

# Acetals as Crosslinking Reagents for Cotton

J. G. FRICK, JR., and ROBERT J. HARPER, JR., *Southern Regional Research Center, \* New Orleans, Louisiana 70179*

## Synopsis

Acetals that react with cotton to form cellulose crosslinks are derived from dialdehydes that can form five- or six-membered tetrahydrofuran or tetrahydropyran rings. These aldehydes themselves are reactive to cotton, but the acetals do not form the aldehyde to react. The acetals were less reactive than the aldehydes and formed crosslinks with a different structure. Intrinsic reactivity of acetals increased with increased branching in the alkoxy group, but the increase was often hidden by the effect from changing solvents. In some instances a greater reactivity with methyl acetals was pronounced. Strength loss in cotton fabric from crosslinking was greater with acetals than with conventional crosslinking agents because even the most reactive acetals were less reactive and required more rigorous reaction conditions than conventional agents.

## INTRODUCTION

In our investigations of crosslinking reactants for cotton that could lead to formaldehyde-free finishing agents, acetals of aldehydes other than formaldehyde were considered. Initial prospects were poor because formal finishing agents had little effectiveness,<sup>1,2</sup> and the first nonformaldehyde acetals tried were no better. However, in our early investigations there was one acetal that did give appreciable crosslinking, at least when it was used with a highly active catalyst. This acetal, 2,5-dimethoxytetrahydrofuran, had been claimed to be an active crosslinking agent for cellulose,<sup>3</sup> but apparently had received no attention among the numerous acetal agents with little reactivity. The example of a nonformaldehyde acetal that gave appreciable crosslinking prompted this study of monomeric acetals to determine the structural features of acetals that govern their reactivity with cellulose, particularly cellulose in cotton.

## EXPERIMENTAL

The reactivity of acetals to cellulose in cotton was tested by using them to treat a scoured and bleached cotton printcloth that weighed 110 g/m<sup>2</sup> (3.2 oz/yd<sup>2</sup>). Treatment of fabric samples consisted of applying a solution of acetal and catalyst in a suitable solvent by padding, placing the samples on pin frames for drying and curing in mechanical convection ovens, and then washing the samples by the AATCC procedure for durable press rating.

The catalysts used in the fabric treatments were 2.0% (on weight of solution) magnesium chloride hexahydrate or 0.5% magnesium chloride with 0.5% citric acid. With magnesium chloride alone the acetal solution was adjusted to pH 5 before adding the catalyst, and the fabric samples were dried 7 min at 70°C

\* One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture.

and cured 3 min at 160°C unless otherwise noted. With the magnesium chloride/citric acid catalyst the acetal and catalyst formed a solution of pH 2.5 that was left unadjusted. The fabric samples with the magnesium chloride/citric acid catalyst were dried 7 min at 70°C and cured 3 min at 120°C.

Fabric samples were tested by methods described in the Technical Manual of the American Association of Textile Chemists and Colorists.<sup>4</sup> Wrinkle recovery angles were determined by the "Recovery Angle Method," durable press ratings by the method for "Appearance of Durable Press Fabrics after Repeated Home Laundering" using a single laundering by procedure IIB, and tear strength by the ASTM Elmendorf method.

Hydrolysis of fabric samples was conducted by placing the samples in 0.1*N* or 0.5*N* hydrochloric acid at 40°C for 30 min with occasional shaking in a water bath. The measured pH of these hydrolysis solutions was 1.5 and 1.2. Samples were then submitted to the laundry procedure and tested.

Proton magnetic resonance (PMR) spectra were obtained with a Varian EM 360L 60 MHz spectrometer. Signals were measured in parts per million from methylsilane standards.

### Agents Applied to Fabric

Dimethyloldihydroxyethyleneurea, 4,5-dihydroxy-1,3-bis(hydroxymethyl)-2-imidazolidinone, was purchased in a 40% solution as a textile finishing agent from a supplier of textile chemicals. Glutaraldehyde was obtained in a 50% solution from Aldrich Chemical Co.

Among the acetals, *dimethoxymethane* and *2,5-dimethoxytetrahydrofuran* were laboratory reagents purchased from Aldrich Chemical Co. The other acetals were prepared in laboratory by the following procedures.

***ρ*-Bis(dimethoxymethyl)benzene.** Terephthalaldehyde, 101 g (0.75 mol), was mixed with 191 g trimethyl orthoformate, and 0.5 g concentrated sulfuric acid was added with shaking. The reaction mixture was cooled in tap water as an exotherm occurred and a solution formed. The solution was allowed to stand 24 h and was then neutralized with sodium methoxide in methanol. The solution was filtered and evaporated under vacuum at room temperature to leave 141 g of solid, mp 49–54°C. The solid was extracted with 300 mL heptane at 50°C. On cooling the extract to room temperature, there crystallized 47 g *ρ*-bis(dimethoxymethyl)benzene, mp 53–55°C (lit.<sup>5</sup> mp 53°). Chilling the heptane liquors yielded a further 65 g, mp 52–54°C. The PMR spectrum of *ρ*-bis(dimethoxymethyl)benzene consisted of three singlets at 3.30, 5.38, and 7.45 ppm.

**1,3-Bis(4,5-dimethyl-1,3-dioxolan-2-yl)propane.** This acetal of glutaraldehyde and 2,3-butanediol was prepared by the method of Sprung and Guenther<sup>6</sup> for glyoxal acetals with the substitution of an equimolar amount of 50% glutaraldehyde for 30% glyoxal. The mixed isomers of 1,3-bis(4,5-dimethyl-1,3-dioxolan-2-yl)propane were distilled at 104°C and 1 torr in 84% of theoretical yield. Analysis of the product showed 64.02% C and 9.79% H; calculated values are 63.90% C and 9.90% H. 1,3-Bis(4,5-dimethyl-1,3-dioxolan-2-yl)propane gave a PMR spectrum with the following signals: two doublets at 1.0–1.4 ppm, a band at 1.4–1.7 ppm, a multiplet at 3.3–3.8 ppm, and a band at 4.8–5.2 ppm.

