

## Crosslinking of Cotton in the Presence of Poly(vinyl Alcohol). Analysis and Composition of Products

B. A. KOTTES ANDREWS and J. G. FRICK, JR., *Southern Regional Research Laboratory, Southern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

### Synopsis

The spectrophotometric method developed by Finley for the determination of poly(vinyl alcohol) in paper coatings has been adapted for analysis of cotton fabrics crosslinked with finishes containing a poly(vinyl alcohol) additive. The effect of time and pH of hydrolysis on the analysis, and the dependency of the durability of the poly(vinyl alcohol) on the crosslinking agent are established. Evidence of chemical attachment to the cellulose of the cotton fiber through the crosslinking agent is offered.

### INTRODUCTION

The use of poly(vinyl alcohol) (PVOH) as a hand-building additive to crosslinking treatments for cotton textiles parallels the history of crease-proofing itself.<sup>1</sup> In the durable-press finishing of knitted cotton fabric, PVOH was found to contribute not only to the hand of the fabric, but also to an improvement in dimensional stability, sharpness of pressed-in crease, and resistance to flat abrasion.<sup>2</sup>

To gain an insight into the effect of PVOH on the finished fabric, the chemistry of its attachment to the cellulose of the cotton fiber was investigated. The spectrophotometric method developed by Finley<sup>3</sup> for analyzing PVOH in paper coatings was adapted for use in analyzing PVOH in the presence of nitrogenous crosslinking agents. The stable, colored complex that PVOH forms with iodine in the presence of boric acid and the absorption maximum of this green complex at 690 m $\mu$  is the basis for this method.

### MATERIALS, TESTS, AND ANALYSES

The fabric used in this study was a 5.2 oz/yd<sup>2</sup> cotton jersey of 25 wales and 34 courses per inch, having a ktk, tkt pattern and knit from 20/1 combed peeler yarn.

Fifty per cent aqueous solutions of N,N'-bis(hydroxymethyl)imidazolidinone-2 and N,N'-bis(methoxymethyl)urea were obtained from com-

mercial sources; methyl bis(hydroxymethyl)carbamate was prepared by the reaction in aqueous solution of commercially obtained methyl carbamate with formaldehyde from reagent-grade formalin as described by Reid, Reinhardt, and Bruno.<sup>4</sup> Inorganic salts were reagent-grade chemicals.

The poly(vinyl alcohol) (PVOH) additive to the crosslinking treatment, of low acetyl content and low molecular weight (approx. 14,000), was obtained from commercial sources.

The following physical tests were used in this study:

Durable-press ratings were determined by comparison with plastic replicas described in AATCC Tentative Test Method 124-1967.<sup>5</sup>

Bursting strength was determined using a Diaphragm Bursting Apparatus, Method 5122, Federal Test Methods Standard No. 191.

Stiffness was determined by a Directional Stiffness Cantilever Bending Apparatus, Method 5202, Federal Test Methods Standard No. 191.

Poly(vinyl alcohol) contents of the hydrolyzates, extracted from treated fabrics, were determined by the spectrophotometric technique of Finley.<sup>3</sup> Nitrogen content of the cloth samples was determined by the Kjeldahl method. Formaldehyde content was determined by the chromotropic acid method of Roff<sup>6</sup> after distillation of formaldehyde from weighed fabric specimens refluxed in 200 ml of 5% sulfuric acid containing 10 g sodium sulfate and simultaneously distilled until 160 ml of the distillate was collected

## EXPERIMENTAL AND RESULTS

### Finishing Procedures

Samples of the knitted cotton were impregnated with 3% poly(vinyl alcohol) (PVOH) and the three crosslinking agents in the following concentrations: 5% N,N'-bis(hydroxymethyl)imidazolidinone-2 (DMEU), 5% N,N'-bis(methoxymethyl)urea (BMMU), and 7% methyl bis(hydroxymethyl)carbamate (DMMC). Catalyst for DMEU and BMMU was magnesium chloride hexahydrate, 30% of agent weight. Catalyst for DMMC was zinc nitrate hexahydrate, 12% of agent weight. Both catalysts produce similar reactions in fabric finishing.

After the impregnation step, the wet fabrics were extended 4% in each direction, on pin frames, dried at 70°C for 10 min, and cured at 160°C for 3 min in mechanical convection ovens. Physical properties and chemical analyses were obtained from fabrics washed once in an automatic washing machine followed by tumble drying. The comparative efficiencies of the agents in binding the PVOH to the cellulose are shown in Table I. The DMEU and BMMU crosslinking agents are more efficient than DMMC in binding PVOH. Fifty per cent more PVOH is bound through treatments with DMEU and BMMU than with DMMC at the levels of treatment used in this study.

