

# Reagent Residues on *N*-Methylolpyrrolidone-Treated Cotton

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## Synopsis

Residues remaining after drying and curing cotton fabric with either sodium bisulfate or zinc nitrate and *N*-methylolpyrrolidone, a monofunctional model durable press agent, have been quantitated by high performance liquid chromatography. The residues were identified as pyrrolidone, *N*-methylolpyrrolidone, *N,N'*-methylene-bis-2-pyrrolidone, and *N,N'*-(oxydimethylene)bis-2-pyrrolidone. The two catalysts fixed approximately the same amount of the *N*-methylolpyrrolidone to cellulose, but generated different ratios of the extractable residues. A comparison of the levels of these residues that are capable of releasing formaldehyde is given. The dominant residue from the NaHSO<sub>4</sub> treatment was *N*-methylolpyrrolidone, while zinc nitrate generated more *N,N'*-(oxydimethylene)bis-2-pyrrolidone.

## INTRODUCTION

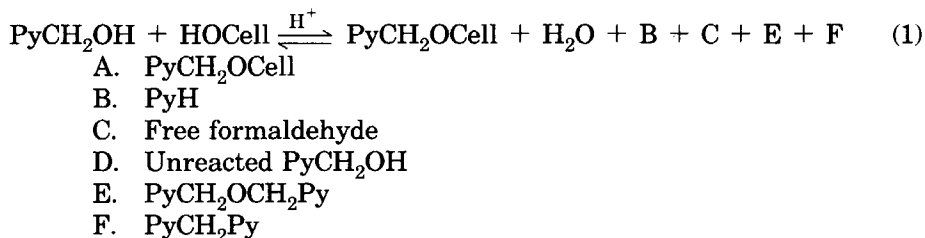
Factors that influence the release of formaldehyde from durable press treated cotton have been investigated in many studies.<sup>1-3</sup> In the preceding paper,<sup>1</sup> we have discussed the effects of various reagent residues on formaldehyde release from cotton fabric treated with *N*-methylolpyrrolidone, a monofunctional model durable press resin. The purpose of that research was to determine how various reagent residues, including catalyst, monofunctional resin, and byproducts generated in the curing step, influence the amount of formaldehyde released from the resin treated fabric. In this paper we report both the identity and the amount of the pyrrolidone residues generated during the curing process.

*N*-Methylolpyrrolidone (PyCH<sub>2</sub>OH; Py =  $\overline{\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}}$ ) was selected as a model because it is a monofunctional compound that provides an unambiguous finish for use in formaldehyde release studies. Since PyCH<sub>2</sub>OH is monofunctional, it cannot impart durable press (DP) characteristics, but it should provide some insight into the behavior of the more complex di- and polyfunctional agents. PyCH<sub>2</sub>OH was applied to cotton fabric, dried, and cured, and the residues on the fabric determined qualitatively and quantitatively by high performance liquid chromatography

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(HPLC). The acid-catalyzed curing step, depicted in eq. (1), could generate products and residues as shown below:



Compounds B, D, E, and F can be quantified by HPLC. Free formaldehyde was shown<sup>1</sup> by low temperature titration to be present at the 10 ppm level. HPLC cannot be used for this determination because the water:methanol (70:30) solution of formaldehyde has a refractive index very close to that of the solvent itself. Therefore, the response factor for formaldehyde is low and this amount (10 ppm) is not registered by the RI detector. Product A represents the fixed reactant and is not extractable.

## EXPERIMENTAL

### Materials

Cotton printcloth (80 × 80, Testfabrics #400, 113 g/m<sup>2</sup>, bleached) was scoured with 2 g/L AATCC detergent, rinsed with water, washed with 0.3% acetic acid, rinsed thoroughly, and dried. All water used was ultrapure as a result of being softened and passed through a reverse-osmosis system followed by total ion removal, charcoal filtration, and final filtration through a submicron filter.