**1,3-Bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)propane.** This acetal of glutaraldehyde and 2,3-dimethyl-2,3-butanediol, pinacol, was prepared as follows. A mixture of 170 g pinacol (1.44 mol), 120 g 50% glutaraldehyde (0.60 mol), 2.0 g *p*-toluenesulfonic acid monohydrate, and 120 mL toluene was refluxed under a Dean and Stark trap. Reflux was stopped after 3.8 h when the temperature of the boiling liquid reached 130°C and was rising rapidly. Water layer collected in the trap was 80.9 g. The reaction mixture was washed twice with 150 mL 9% sodium bicarbonate. The washings were extracted with toluene which was added to the reaction mixture. The mixture was dried over anhydrous potassium carbonate and evaporated under vacuum at room temperature to leave a wet solid. The solid was recrystallized from heptane to give 37 g 1,3-bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)propane, mp 38–40°C. Concentration of the heptane liquors gave an additional 53 g, mp 39–40°C. Analysis of the product showed 68.39% C and 10.87% H; calculated values are 67.96% C and 10.74% H. 1,3-Bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)propane gave a PMR spectrum with the following signals: a singlet at 1.20 ppm, a band at 1.5–1.7 ppm, and a band at 4.9–5.1 ppm.

**2-*tert*-Butoxy-5-methoxytetrahydrofuran.** This acetal was prepared in an attempt to prepare 2,5-di-*tert*-butoxytetrahydrofuran.

A mixture of 106 g 2,5-dimethoxytetrahydrofuran, 711 g *tert*-butanol, and 4.0 g *p*-toluenesulfonic acid monohydrate was boiled, and a distillate was collected through a Snyder column at 72–78°C. After 7 h, 55 g *tert*-butanol, the weight of the distillate at that time, was added, and distillation was continued another 7 h. A total of 150 g distillate was collected. The residual reaction mixture was neutralized with sodium *tert*-butoxide in hot *tert*-butanol, filtered, and concentrated under a distilling column until it boiled at 50°C and 25 torr. The residue was extracted twice with 150 and 100 mL portions of petroleum ether. The petroleum ether was evaporated, and the residual liquid, about 80 g, distilled through a Snyder column. A fraction of 22 g was collected at 31–33°C and 2 torr, and another of 11 g at 33–50°C and 2 torr. The lower boiling fraction gave a PMR spectrum with the following signals: a singlet at 1.22 ppm, a band at 2.0 ppm, a singlet at 2.76 ppm, a multiplet at 3.4 ppm, a band at 5.1 ppm, a band at 5.5 ppm, and a singlet at 9.80 ppm. Integration ratios of the signals in the above order were 60:44:05:28:09:09:02. The equal integration of butoxy CH and methoxy CH (5.1 and 5.5 ppm) indicated about equal molar amounts of both groups. Integration relative to total integration of butoxy CH<sub>3</sub> and methoxy CH<sub>3</sub> (1.22 and 3.4 ppm) was equivalent to 30 mol % di-*tert*-butoxytetrahydrofuran and 40 mol % dimethoxytetrahydrofuran. It was concluded that this fraction consisted of about 60 mol % 2-*tert*-butoxy-5-methoxytetrahydrofuran with 10 mol % dimethoxytetrahydrofuran, 10 mol % succinaldehyde (2.76 and 9.80 ppm), and 20 mol % aldehyde polymer (1.96 ppm integration excess). This fraction was applied to fabric as 2-*tert*-butoxy-5-methoxytetrahydrofuran.

The higher boiling fraction, from its PMR spectrum, contained a higher *tert*-butoxy content but still contained an appreciable methoxy content and similar contents of aldehyde and polymer.

**2,6-Diethoxytetrahydropyran.** This acetal was prepared by the method of Kankaanpera and Miiki<sup>7</sup> from 3,4-dihydro-2-ethoxypyran and ethanol. The product of mixed isomers was distilled at 58–63°C and 4 torr in 67% of theoretical yield. The mixed isomers of 2,6-diethoxytetrahydropyran gave a PMR spectrum

with the following signals: a triplet at 1.14 ppm, a band at 1.3–1.9 ppm, a multiplet at 3.1–4.1 ppm, and a band at 4.3–4.9 ppm.

**2,5-Diisopropoxytetrahydrofuran.** 2,5-Dimethoxytetrahydrofuran, 100 g, was mixed with 545 g isopropanol and 3.0 g *p*-toluenesulfonic acid monohydrate. The mixture was boiled 13 h while a distillate was collected slowly through a Snyder column. Total distillate, collected at 73–80°C, was 110 g; theoretical yield of methanol was 48.4 g. The residue was neutralized with sodium isopropoxide in isopropanol and evaporated to 112 g liquid and solid. The liquid was filtered and distilled. The product, 58 g, was collected at 38°C and 1 torr. The last fraction of the distillate contained 63.93% C and 10.53% H; calculated values for 2,5-diisopropoxytetrahydrofuran are 63.79% C and 10.71% H. This fraction gave a PMR spectrum with clusters of signals of 0.9–1.3 ppm, 1.6–2.2 ppm, 3.5–4.2 ppm, and 5.1–5.4 ppm. Integration ratios were 5.8:2.1:1.0:1.0; theoretical ratios are 6:2:1:1 for the mixed isomers of 2,6-diisopropoxytetrahydrofuran. The bulk of the distillate that was used for application to fabric had additional signals from methoxy groups at 3.2–3.4 ppm. Integration ratios were 5.8:2.4:0.9:1.0 for the original four signals, and 0.4 for the additional signals. This was calculated to be the spectrum from a mixture of 74 mol % diisopropoxytetrahydrofuran and 26% isopropoxymethoxytetrahydrofuran.