The textile properties of these fabrics are shown in Table II. There is the usual inverse relationship between dimensional stability and bursting strength that is produced by crosslink finishing of cotton cellulose. Dur-

TABLE I  
Chemical Properties of Finished Fabrics Before Hydrolysis

Treating bath	PVOH, %	HCHO, %	Nitrogen, %
DMEU	0.00	1.49	1.03
DMEU-PVOH	2.75	1.68	1.05
BMMU	0.00	2.46	1.03
BMMU-PVOH	2.70	2.51	1.00
DMMC	0.00	2.38	0.78
DMMC-PVOH	1.92	2.34	0.69

TABLE II  
Textile Properties of Finished Fabrics Before Hydrolysis

Treating bath	Durable-press rating	Burst. str., psi	Stiffness $W$ , $\times 10^{-4}$ -in. lb.	Shrinkage $W$ , %
Untreated	1.7	94	2.2	16.0
DMEU	4.0	56	2.2	3.5
DMEU-PVOH	3.6	54	4.0	2.0
BMMU	3.9	49	2.2	6.5
BMMU-PVOH	3.0	49	2.8	4.2
DMMC	4.2	46	2.5	4.2
DMMC-PVOH	3.4	56	3.2	3.2

able-press ratings are increased by the finishing treatments; fabric stiffness is increased only by the treatments containing PVOH.

### Hydrolytic Removal of Finishes

One-gram fabric samples were hydrolyzed at pH 2, 4, 7, and 10 in stoppered 250-ml Erlenmeyer flasks using buffer mixtures reported by Clark and Lubs.<sup>7</sup> A pH of 1 was obtained with 1*N* HCl; a pH of 14, with 1*N* sodium hydroxide. The samples were hydrolyzed at 80°C for the indicated times using a 50:1 ratio of buffer solution to sample. After hydrolysis of each sample, the hydrolyzate was washed with distilled water into a 1-liter volumetric flask along with several distilled water washings from the hydrolyzed sample. The hydrolyzate and combined washings were diluted to 1 liter with distilled water. Poly(vinyl alcohol) content was determined on 20-ml aliquots transferred to 50-ml volumetric flasks.

### Influence of Crosslinking Agent and pH of Hydrolyzate on PVOH Analysis

The presence of hydrolyzed crosslinking agent and the pH of the hydrolyzate were examined to determine whether these variables affected the accuracy of the PVOH determination. A 10% stock solution was prepared by dissolving 10.00 g PVOH in 90.00 g H<sub>2</sub>O. To 3% solutions diluted from the 10% stock solution was added 1 g of fabric crosslinked with the three finishing agents. The fabric samples in the presence of the aliquots of PVOH of known concentration were then hydrolyzed at pH 2 for 30 min at

80°C. In all cases the differences in PVOH content of the hydrolyzates were within experimental error ( $\pm 0.03\%$ ).

Aliquots of known PVOH content were added to 20 ml of buffer solutions of the pH's used in this study. Analysis of these aliquots for PVOH were within experimental error of the calculated value. The presence of starch on the fabric does, however, affect the accuracy of the PVOH analysis.<sup>3</sup>

### Effect of Crosslinking Agent on Durability of PVOH in Cotton

Figure 1 compares the resistance to hydrolytic removal at 80°C of PVOH applied to cotton with the three finishing agents. A sample treated with 3% PVOH alone was included in the study. The PVOH in the DMMC-PVOH finish was extremely stable to both acid and alkali hydrolysis. The BMMU-PVOH finish was the only one from which the PVOH was removed by alkali. The sensitivity of PVOH to removal by acid hydrolysis, however, was greater in the DMEU-PVOH finish. The PVOH applied alone showed poor resistance to both acid and alkali.

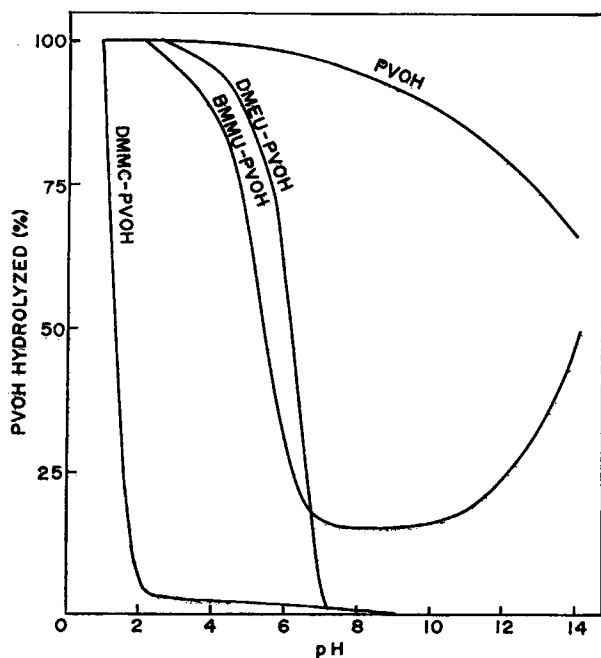


Fig. 1. Effect of pH on 30 min hydrolysis at 80°C.

