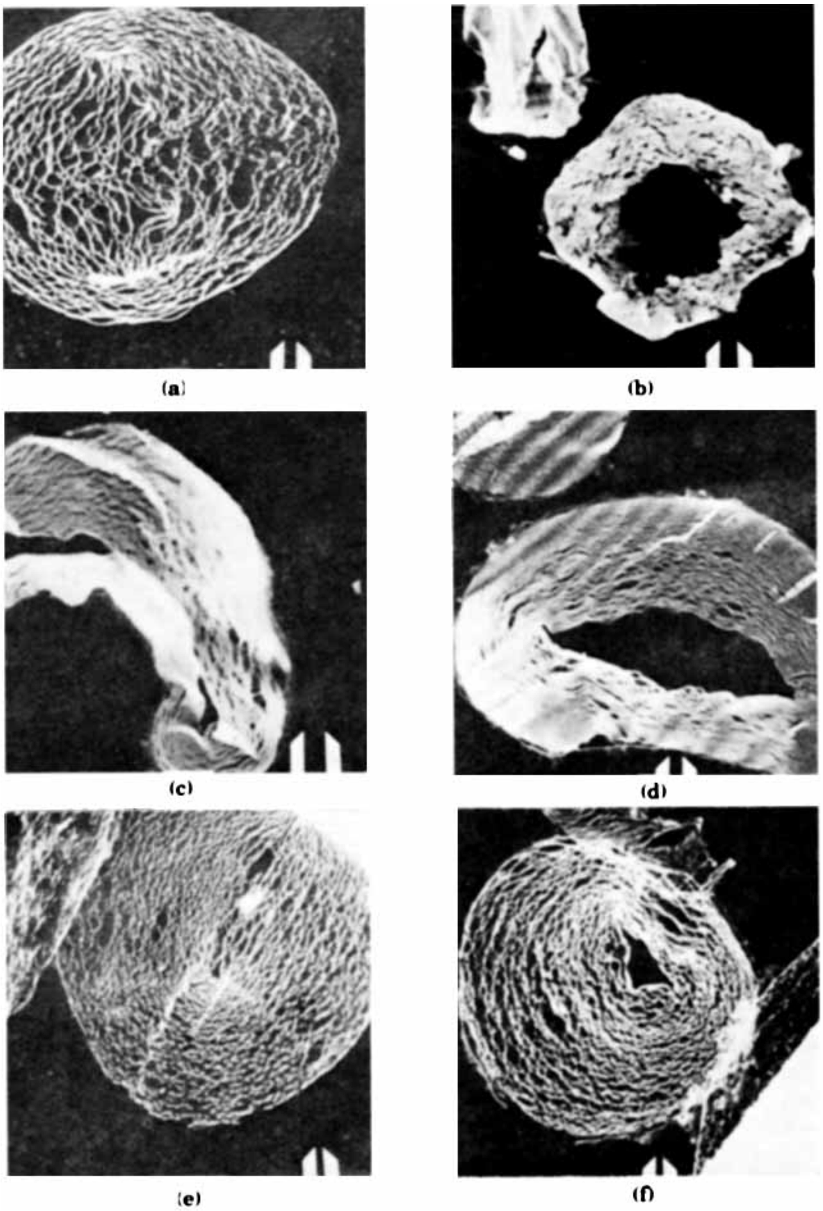

Fig. 3. Electron micrographs showing layer expansion of: untreated cotton (a) and cotton treated to 237–244° ($w + f$) conditioned wrinkle recovery angle with 2% DMDHEU (b), 2% DMEU (c), 2% CHO (d), 12% DHDMI (e), and 10% TMB (f).

with no layer separation, acetylation before crosslinking with the formaldehyde-based agent dimethylolethyleneurea reduced interlayer bonding to give a partial restriction of layer separation and lowered the wrinkle recovery angle below 200°. The present work indicates that the absence of interlayer bonding has no effect on wrinkle recovery angle below a moderate value, about 240° on the fabric used in this work. This value represents about two-thirds of the maximum increase obtained with the most effective agents.

Although the methacrylate "expansion" showed that crosslink distribution within the cotton fiber differed considerably, all agents readily insolubilized cotton in cupriethylenediamine hydroxide. Gel formation in cupriethylenediamine hydroxide by the method of Rowland and Post[15] was greater than 95% for cotton treated with all agents, even at the lowest levels of application. Also, the swelling of the gel in the cupriethylenediamine hydroxide was essentially the same among the cottons treated with different agents. The distention index of Stark and Rowland[16] is shown in Table III as a measure of this swelling of the gel. The distention index decreased as wrinkle recovery angle increased, but with different agents at 237–244° wrinkle recovery angle, the distention index ranged only from 14 to 18, and at molar substitutions of 4.5–5.0/10,000 g cellulose, ranged only from 13 to 15.

The difference in distribution of crosslinks from the various agents affected extensibility of the crosslinked fabrics similarly to the way it affected wrinkle recovery angle. In Figure 4 there was a highly significant inverse relationship between elongation at break and wrinkle recovery angle and no distinction based on agent could be made.