Sodium bisulfate monohydrate (Baker) was Analytical Reagent grade. 2-Pyrrolidone (Aldrich) was distilled under vacuum through a Vigreux column prior to use. Paraformaldehyde, zinc nitrate hexahydrate, and *p*-toluenesulfonic acid monohydrate were from Matheson, Coleman, and Bell. Pure *N*-methylolpyrrolidone (D) was prepared by a modification of the method of Scheuerl.<sup>4</sup> 2-Pyrrolidone (B) (3.74 mol) and KOH (3.6 g) were mixed in a 600-mL beaker. Paraformaldehyde (3.74 mol) was added and the temperature kept at 80°C for 15 min. The pH was adjusted to 7 with concd HCl and the melt poured into a large Pyrex pan. Recrystallization of the crude product from benzene gave pure (D) as shown by IR, HPLC, and melting point (82–83°C).

*N,N'*-Methylene-bis-2-pyrrolidone (F) was prepared from a modified literature procedure<sup>5</sup> by stirring B (0.8 mol), paraformaldehyde (0.47 mol), and concd HCl (16 drops) at 70°C for 19 h. The product was fractionally distilled under vacuum without further workup. The product melted at 72–73°C and was pure by IR, <sup>1</sup>H NMR, and HPLC.

*N,N'*-(Oxydimethylene)bis-2-pyrrolidone (E) is a new compound. The synthesis, from D and *p*-toluenesulfonic acid, and its properties will be reported in a later publication. Its boiling point was 167–169°C at 0.15–0.20 mm. Spectral (IR, <sup>1</sup>H, <sup>13</sup>C, and mass) characteristics and elemental analysis con-

firmed the structural assignment. The most interesting property of this ether was the ease with which it decomposed to C and F in the presence of an acid.

### Fabric Treatment

Pad baths were prepared by diluting 4.50 g of PyCH<sub>2</sub>OH and 0.20 g of NaHSO<sub>4</sub> · H<sub>2</sub>O [or 0.25 g of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O] to 50.0 g with water. Samples were padded (squeezed between pressure rolls) to 80% wet pickup and then either dried at room temperature or at 60°C for 7 min. Some of the samples dried at 60°C were cured at 160°C for 3 min in a convection oven. All samples were conditioned (65% RH and 21°C) for at least 18 h and then milled. The samples were extracted as previously described<sup>6</sup> using water:methanol (70:30, v/v) as the solvent. Extracts were analyzed directly by HPLC as described later. Nitrogen analyses were by the micro-Kjeldahl method.

### Liquid Chromatography and Calculations

An Adsorbosphere C<sub>18</sub>, 5 μm column (250 × 4.6 mm) was used with a pellicular C<sub>18</sub> guard column. The mobile phase was 70:30 (v:v) water:methanol pumped at 1.0 mL/min by a Constametric I pump. The differential refractometer was thermostated by circulating water at 31°C. Peak heights in the chromatograms were determined manually. Molar response factors relative to PyCH<sub>2</sub>OH were determined using pure materials and peak heights were corrected accordingly. From the corrected peak heights ( $p_c$ ), molar amounts of the components of the mixture were calculated by multiplying with the slope ( $m$ ) (determined by linear regression) of a peak height ( $x$ -axis) vs. the concentration ( $y$ -axis) calibration curve for PyCH<sub>2</sub>OH. Division of the resulting concentration by the weight (ca. 200 mg weighed to the nearest 0.1 mg) of the conditioned sample ( $w$ ) gave units (μmol/mg) of fabric for the reagent residues.

$$\mu\text{mol/mg} = (p_c \times m)/w$$

The calibration curve was run just prior to the analytical runs. Retention times for D, B, F, and E residues were 178, 188, 235, and 305 s, respectively. Detection limits for these compounds (D, B, E, and F) under the described conditions were 0.0037, 0.0057, 0.0032, and 0.0037 μmol/mg, respectively. These limits in mg/L (ppm) are 8, 10, 14, and 13, respectively.