### Time of Hydrolysis

A sample of knitted fabric was treated with 5% DMEU-3% PVOH to produce a fabric with 2.75% bound PVOH. The fabric was divided into several specimens which were subjected to hydrolysis at pH 2, 4, and 7 for times ranging from 5 to 30 min. The results of these hydrolyses are shown

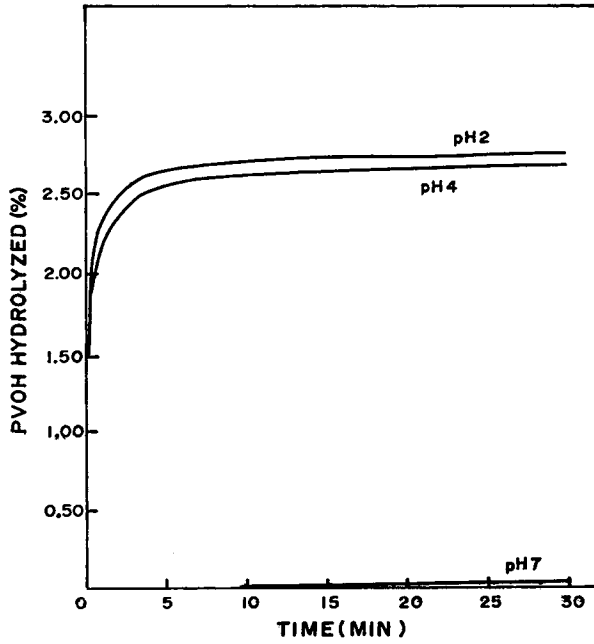


Fig. 2. Hydrolysis of DMEU—PVOH finish at 80°C; removed PVOH expressed as per cent of fabric weight.

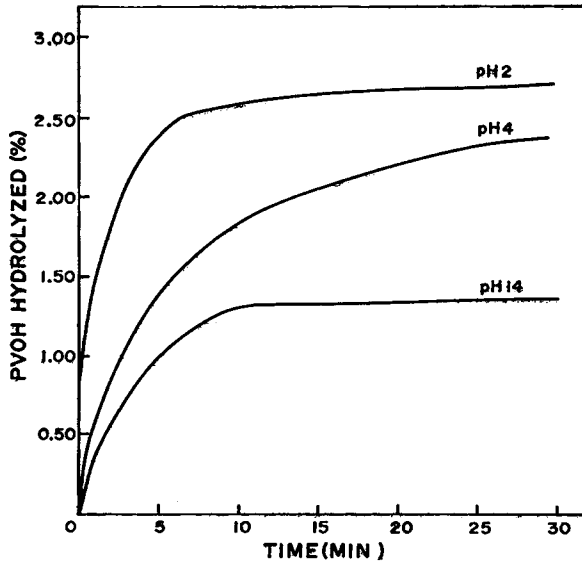


Fig. 3. Hydrolysis of BMMU—PVOH finish at 80°C; removed PVOH expressed as per cent of fabric weight.

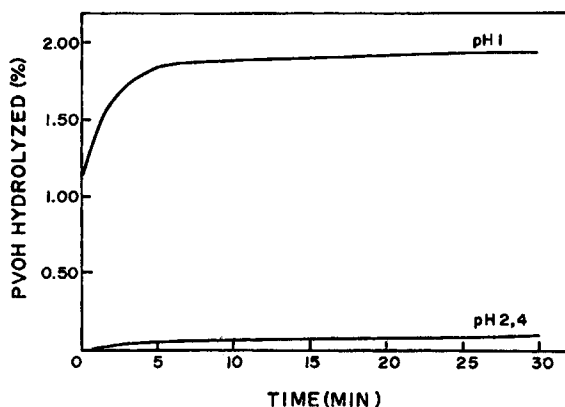


Fig. 4. Hydrolysis of DMMC-PVOH finish at 80°C; removed PVOH expressed as per cent of fabric weight.

in Figure 2. Most of the hydrolysis occurred within the first 5 min at both pH 2 and 4, with the initial rates the same at both.

A similar relationship between time and extent of hydrolysis for fabric treated with 5% BMMU-3% PVOH is shown in Figure 3. The initial concentration of PVOH was 2.70%. At pH 2 and 14, the maximum PVOH hydrolyzed was approached within the first 10 min. The rate of hydrolysis at pH 4 was much slower.

A sample treated with 7% DMMC-3% PVOH, the most stable of the systems studied, had an initial PVOH content of 1.92%. The results of hydrolysis of portions of this sample at pH 1, 2, and 4 for times of 5 to 30 min are shown in Figure 4. Only at pH 1 did appreciable hydrolysis occur. Again, the maximum hydrolysis was approached within the first 10 min.