**2,6-Diisopropoxytetrahydropyran.** A mixture of 100 g 50% glutaraldehyde (0.50 mol), 180 g isopropanol (3.0 mol), 1.7 g *p*-toluenesulfonic acid monohydrate, and 100 mL benzene were refluxed under a Dean and Stark trap. The mixture was refluxed 27 h during which time an aqueous layer of 58 g was collected. Theoretical yield of water was 68 g. The mixture was neutralized with sodium isopropoxide in isopropanol, the isopropanol evaporated, and the residual liquid filtered and distilled. A distillate of 60 g was collected at 42–57°C and 1 torr. The distillate was redistilled to give 53 g at 48–49°C and 1 torr. The PMR spectrum of the product had four major signals: a multiplet at 0.9–1.3 ppm, a band at 1.3–1.9 ppm, a septet at 3.95 ppm, and a band at 4.7–5.1 ppm. Integration ratios were 6.2:3.0:1.0:1.1; theoretical ratios were 6:3:1:1. There were two minor signals at 4.3–4.7 ppm and 9.76 ppm with integration ratios of 0.14 and 0.07. The spectrum indicated that the product was 2,6-diisopropoxytetrahydropyran contaminated with about 5 mol % aldehyde. Analysis showed 65.24% C and 10.76% H; calculated values for 2,6-diisopropoxytetrahydropyran are 65.31% C and 10.96% H.

**1,1-Dimethoxyhexane.** Hexanal, 100 g (1.0 mol), was added slowly with stirring and cooling to a mixture of 64.0 g methanol (2.0 mol) and 19 g anhydrous calcium chloride. The mixture was allowed to stand 24 h with occasional shaking. Two layers formed. The upper layer was separated, washed with 20 mL water, placed over anhydrous potassium carbonate overnight, and then distilled. 1,1-Dimethoxyhexane, 60 g, was collected at 65°C and 25 torr (lit.<sup>8</sup> 52–53°C and 12 torr). 1,1-Dimethoxyhexane gave a PMR spectrum with the following signals: a multiplet at 0.8–1.1 ppm, a band at 1.1–2.4 ppm, a singlet at 3.30 ppm, and a triplet at 4.33 ppm.

**2,6-Dimethoxytetrahydropyran.** This acetal was prepared from equimolar amounts of 3,4-dihydro-2-methoxypyran and methanol by the method used for preparing 2,6-diethoxytetrahydropyran. A 69% yield of 2,6-dimethoxytetrahydropyran mixed isomers was obtained, distilling at 63–66°C and 16 torr

(lit.<sup>9</sup> 65–67°C and 21 torr). The product gave a PMR spectrum with the following signals: a band at 1.2–2.0 ppm, a singlet at 3.39 ppm, a singlet at 3.41 ppm, a band at 4.2–4.5 ppm, and a band at 4.6–4.8 ppm. Integration ratios were 3.6:3.7 (both singlets): 0.22:1.0. The spectrum indicated that the product was 2,6-dimethoxytetrahydropyran with an unknown contaminant.

**1,1,5,5-Tetraacetylpentane.** A quantity of 50% glutaraldehyde was concentrated under vacuum at room temperature to 63% of original weight. A 56 g portion of this concentrate was dissolved in 390 g acetic anhydride, and the solution was refluxed 25 h. The solution was heated to 120°C and 40 torr to remove volatiles and was then distilled without a column. Product, 31 g, was collected at 166–170°C and 1 torr. The distillate on standing went to a solid, mp 61–63°C. Recrystallization from 50% toluene/50% petroleum ether gave 1,1,5,5-tetraacetylpentane, mp 64–65°C. Analysis showed 51.47% C and 6.34% H; calculated values are 51.31% C and 6.63% H. 1,1,5,5-Tetraacetylpentane gave a PMR spectrum with the following signals: a band at 1.2–2.5 ppm, a singlet at 2.06 ppm, and a triplet at 6.76 ppm.

**1,1,5,5-Tetraethoxypentane.** A solution of 38.2 g 2,6-diethoxytetrahydropyran in 51 g ethanol was added slowly to 1.4 g concentrated sulfuric acid in 51 g ethanol. The solution was allowed to stand 26 h over 4 g anhydrous magnesium sulfate. The mixture was filtered and neutralized with sodium ethoxide in ethanol. The ethanol was evaporated, and the residual liquid was distilled. 1,1,5,5-Tetraethoxypentane, 18 g, was collected at 85–87°C and 1 torr (lit.<sup>10</sup> 85–86°C and 0.3 torr). Analysis showed 62.70% C and 11.35% H; calculated values for tetraethoxypentane are 62.87% C and 11.36% H. 1,1,5,5-Tetraethoxypentane gave a PMR spectrum with the following signals: a triplet at 1.19 ppm, a multiplet at 1.3–1.8 ppm, a cluster at 3.2–3.9 ppm, and a triplet at 4.46 ppm.

**1,1,4,4-Tetramethoxybutane.** A solution of 93 g 2,5-dimethoxytetrahydrofuran and 3.0 g *p*-toluenesulfonic acid monohydrate in 179 g methanol was mixed with 12 g anhydrous magnesium sulfate. The mixture was allowed to stand 2 days with occasional shaking. The mixture was filtered and neutralized with sodium methoxide in methanol. The methanol was evaporated, and the residual liquid was distilled. 1,1,4,4-Tetramethoxybutane, 41 g, was collected at 45°C and 2 torr (lit.<sup>11</sup> 77–78°C and 12 torr).

ANAL. Calcd for tetramethoxybutane: C, 53.91%; H, 10.18%. Found: C, 54.17%; H, 10.01%. 1,1,4,4-Tetramethoxybutane gave a PMR spectrum with the following signals: a multiplet at 1.4–1.7 ppm, a singlet at 3.29 ppm, and a band at 4.1–4.5 ppm.