The amount of PyCH<sub>2</sub>OH (μmol/mg) ( $\mu_A$ ) fixed to the cellulose was calculated from the following formula:

$$\mu_A = (\%N \times 10)/14$$

where %N is the percent nitrogen in the sample (from Kjeldahl determination), 14 is the atomic weight of nitrogen, and 10 is the conversion factor to give units (μmol/mg). The amount of PyCH<sub>2</sub>OH initially applied ( $T$ ) was calculated (μmol/mg) using the following formula:

$$T = \mu_A + \mu_B + \mu_D + 2\mu_E + 2\mu_F$$

where  $\mu_X$  represents mol compound  $X$ /mg fabric. Since compounds E and F each contain two Py units, these concentrations were multiplied by two to correlate  $T$  with the amount of starting D. The calculated total ( $T$ ) agreed with the value obtained from the determination of nitrogen content of the unextracted fabric. The amount of each residue as a percent of the initially applied  $\text{PyCH}_2\text{OH}$  ( $T$ ) was then calculated as follows:

$$\%X = (\%X \times 100)/T$$

## RESULTS AND DISCUSSION

Two sets of preliminary experiments were run to determine the effects of drying conditions on the residues. Table I shows the results of these experiments.

It can be concluded from these data that only the Brønsted acid,  $\text{NaHSO}_4$ , lowers the energy of activation sufficiently to catalyze the generation of the ether (E) when drying is effected at ambient temperature.

The second experiment was designed to determine the effect of drying and curing conditions on evaporation of pyrrolidone. Fabric was padded with a solution (0.592 g of  $\text{PyH}$ /50 mL of  $\text{H}_2\text{O}$ ), dried at room temperature and  $60^\circ\text{C}$ , and cured at  $160^\circ\text{C}$  as described in the Experimental section. The residual  $\text{PyH}$  from the two dried samples was identical (as determined by HPLC) to that found on the cured sample. Certainly some  $\text{PyH}$  may have been volatilized by the curing conditions, but that small a change was not detectable by this HPLC method. The other residues are less volatile than  $\text{PyH}$  and should not be appreciably volatilized during the treatment.

For the actual resin application, cotton fabric was given a pad-dry-cure treatment with a catalyst and  $\text{PyCH}_2\text{OH}$ . The catalysts used were  $\text{NaHSO}_4$ , a Brønsted acid, and  $\text{Zn}(\text{NO}_3)_2$ , a Lewis acid. Table II shows the results of the experiments in which the residues, after curing, were extracted and quantitated by HPLC. Even though the data reported in Table II are from a single run, the experiments were carried out earlier in duplicate at a lower (7.4% vs. 9.0%) concentration of  $\text{PyCH}_2\text{OH}$  and give similar, but correspondingly smaller, amounts of residues. The  $\text{Zn}(\text{NO}_3)_2$  treated fabric gave 0.505 and 0.485  $\mu\text{mol}/\text{mg}$   $\text{PyCH}_2\text{OH}$  in duplicate runs at 7.4% com-

TABLE I  
Effects of Drying Conditions on Residues<sup>a</sup>

Condition	A	B	D	E	F
Dried at RT, <sup>b</sup> no catalyst	—	—	100	—	—
Dried at $60^\circ\text{C}$ , <sup>b</sup> no catalyst	—	—	100	—	—
Dried at RT, <sup>c</sup> $\text{NaHSO}_4$	—	—	84	16	—
Dried at RT, <sup>b</sup> $\text{Zn}(\text{NO}_3)_2$	—	—	100	—	—

<sup>a</sup> Expressed as a % of initial  $\text{PyCH}_2\text{OH}$  applied.

<sup>b</sup> Pad bath was 7.4% (w/w)  $\text{PyCH}_2\text{OH}$ .