The relationship of breaking strength to wrinkle recovery angle was also linear. Fabrics treated with dimethyloldihydroxyethyleneurea, dimethylolethyleneurea, or tetramethoxybutane fell within the range enclosed by the dotted lines in Figure 5 and showed no significant differences. Previous work indicating lower strength with tetramethoxybutane than with dimethyloldihydroxyethyleneurea[2] was not confirmed here. Breaking strengths within this range are the usual values for fabric finished with practical crosslinking agents. Formaldehyde, as expected, consistently gave fabric with lower strength at a given wrinkle recovery angle. Dihydroxydimethylimidazolidinone, over the range of wrinkle recovery angles produced, gave fabric with a slightly higher strength. However, more extensive testing would be required to assure that the increase is inherent to finishing with dihydroxydimethylimidazolidinone. A comparison of tearing strengths

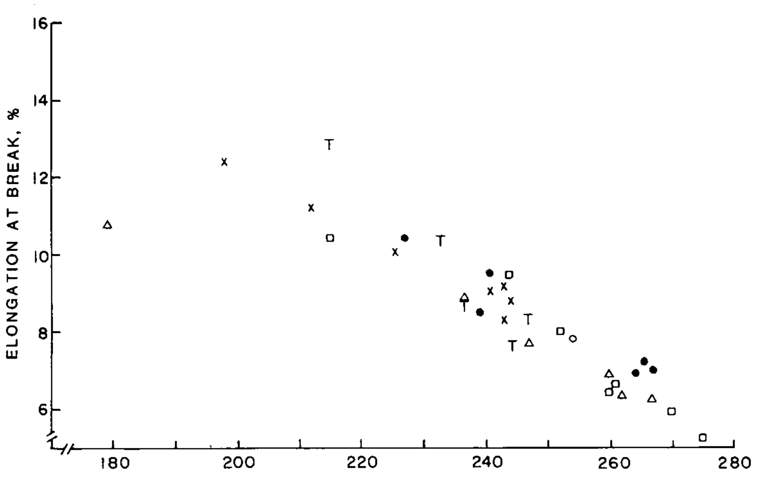

Fig. 4. Relationship of extensibility to wrinkle recovery angle for crosslinked cottons. Crosslinking agents were (•) DMDHEU; (□) DMEU; (△) CHO; (×) DHDMI; (T) TMB.

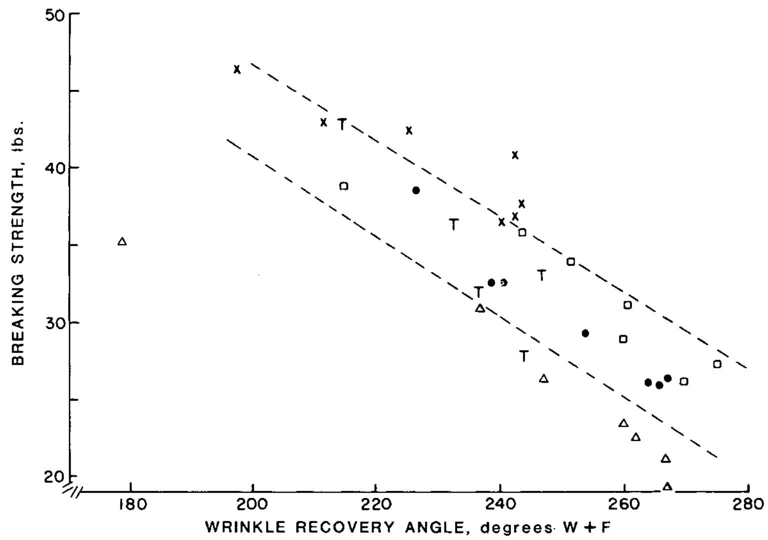

Fig. 5. Relationship of breaking strength to wrinkle recovery angle for crosslinked cottons. Crosslinking agents are: (•) DMDHEU; (□) DMEU; (△) CHO; (×) DHDMI; (T) TMB.

in a previous work did not show higher values with dihydroxydimethylimidazolidinone.[17]

SUMMARY AND CONCLUSIONS

Two formaldehyde-free crosslinking agents, 4,5-dihydroxy-1,3,-dimethyl-2-imidazolidinone and 1,1,4,4-tetramethoxybutane, were less efficient in reaction with cotton than conventional, formaldehyde-based agents, that is, they formed fewer crosslinks for mole of applied agent. The formaldehyde-free agents generated less crosslink bonding between layers in the laminated structure of the cotton fiber. The decreased interlayer bonding was pronounced with dihydroxydimethylimidazolidinone and less pronounced with tetramethoxybutane. The decreased interlayer bonding placed limits on the attainable wrinkle recovery angles and durable press ratings that were lower than the limits with formaldehyde-based agents. Maximum wrinkle recovery angles were about 240° and 270° ($w + f$) on the cotton printcloth used. Unexpectedly, the absence of interlayer bonding did not reduce the effectiveness of the crosslinks below 240° wrinkle recovery angle; similar molar substitutions of either type agent produced similar wrinkle recovery angles. With no interlayer bonding, moisture regain and dye receptivity were not reduced by crosslinking. This indicates that sites for these absorptions are not within but are the surface of the fiber lamellae. The extent of interlayer bonding had no influence on the dissolution or swelling of crosslinked cotton in cupriethylenediamine hydroxide solution, an indication that such swelling occurs within and not between the fiber lamallae. The extent of interlayer bonding also had no influence on the extensibility of fabric at a given wrinkle recovery angle. Fewer interlayer bonds may have contributed to higher strength in wrinkle-resistant fabric, but the effect was small at best.

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