**1,1,2,2-Tetramethoxyethane.** A mixture of 69.9 g glyoxal trimer dihydrate (1.0 mol), 129 g methanol (4.0 mol), and 5.0 g *p*-toluenesulfonic acid monohydrate was refluxed until a solution formed; about 1 hr was required. The solution was mixed with 500 mL chloroform, and the resultant solution was refluxed under a water trap that returned the heavier layer of the heterogeneous distillate to the boiling solution. Every 7.5 h an amount of methanol equal to 30% of the lighter layer removed during the period was added. The solution was refluxed for 37.5 h, during which time 71 g of the lighter layer was removed and 21 g methanol was added. At this time the lighter layer was still being formed at a slow rate. Methanol, 43 g, was added and reflux was continued for 2.5 h; during this period the distillate was homogeneous. The solution was neutralized with

sodium methoxide in methanol and filtered. Volatiles were removed by vacuum distillation through a Snyder column, with the vacuum controlled to keep a reflux in the column, until the liquid was boiling at 62°C and 50 torr. The residual liquid was filtered and distilled. 1,1,2,2-Tetramethoxyethane, 34 g, was collected at 50–52°C and 12 torr after 33 g of forerun.

ANAL. Calcd for tetramethoxybutane: C, 47.99%; H, 9.40%. Found: C, 47.81%; H, 9.54%.

The product gave a PMR spectrum with singlets at 3.34 and 4.21 ppm. Integration ratio of the signals was 5:1 instead of the calculated 6:1. The product was yellow when freshly distilled and became colorless on standing. The color change was probably from the presence of glyoxal that polymerized on standing. The PMR spectrum and the color change suggested contamination of the product with about 7% glyoxal polymer.

**1,1,8,8-Tetramethoxyoctane.** Magnesium turnings, 34.0 g (1.4 mol), were placed in 205 g diethyl ether, and a small amount of 1,6-dibromohexane and a crystal of iodine were added. The mixture was heated until the reaction started. 1,6-Dibromohexane was then added with stirring at a rate to keep the mixture at reflux until 171 g (0.70 mol) were added. After addition was complete, in about 3 h, the mixture was refluxed 2 h more and allowed to stand overnight. Trimethyl orthoformate, 149 g (1.4 mol), was added with stirring at a rate to keep the mixture refluxing. Addition was complete in 3 h, and the mixture was allowed to stand 1 h more while the exotherm continued. A precipitate formed during the course of the reaction. The liquid was poured over ice, and the organic layer separated. The solid was washed with ether, and the ether extract poured into ice water and separated. The remaining solid was dissolved in 1% NaHCO<sub>3</sub>, and the solution was extracted with ether. All ether extracts and the original organic layer were combined and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. The solution was allowed to evaporate at room temperature, and the residue was distilled through a Vigreux column. After collecting a lower boiling material, apparently 1,1-dimethoxyheptane, 1,1,8,8-tetramethoxyoctane was collected at 112–125°C and 3–4 torr.

ANAL. Calcd for tetramethoxyoctane: C, 61.50% H, 11.19%. Found: C, 61.89%; H, 11.28%.

1,1,8,8-Tetramethoxyoctane gave a PMR spectrum with the following signals: a band at 1.1–1.8 ppm, a singlet at 3.29 ppm, and a triplet at 4.32 ppm.

**1,1,5,5-Tetramethoxypentane.** A solution of 114 g 2-methoxy-3,4-dihydroxypropan in 190 g methanol was added to a solution of 10 g *p*-toluenesulfonic acid monohydrate in 194 g methanol with stirring and cooling. The mixture was allowed to stand 20 h and was then neutralized with sodium methoxide in methanol. Methanol was evaporated to leave two immiscible liquids. The lighter liquid was dried over anhydrous potassium carbonate and distilled. 1,1,5,5-Tetramethoxypentane, 106 g, was collected at 60–61°C and 1 torr (lit.<sup>12</sup> 75–77°C and 3 torr). 1,1,5,5-Tetramethoxypentane gave a PMR spectrum with the following signals: a multiplet at 1.2–1.9 ppm, a singlet at 3.30 ppm, and a multiplet at 4.1–4.6 ppm.

## RESULTS AND DISCUSSION

In this work the distinction was made between acetals that react to form cellulose crosslinks and unreactive acetals on the basis of their ability to increase the resiliency of cotton printcloth as shown by increases in wrinkle recovery angle

and durable press rating.<sup>13</sup> The wrinkle recovery angle was given greater weight because durable press rating at the low values obtained with the lower levels of reactivity varied enough to make distinctions difficult. Durable press ratings below 2.5 appeared to have little meaning. Increases in wrinkle recovery angle and durable press rating are, after all, the changes desired in commercial crosslinking treatments of cotton. Although other criteria for determination of agent reactivity in addition to these values were desirable, no other property or measurement was found to be directly pertinent. With reactive acetals of higher molecular weight, there was an obvious and measurable weight gain on treatment; but, considering the variability of the measured weight gain and the small amount of cellulose crosslinking necessary to change wrinkle recovery and durable press rating,<sup>13,14</sup> reaction of lower molecular weight acetals could not be excluded by lack of measurable weight gain. Similarly, the change in the elemental composition of the cotton on treatment with reagents composed only of carbon, hydrogen, and oxygen was too small to provide a measure of reaction. Insolubility of the treated cotton in cellulose solvents, on the other hand, was too sensitive; insolubility could be conferred by an extent of reaction too small to affect other properties.<sup>15,16</sup> Moisture absorption was unreliable as a criterion; we have found that it can vary with the agent at apparently similar levels of crosslinking. An increase in wrinkle recovery angle and durable press rating has been noted with treatments other than crosslinking,<sup>17</sup> but such an effect is unlikely with the conditions used here.

To test reactivity of the acetals, cotton printcloth was impregnated with a solution of acetal and catalyst, dried, cured, and washed. Two conditions of treatment were used: 2.0% (on weight of solution) magnesium chloride hexahydrate as catalyst with curing at 160°C; and 0.5% magnesium chloride hexahydrate and 0.5% citric acid as catalyst with curing at 120°C. These two conditions were chosen because of their suitability for crosslinking with agents of usual activity and for crosslinking under strenuous conditions that are effective with less active agents.<sup>18</sup> Indeed, some acetals were found to react with magnesium chloride/citric acid but not with magnesium chloride alone.