<sup>c</sup> Pad bath was 9.0% (w/w)  $\text{PyCH}_2\text{OH}$ .

TABLE II  
 Residues as Percentage of Initial PyCH<sub>2</sub>OH Applied

Sample	Catalyst	A	B	D	E	F	T <sup>c</sup>
Dried <sup>a</sup>	NaHSO <sub>4</sub>	12	0	71	17	0	0.65
Cured <sup>b</sup>	NaHSO <sub>4</sub>	81	0	12	4	3	0.59
Dried <sup>a</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	1	0	99	0	0	0.61
Cured <sup>b</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	80	4	3	10	3	0.58

<sup>a</sup> 60°C for 7 min.

<sup>b</sup> 160°C for 3 min.

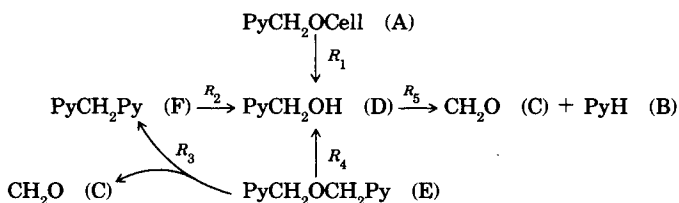
<sup>c</sup> Initial PyCH<sub>2</sub>OH applied, μmol/mg. A, B, D, E, and F are reported as % of T. In the case of E and F, the actual molar quantities were multiplied by 2 before calculation of % because they (E and F) were obtained from two molecules of PyCH<sub>2</sub>OH.

pared to 0.600 for a single run at 9%. Thus, the amount of PyCH<sub>2</sub>OH extracted increased in the same proportion as the increase in PyCH<sub>2</sub>OH applied. As expected, the precision of the amounts of residues that were extracted at higher concentrations was better than that observed at levels that were near the limits of detection. The data from the higher concentration run (9%) are reported here to be consistent with the procedures reported in the previous work.<sup>1</sup>

It is apparent from the data in Table II that the two catalysts exert some different and some similar effects on the nature and amounts of the residues.

During curing, 81% of PyCH<sub>2</sub>OH is fixed on cellulose in the presence of NaHSO<sub>4</sub> and 80% in the presence of Zn(NO<sub>3</sub>)<sub>2</sub>. Thus, the efficiencies of NaHSO<sub>4</sub> and Zn(NO<sub>3</sub>)<sub>2</sub> (at these concentrations) in catalyzing the cellulose-PyCH<sub>2</sub>OH reaction at 160°C are the same. The extractable residues capable of releasing formaldehyde (D, E, and F) are only slightly smaller on the Zn(NO<sub>3</sub>)<sub>2</sub> treated fabric than on the fabric treated with NaHSO<sub>4</sub>. Residual PyCH<sub>2</sub>OH is significantly higher with NaHSO<sub>4</sub> than with Zn(NO<sub>3</sub>)<sub>2</sub>, while Zn(NO<sub>3</sub>)<sub>2</sub> leaves more B and E. Both catalysts generate the same amount of F, which, as previously noted,<sup>1</sup> decreases the amount of formaldehyde released.

The modes by which each of these residues releases formaldehyde warrant further discussion. The actual formaldehyde donors are PyCH<sub>2</sub>OH and PyCH<sub>2</sub>OCH<sub>2</sub>Py. The byproducts of formaldehyde release from these two species are PyH and PyCH<sub>2</sub>Py, respectively, as shown in the following scheme:



The hydrolysis of PyCH<sub>2</sub>Py (R<sub>2</sub>) is highly unlikely either under the curing or formaldehyde release test conditions. Hydrolysis of PyCH<sub>2</sub>OCell is assumed to proceed via C—O cleavage (R<sub>1</sub>) to give cellulose and PyCH<sub>2</sub>OH. This is followed by C—N cleavage (R<sub>5</sub>) during demethylation to yield for-

maldehyde and PyH. This suggested sequence is supported by the works of Vail<sup>7</sup> and Petersen.<sup>8</sup>