In all systems where the hydrogen ion concentration was sufficient to totally remove the finish, hydrolysis was complete after 20 min.

## DISCUSSION

It has been established by other workers that poly(vinyl alcohol) in paper coatings can be accurately determined. The fact that the determination of known quantities of PVOH is unaffected by the presence of hydrolyzed crosslinking agent residues led to an investigation of the behavior of PVOH during both acid and alkali hydrolysis of finishes containing a nitrogenous crosslinking agent and PVOH on cotton. A formaldehyde-PVOH finish was not included because formaldehyde alone does not attach PVOH to cotton to any great extent. Possibly the formaldehyde reacts preferentially with PVOH to form cyclic formals.

The order of resistance to hydrolysis for the 2-imidazolidinone, urea, and carbamate classes of finishing agents was established previously,<sup>8,9</sup> and each exhibited differing resistance to both acid and alkali. In this study, the DMEU finish showed poor acid stability and excellent alkali stability,



The acid hydrolysis of the methylamido ether of cellulose (II) proceeds via a carbonium ion mechanism as proposed by Reeves, Vail, and Frick.<sup>13</sup> A similar mechanistic scheme is followed for hydrolysis of the etherified PVOH (I). This mechanism is essentially the reverse reaction of those shown above for the etherifications.

The mechanism for alkali hydrolysis of the methylamido ether of cellulose also has been previously proposed,<sup>8</sup> and the hydrolysis of the etherified PVOH follows a similar mechanism.

For the determination of PVOH it is important to choose a pH and digestion time for the hydrolysis step of the PVOH analysis which completely removes the nitrogenous crosslinking agent, because, as mentioned above, the hydrolysis resistance of the PVOH in a creaseproofing finish is dependent on the ease of hydrolysis of the crosslinking agent. For the three classes of agents studied in this investigation, a digestion time of 20 min would be adequate, although 30 min would not affect the subsequent PVOH analysis.

### SUMMARY

A method has been developed for determining PVOH in cotton fabric finished from crosslinking baths containing both a nitrogenous crosslinking agent and PVOH. The method uses the spectrophotometric determination of Finley on hydrolyzates obtained from acid digestion of the finished fabrics. The hydrolyzing bath must have a pH at which the nitrogenous finish is completely removed.

The stability of the PVOH to hydrolysis is dependent on the stability of the nitrogenous finish. A mechanism for this dependency is proposed. The PVOH is etherified by an N-methylol (or N-methoxymethyl) group of the nitrogenous crosslinking agent. Another N-methylol group may also react to form an amidomethyl ether of cellulose. For N,N'-bis(hydroxymethyl)imidazolidinone-2 and N,N'-bis(methoxymethyl)urea, pH 2 must be attained before complete hydrolysis of the finish occurs; for methyl bis(hydroxymethyl)carbamate, pH 1 must be reached. Complete hydrolysis with all finishes occurs in 20 min at 80°C. The pH of the digesting bath does not affect subsequent analysis of the hydrolyzate.

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### References

1. M. D. Hurwitz, *Text. Res. J.*, **27**, 267 (1957).
2. B. A. K. Andrews, J. G. Frick, Jr., and J. D. Reid, *The Knitter*, **33**, 26, 28, 30 (1969).
3. J. H. Finley, *Anal. Chem.*, **33**, 1925 (1961).
4. J. D. Reid, R. M. Reinhardt, and J. S. Bruno, *Amer. Dyestuff Reprtr.*, **54** (13), 54 (1965).



5. Amer. Assoc. Textile Chemists and Colorists, *AATCC Technical Manual*, **46**, (1970).
6. W. J. Roff, *Text. Inst.*, **47**, T308 (1956).
7. N. A. Lange, Ed., *Handbook of Chemistry*, 5th ed., McGraw-Hill, New York, 1944.
8. B. A. K. Andrews, R. L. Arceneaux, J. G. Frick, Jr., and J. D. Reid, *Text. Res. J.*, **32**, 489 (1962).
9. R. L. Arceneaux, J. G. Frick, Jr., J. D. Reid, and G. A. Gautreaux, *Amer. Dyestuff Repr.*, **50**(22), 37 (1961).
10. C. M. Welch, *Text. Res. J.*, **33**, 165 (1963).
11. J. T. Lofton, R. J. Harper, H. W. Little, and E. J. Blanchard, *Text. Ind.*, **134**(1), 56 (1970).
12. R. J. Harper, E. J. Blanchard, and M. J. Donoghue, *Amer. Dyestuff Repr.*, **59**(13), 15 (1970).
13. W. A. Reeves, S. L. Vail, and J. G. Frick, Jr., *Text. Res. J.*, **32**, 305 (1962).

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