**Characteristics of Reactive Acetals.** In Table I are the wrinkle recovery angles and durable press ratings from application to cotton printcloth of a series of methyl acetals at similar molar concentration. The aldehydes from which these acetals were derived include aliphatic monoaldehydes and dialdehydes and aromatic dialdehydes. The acetals were applied from water when they were water-soluble; otherwise, they were applied from a mixture of water and methanol containing the minimum amount of methanol.

The only acetals in this series that showed substantial reactivity were those derived from succinaldehyde and glutaraldehyde, that is, the methoxy butane and tetrahydrofuran, and the methoxy pentane and tetrahydropyran. The reactive acetals are derived from aldehydes that are, themselves, reactive to cotton; glutaraldehyde has been shown to be reactive and succinaldehyde has the structure needed for reactivity.<sup>19</sup> Yet, dimethoxymethane was unreactive, although it is derived from formaldehyde, another aldehyde that is reactive to cotton. It is possible that dimethoxymethane is too volatile and evaporates before reaction can occur. However, less volatile formals have not shown noticeable effectiveness.<sup>1,2</sup> Volatility does not seem to be a major factor in determining reactivity to cotton. 1,1-Dimethoxyhexane was chosen as an example

TABLE I  
 Crosslinking of Cotton Printcloth with Methyl Acetals

Acetal applied <sup>a</sup>	Parent aldehyde	Solvent <sup>b</sup> (% water)	Durable press rating	Wrinkle recovery angle (degrees, w + f)
Applied with magnesium chloride/citric acid and cured at 120°C				
Dimethoxymethane	Formaldehyde	100	2.2	211
1,1-Dimethoxyhexane	Hexanal	30	2.3	208
1,1-Dimethoxyhexane <sup>c</sup>	Hexanal	1	1.4	195
<i>p</i> -Bis(dimethoxymethyl)benzene	Terephthalaldehyde	0	2.5	214
1,1,2,2-Tetramethoxyethane	Glyoxal	100	2.0	200
1,1,4,4-Tetramethoxybutane	Succinaldehyde	100	3.9	275
1,1,5,5-Tetramethoxypentane <sup>d</sup>	Glutaraldehyde	80	3.4	268
2,5-Dimethoxytetrahydrofuran	Succinaldehyde	100	3.7	274
2,6-Dimethoxytetrahydropyran	Glutaraldehyde	50	2.4	235
Applied with magnesium chloride and cured at 160°C				
Dimethoxymethane	Formaldehyde	100	1.9	198
1,1-Dimethoxyhexane	Hexanal	30	1.7	184
1,1-Dimethoxyhexane <sup>c</sup>	Hexanal	3	1.4	196
<i>p</i> -Bis(dimethoxymethyl)benzene	Terephthalaldehyde	10	2.2	205
1,1,2,2-Tetramethoxyethane	Glyoxal	100	1.3	205
1,1,8,8-Tetramethoxyoctane	Octanedial	2	2.3	217
1,1,4,4-Tetramethoxybutane	Succinaldehyde	100	3.4	247
1,1,5,5-Tetramethoxypentane	Glutaraldehyde	40	3.3	246
2,5-Dimethoxytetrahydrofuran	Succinaldehyde	100	2.0	193
2,6-Dimethoxytetrahydropyran	Glutaraldehyde	50	2.5	225
(Untreated fabric)		—	1.2	188

<sup>a</sup> Acetals were applied from solution of 0.76 mol/1000 g solution with 0.5% MgCl<sub>2</sub>·6H<sub>2</sub>O and 0.5% citric acid, or with 2.0% MgCl<sub>2</sub>·6H<sub>2</sub>O.

<sup>b</sup> Solvent was a mixture of water and methanol with maximum amount of water allowed by the solubility of the acetal.

<sup>c</sup> Concentration of acetal was 1.5 mol/1000 g solution.

<sup>d</sup> Concentration of acetal was 0.67 mol/1000 g solution.

of a methyl acetal from a simple aliphatic monoaldehyde because it had the lowest molecular weight with a relatively high boiling point, 158°C. It was unreactive even at high concentrations. 2,5-Dimethoxytetrahydrofuran with a boiling point of 146°C, however, was reactive.

The reactive acetals, like the reactive aldehydes, were those that exist in or can form five-membered or six-membered rings by an internal ether link. 1,1,2,2-Tetramethoxyethane and 1,1,8,8-tetramethoxyoctane are similar to re-



TABLE II  
 Reactivity of Acetals with Different Alkoxy Groups

Acetal <sup>a</sup>	Catalyst <sup>b</sup>	Solvent	Durable press rating	Wrinkle recovery angle (degrees, <i>w + f</i> )
2,5-Dimethoxytetrahydrofuran	MC	60% Methanol	2.8	232
2,5-Diisopropoxytetrahydrofuran	MC	60% Isopropanol	3.1	243
2- <i>Tert</i> -butoxy-5-methoxytetrahydrofuran	MC	60% <i>tert</i> -Butanol	3.4	266
2,6-Dimethoxytetrahydropyran	MC	50% Methanol	2.4	235
2,6-Diethoxytetrahydropyran	MC	50% Ethanol	2.2	240
2,6-Diisopropoxytetrahydropyran	MC	60% Isopropanol	2.3	210
1,1,5,5-Tetramethoxypentane <sup>c</sup>	M	60% Methanol	3.1	246
1,1,5,5-Tetraethoxypentane <sup>c</sup>	M	60% Ethanol	1.4	185
1,1,5,5-Tetramethoxypentane <sup>c</sup>	M	60% Ethanol	3.0	244
1,3-Bis(4,5-dimethyl-1,3-dioxolan-2-yl)propane	MC	100% Isopropanol	2.4	205
	MC	50% Ethanol	1.5	175
1,3-Bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)propane	MC	100% <i>tert</i> -Butanol	2.0	203
	M	65% Ethanol	1.3	195
1,1,5,5-Tetraacetoxypentane	MC	85% Ethanol	1.8	205

<sup>a</sup> Concentration of acetal applied was 0.76 mol/1000 g except where noted.