The other route ( $R_3$ ) to formaldehyde involves decomposition of the ether (E). Fragmentation of E to formaldehyde and F was quite facile under certain conditions, e.g., standing at room temperature in the presence of *p*-toluenesulfonic acid, chromatography on silica gel, and distillation, if all acid is not removed. This is strange behavior for an ether (an acetal here), but in this case it is not entirely unexpected since protonation of the oxygen would generate a neutral leaving group (PyCH<sub>2</sub>OH) and a resonance stabilized carbonium-immonium ion (PyCH<sub>2</sub><sup>+</sup>). That this process occurs readily, even in the nonstabilizing environment of a mass spectrometer, is evidenced by the production of PyCH<sub>2</sub><sup>+</sup> ion as the base peak in the mass spectrum of E. The fact that E is generated with NaHSO<sub>4</sub> at room temperature and at 60°C, but does not decompose to F, indicates that the cellulose may be inhibiting the reaction under these mild conditions.

In addition to E, both B and F are generated during curing at 160°C. Residue F can arise from the decomposition of E or by nucleophilic attack of B on the conjugate acid of D (PyCH<sub>2</sub>OH<sub>2</sub><sup>+</sup>). This, as well as the previously mentioned detection limits, may account for the absence of PyH on the NaHSO<sub>4</sub>-cured fabric, i.e., the PyH may have been scavenged by D to form F. The loss of E during curing of the bisulfate sample may be due to formation of some F, but since the residual F is significantly smaller, most of the PyCH<sub>2</sub><sup>+</sup> is probably reacting with cellulose to give A.

Since the total of the residues capable of releasing formaldehyde (A, D, E, and F) on NaHSO<sub>4</sub>- and Zn(NO<sub>3</sub>)<sub>2</sub>-cured fabrics is not significantly different, the difference in formaldehyde release from these fabrics must be due to other factors, such as the following: 1. pH of the pad baths (see Tables V and VI in Ref. 1).

2. Inhibitory effect of Zn(NO<sub>3</sub>)<sub>2</sub> (see Tables V and VI in Ref. 1.)

3. Extent of formaldehyde release from PyCH<sub>2</sub>OH and PyCH<sub>2</sub>OCH<sub>2</sub>Py, the dominant extractable residues on the NaHSO<sub>4</sub>- and Zn(NO<sub>3</sub>)<sub>2</sub>-cured fabrics, respectively.

## CONCLUSIONS

Cotton fabric was treated with catalyst [NaHSO<sub>4</sub> or Zn(NO<sub>3</sub>)<sub>2</sub>] and *N*-methylolpyrrolidone, a monofunctional model durable press agent, and the nature and amount of residues on the dried and cured fabrics were determined by HPLC. When cured on cotton fabric and NaHSO<sub>4</sub>, PyCH<sub>2</sub>OH leaves residues in the order (molar quantities) PyCH<sub>2</sub>OH > PyCH<sub>2</sub>Py ~ PyCH<sub>2</sub>OCH<sub>2</sub>Py, while Zn(NO<sub>3</sub>)<sub>2</sub> leaves residues in the order PyCH<sub>2</sub>OCH<sub>2</sub>Py > PyH ~ PyCH<sub>2</sub>OH ~ PyCH<sub>2</sub>Py. The amount of residues most likely to release formaldehyde (PyCH<sub>2</sub>OH and PyCH<sub>2</sub>OCH<sub>2</sub>Py) was slightly higher on the NaHSO<sub>4</sub>-treated fabric than on the Zn(NO<sub>3</sub>)<sub>2</sub>-treated fabric. The efficiency of fixation of the resin during curing was the same for both catalysts, but the ratio of the residues was different.

Work of a similar nature on dimethyloldihydroxyethyleneurea, a commonly used durable press agent, is in progress.

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