<sup>b</sup> Catalysts were: M, 2.0% MgCl<sub>2</sub>·6H<sub>2</sub>O; MC, 0.5% MgCl<sub>2</sub>·6H<sub>2</sub>O, and 0.5% citric acid.

<sup>c</sup> Concentration was 0.67 mol/1000 g.

active acetals but are derived from dialdehydes that cannot form a monomeric five- or six-membered ring, and they showed no more than a little reactivity. However, the linear acetals were more reactive than the cyclic acetals. Tetramethoxybutane and tetramethoxypentane reacted with magnesium chloride catalysis while dimethoxytetrahydrofuran and tetrahydropyran required the more active catalysis of magnesium chloride and citric acid. Although the two acetal groups needed to be in proximity for reaction with cellulose, the reaction apparently did not go through the ring structure.

**Influence of Alkoxy Group on the Reactivity of Acetals.** In Table II are the wrinkle recovery angles and durable press ratings obtained from acetals of succinaldehyde and glutaraldehyde containing different alkoxy groups. Solvents

TABLE III  
Application of 2,5-Dimethoxytetrahydrofuran from Different Solvents

Solvent, alcohol content <sup>a</sup>	Viscosity of solvent <sup>b</sup> (cP at 25°C)	Durable press rating	Wrinkle recovery angle (degrees, <i>w + f</i> )
Nil	0.89	3.6	265
50% Methanol	1.58	3.2	238
60% Methanol	—	2.8	232
100% Methanol	0.56	3.4	263
60% Isopropanol	3.03	2.3	199
100% Isopropanol	2.06	2.2	195

<sup>a</sup> Remainder of solvent was water. Catalyst was 0.5% MgCl<sub>2</sub>·6H<sub>2</sub>O and 0.5% citric acid.

<sup>b</sup> Viscosities were obtained from Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd ed., vol. 13, p. 371 and vol. 16, p. 565.

for application were alcohols or mixtures of alcohols and water, with the alcohol chosen to match the alkoxy group of the acetal. Where the same alkoxy group could not be used, the alcohol was of the same type—primary, secondary, or tertiary. In a few instances other alcohols were used also to allow use of an aqueous mixture or to demonstrate the effect of solvent.

In the tetrahydrofuran series reactivity increased in the order: methoxy, isopropoxy, *tert*-butoxy—that is, primary, secondary, tertiary. Differences, however, were small. Also, the solvent for application had an effect; the extent of crosslinking with the methoxy compound was less than obtained with application from water in Table I.

In the tetrahydropyran series the isopropoxy compound seemed less reactive than the methoxy or ethoxy compound. The effect of the solvent appeared to be strong here. Between the methoxy and the ethoxy compound there was little difference in reactivity.

In the tetraalkoxypentanes the methoxy compound showed a markedly greater reactivity than the ethoxy compound. The reactivity of tetramethoxypentane with application from a mixture of ethanol and water showed that this difference in reactivity was not an effect of solvent. This large difference in reactivity is surprising. It did not occur with the tetrahydropyrans and has not been explained.

Two glutaraldehyde acetals with cyclic alkoxy groups were tested. One was derived from a di-secondary glycol (2,3-butanediol), and the other from a di-tertiary glycol (2,3-dimethyl-2,3-butanediol). Both had little or no reactivity. The five-membered cyclic structure conferred enough stability that cleavage to react with cellulose did not occur.

Also tested was 1,1,5,5-tetraacetoxy-pentane as an example of an acylal from an aldehyde that gave reactive acetals. It showed no discernable reactivity.

**Influence of Solvent on Reactivity of Acetals.** It was noted that the reactivity of 2,5-dimethoxytetrahydrofuran was less when it was applied from methanol/water (Table II) than when it was applied from water (Table I). In Table III are the properties obtained from dimethoxytetrahydrofuran applied from a series of solvents. Reactivity from application in methanol about equaled the reactivity from application in water, but reactivity from application in a

TABLE IV  
Strength of Crosslinked Fabric

Crosslinking agent	Cure temperature (°C)	Durable press rating	Wrinkle recovery angle (degrees, $w + f$ )	Tear strength (g, $w$ )
1,1,4,4-Tetramethoxybutane, 14%	160	3.2	249	528
	140	3.2	229	600
	120	2.8	208	708
1,1,5,5-Tetramethoxypentane, 15%	160	3.3	246	504
	140	2.5	214	624
	120	2.5	203	712
Dimethyloldihydroxyethyleneurea, 4%	160	3.3	256	580
Dimethyloldihydroxyethyleneurea, 2%	160	3.0	248	632
(Untreated)	—	1.2	184	848

mixture of methanol and water was noticeably less. Reactivity from application in isopropanol or in a mixture of isopropanol and water was still less. Viscosities of the solvents are also included in Table III, and reactivity is seen to decrease as viscosity of the solvent for application increased. This relationship suggests that the penetration of acetal into the cotton fiber necessary for reaction is hindered by increasing viscosity of solvent.

The low reactivity of dimethoxytetrahydrofuran applied from isopropanol/water indicates that 2,5-diisopropoxytetrahydrofuran must have a high intrinsic or potential reactivity even though observed reactivity from this solvent is relatively low (Table II). Also, 2,6-diisopropoxytetrahydropyran should have a higher potential reactivity than indicated.

**Strength of Fabric Crosslinked with Acetals.** The data in Table IV showed that the loss of fabric strength on crosslinking with acetals was high when using the usual conditions of treatment—curing at 160°C with magnesium chloride catalyst. Comparison of data from treatments with acetals and with the conventional crosslinking agent dimethyloldihydroxyethyleneurea showed lower tear strength with the acetal treatment at the same wrinkle recovery angle.

Strength loss from treatment with acetals was closer to that experienced from treatment with aldehydes, such as formaldehyde or glutaraldehyde. The greater strength loss from treatment with aldehydes has been ascribed to greater acid degradation of cellulose than occurs in treatment with conventional agents, even though the same catalyst and curing conditions are used.<sup>13</sup> If acetals behave similarly, a more reactive acetal could be applied with less rigorous curing conditions and would cause less cellulose degradation and less loss of fabric strength. Therefore, 1,1,4,4-tetramethoxybutane and 1,1,5,5-tetramethoxypentane, the most active of the acetals examined, were applied with 2.0% magnesium chloride hexahydrate using progressively lower curing temperatures. The results, also in Table IV, showed that the wrinkle recovery angle and durable press rating of the fabric dropped rapidly as curing temperature was lowered. Even so, at a given performance level obtained with acetal and milder curing, tear strength was less than that obtained with a conventional agent.

For the data in Table IV concentrations of dimethyloldihydroxyethyleneurea were varied to get different wrinkle recovery angles and durable press ratings. The results, then, also demonstrate the low efficiency of the acetals as compared with the conventional crosslinking agent.

**Mechanism of Acetal Reactivity.** It was noted that all the reactive acetals were derived from aldehydes that were themselves reactive to cotton. In fact, the free aldehydes had greater reactivity.<sup>19</sup> This suggested that the acetals reacted by hydrolyzing to aldehydes in solution before application and that the free aldehydes were the reactive crosslinking agents. This concept was supported by the reactivity of 2,5-dimethoxytetrahydrofuran when applied with magnesium chloride and citric acid, which formed a pad solution of pH 2.5, and lack of reactivity when applied with magnesium chloride alone, from a pad solution of pH 5.0. The concept of hydrolysis to aldehydes was further supported when dimethoxytetrahydrofuran was applied with magnesium chloride at pH 2.5 and cured at 120°C to give 249° wrinkle recovery angle and 3.4 durable press rating. This showed a reactivity that was appreciable, if not to the level shown by the stronger catalyst.

Later work, however, indicated that hydrolysis of the acetal in the pad solution was not a general requirement for activity, if it was needed at all. The free aldehydes are reactive when applied at pH 5.0. However, part of the reactivity of 2,5-dimethoxytetrahydrofuran noted from application with magnesium chloride at pH 2.5 was lost when the solution for application was adjusted to pH 5.0 after standing at pH 2.5. Fabric impregnated with the readjusted solution of dimethoxytetrahydrofuran and cured at 160°C had 236° wrinkle recovery angle and 3.0 durable press rating. Dimethoxytetrahydrofuran, as well as some other acetals, were reactive when applied from methanol in which hydrolysis could not occur. Dimethoxymethane showed little reactivity when applied with magnesium chloride and citric acid although hydrolysis should lead to formaldehyde, a reactive aldehyde. Further, 1,1,5,5-tetramethoxypentane was examined by PMR spectroscopy after standing in CD<sub>3</sub>OD/water solution with the 2,2-dimethyl-2-silapentane-5-sulfonate standard at pH 8 and at pH 3 for 0.5 h, and it showed no sign of hydrolysis. No signal from aldehydic hydrogen ap-

TABLE V  
Acid Hydrolysis of Crosslink Finishes

Crosslinking agent	Catalyst <sup>a</sup>	Solvent	Wrinkle recovery angles (degrees, <i>w + f</i> )		
			Original	After <sup>b</sup> 0.1N HCl	After 0.5N HCl
2,5-Dimethoxytetrahydrofuran, 10%	MC	water	272	203	189
	MC	methanol	263	206	185
1,1,4,4-Tetramethoxybutane, 14%	M	water	249	190	197
	M	methanol	257	192	186
Glutaraldehyde, 8%	M	water	264	224	190
	MC	water	275	230	184
Dimethyloldihydroxyethyleneurea, 12%	M	water	283	267	236
Dimethyloldihydroxyethyleneurea, 4%	M	water	253	230	212

<sup>a</sup> Catalysts are: M, 2.0% MgCl<sub>2</sub>·6H<sub>2</sub>O; MC, 0.5% MgCl<sub>2</sub>·6H<sub>2</sub>O, and 0.5% citric acid.

<sup>b</sup> Hydrolyses were in hydrochloric acid at 40°C for 30 min.

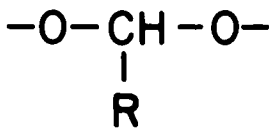


Fig. 1. Crosslink from aldehydes.

peared at 8–10 ppm, and there was no signal from methoxy of methanol appearing near the signal from methoxy of the acetal.

Although it was concluded that hydrolysis of acetal to aldehyde in the pad solution was not a major factor in determining reactivity, hydrolysis on the fabric during drying is not excluded. Indeed, an acetal must cleave sometime in order to react with cellulose, although the cleavage is not necessarily hydrolytical.

**Resistance of Acetal Finishes to Acidic Hydrolysis.** To obtain some clue to the structure of the finish from acetals on cotton, the resistance of acetal finishes to hydrolysis by acid was compared with the acid resistance of other crosslinking finishes. Properties of crosslinked fabric were determined before and after hydrolysis in 0.1*N* and 0.5*N* hydrochloric acid for 30 min at 40°C. Results are shown in Table V.

The data showed that the acid resistance of finishes from 2,5-dimethoxytetrahydrofuran and from 1,1,4,4-tetramethoxybutane was less than the acid resistance of finishes from dimethyloldihydroxyethyleneurea, a conventional nitrogenous agent, and from glutaraldehyde. This showed most clearly in results from hydrolysis with 0.1*N* acid. Neither catalyst nor solvent for application had a noticeable influence on hydrolysis resistance. It should be noted in the comparison of agents that dimethyloldihydroxyethyleneurea gives a finish with high resistance to acid. Finishes from acetals will have greater acid resistance than finishes from most other nitrogenous agents.<sup>20</sup>

The hydrolysis data indicated that the acetals formed crosslinks with a structure different from that formed by glutaraldehyde. It has been claimed that aldehydes, whether monoaldehydes or dialdehydes, form methylene crosslinks with a substituent group on those from aldehydes other than formaldehyde.<sup>21</sup> This structure is shown in Figure 1. Because all reactive acetals are derived from dialdehydes and the less reactive ring structure is not likely in the crosslink, it is suggested that the acetals form crosslinks with a carbon chain between sites of reaction with cellulose. The proposed structure is shown in Figure 2.

## SUMMARY AND CONCLUSIONS

Acetals that were effective crosslinking agents for cellulose in cotton were derived from dialdehydes that can form five-membered tetrahydrofuran or six-membered tetrahydropyran rings, such as succinaldehyde and glutaral-

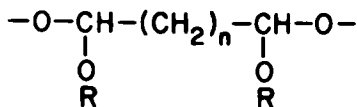


Fig. 2. Proposed crosslink from acetals.

dehyde. These aldehydes themselves are reactive to cotton. Formals are not reactive. Even though formals are derived from a reactive aldehyde, formaldehyde, they cannot form a monomeric ring.

The reactive acetals, however, do not react with cellulose primarily through formation of a free aldehyde. The acetals form crosslinks with a different structure than those formed by aldehydes. And, although two acetal groups must be in proximity for reaction, the reaction does not proceed through the ring structure. Linear tetraalkoxy acetals from the same aldehydes were more reactive than the cyclic dialkoxo acetals and reacted under milder conditions of treatment. Therefore, a linear polymethylene structure is suggested for the crosslink from an acetal, in contrast to the substituted monomethylene structure that has been proposed for the crosslink from aldehydes.

Reactivity of acetals varied with the alkoxy group and increased in the order: primary, secondary, tertiary. However, cyclic alkoxy groups were inert. The effect of the alkoxy group was small and often hidden by the effect of solvent. Many of the acetals were insoluble in water, and the higher viscosity of alcohol or alcohol/water solvents decreased reactivity. Among the glutaraldehyde acetals, the tetramethyl acetal was much more reactive than the tetraethyl acetal. Even the most reactive acetal, however, was less reactive than a conventional crosslinking agent, such as dimethyloldihydroxyethyleneurea.

Acetal crosslinking agents gave lower fabric strength than a conventional methylolamide crosslinking agent at the same wrinkle recovery angle. The reason is believed to be that the reaction conditions required by the low reactivity of even the most reactive acetal did more chemical damage to the cotton than the milder conditions required by the more reactive conventional agents.

The authors thank R. S. Richard and other members of the Cotton Quality Control Unit of the Center for physical testing of fabric, J. E. Helfrich for assistance in laboratory procedures, and N. L. Meadow for drawings of the figures. Mention of companies or commercial products does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

## References

1. H. B. Goldstein, "New Developments in the Technology of Cellulose and Its Derivatives, A. Durable-Press Treatments," in *Cellulose and Cellulose Derivatives, Part V*, N. M. Bikales and L. Segal, Eds., Wiley-Interscience, New York, 1971, p. 1101.
2. G. C. Tesoro and J. J. Willard, "Crosslinked Cellulose," in *Cellulose and Cellulose Derivatives, Part V*, N. M. Bikales and L. Segal, Eds., Wiley-Interscience, New York, 1971, p. 838.
3. J. F. Walker and S. E. Kokowicz, U.S. Pat. 2,548,455 (1951).
4. American Association of Textile Chemists and Colorists, *Technical Manual*, Vol. 57, Research Triangle Park, N.C., 1981-1982.
5. E. Schmitz, *Angew. Chem.*, **68**, 375 (1956); *Chem. Abstr.*, **51**, 12854 (1957).
6. M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, **73**, 1884 (1951).
7. A. Kankaanpera and K. Miiki, *Acta Chem. Scand.*, **23**, 1471 (1969).
8. A. Kirrmann, *Ann. Chim.*, [10], **11**, 223 (1929); *Chem. Abstr.*, **24**, 337 (1930).
9. R. I. Longley, Jr., W. S. Emerson, and T. S. Shafer, *J. Am. Chem. Soc.*, **74**, 2012 (1952).
10. S. M. Makin, V. M. Likhosherstov, and M. I. Berezhnaya, *Zh. Org. Khim.*, **3**(8), 1419 (1967); *Chem. Abstr.*, **67**, 116787 (1967).
11. W. E. Thiele, U.S. Pat. 2,695,318 (1951).
12. E. Kobayashi and A. Yasawa, *Yakugaku Zasshi*, **82**, 451 (1962); *Chem. Abstr.*, **58**, 4552 (1963).
13. J. G. Frick, Jr., B. A. K. Andrews, and J. D. Reid, *Text. Res. J.*, **30**, 495 (1960).

14. J. L. Gardon, *J. Appl. Polym. Sci.*, **5**, 734 (1961).
15. J. L. Gardon and R. Steele, *Text. Res. J.*, **31**, 160 (1961).
16. S. P. Rowland and A. W. Post, *J. Appl. Polym. Sci.*, **10**, 1751 (1966).
17. R. R. Benerito, *Text. Res. J.*, **38**, 279 (1968).
18. A. G. Pierce, Jr., and J. G. Frick, Jr., *Am. Dyestuff Rep.*, **57**(22), 47 (1968).
19. J. G. Frick, Jr., and R. J. Harper, Jr., *J. Appl. Polym. Sci.*, **27**, 983 (1982).
20. J. G. Frick, Jr. and G. A. Gautreaux, *Text. Bull.*, **94**(10), 77 (1968).
21. M. D. Hurwitz and L. E. Colon, *Text. Res. J.*, **28**, 257 (1958).

Received July 29, 1983

Accepted September 28, 1983