Formaldehyde Release from a Model *N*-Methylol System

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Synopsis

A model *N*-methylol reactant system based on pyrrolidone derivatives has been used to study the chemical factors that control formaldehyde release. Fabric samples of known composition were prepared from chemically pure reactants and formaldehyde release was determined by the AATCC Sealed Jar Test. This work provides support for prior suggestions and a more direct approach for understanding unexpected results from tests on post- and precure fabrics. In addition, new findings demonstrate that the *N*-methylol reactant, its byproducts, and pure zinc nitrate are capable of reducing the level of formaldehyde release.

INTRODUCTION

Although much research has been performed on the topic of formaldehyde release from resin-treated cellulosic fabrics,[1] very little effort has been directed toward release from a clearly defined unambiguous substrate. The di- and polyfunctional urea, cyclic urea, or carbamate reactant systems, which have been used for most formaldehyde release studies, do not produce such a clearly defined substrate. These reactants are capable of crosslinking cellulose, polymerization, incomplete attachment to cellulose, and/or a number of other possibilities made even more complicated by release of formaldehyde during the finishing process. Further, unknown inorganic compounds are strongly bound to a finished fabric when metal salts are used as curing catalysts.[2] Therefore, studies[3] to determine the source of formaldehyde from the various groups in the finish have had to rely on estimates of those sources because of an inability to describe the composition of the finish or catalyst residues on the treated fabric.

In this research we have sought to avoid this problem by using an *N*-methylol reactant and catalyst system that would produce an unambiguous finish with no catalyst residues after laundering. Pure samples of various reagents were added to that treated laundered fabric to give a well-defined substrate for evaluation for formaldehyde release. *N*-Methylolpyrrolidone was selected for this study. The products expected from an acid-catalyzed pad-dry-cure treatment are as follows ($\text{Py} = -\underline{\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}}{=}\text{O}$):

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$$\mathrm{PyCH_2OH + CellOH \xrightleftharpoons{H^+} PyCH_2OCell + H_2O} \quad (1)$$

A. $CellOCH_2Py$
B. PyH
C. Free Formaldehyde
D. Unreacted $PyCH_2OH$
E. $PyCH_2OCH_2Py$
F. $PyCH_2Py$

No other products are expected to form, and this was verified by the identification of the solvent (water–methanol) extractable products from the cured fabrics.[4] Products A, C, D, E, and F are potential sources of formaldehyde release. The oxydimethylene ether, E, has been shown to decompose in the presence of mild acids to produce C and F.[5] Because of difficulties inherent in the Sealed Jar Test, overall trends are emphasized in the discussions, rather than small differences in individual samples.

EXPERIMENTAL

Materials

N-Methylolpyrrolidone, *N*-methyoxymethylpyrrolidone, *N*-isopropoxymethylpyrrolidone, and *N,N'*-methylenebispyrrolidone were prepared in 99% or greater purity using known synthetic procedures (see Table I for properties). An aqueous solution containing these compounds is easily prepared, and these solutions are stable except in those experiments involving sodium bisulfate as catalyst. Examination of solutions and aqueous extracts from fabrics that had been padded and dried with these solutions established that the above methoxy and isopropoxy ethers were essentially completely hydrolyzed during the pad-dry procedures using sodium bisulfate. The method used for this examination has been described previously[6] and involves

TABLE I
Properties of Pyrrolidone Derivatives

Compound	Melting or boiling point	Nitrogen analysis		NMR[a] (ppm)
		Calcd	Found	
$Py\underline{CH_2}OH$	80.5–82.6°C (lit.[b] 83–84°C)	12.17	12.00	4.77
$Py\overline{CH_2}O\underline{CH_3}$	79°C at 4 mm Hg (lit.[c] 225°C)	10.85	10.78	3.31
$PyCH_2OCH(\underline{CH_3})_2$	87–88°C at 0.8 mm Hg	8.90	8.72	1.10,1.20
$Py\underline{CH_2}Py$	72–73°C (lit.[d] 73–74°C)	—	—	4.75

[a] Positions of peaks are given in ppm downfield from an internal reference in deuterium oxide (*N*-methylol and *N*-methoxymethyl derivatives) and in $CDCl_3$ (*N*-isopropoxymethyl and *N,N'*-methylenebis derivatives) for the protons underlined under the heading Compound, using a 60-MHz instrument.

[b] H. Böhme, G. Driesen, and D. Schünemann, *Arch. Pharm.*, **294**, 344 (1961); *Chem. Abstr.*, **55**, 22335h (1962).

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examination of the pad bath contents and extracts of residues from the dried fabric using nuclear magnetic resonance. A similar, more thorough study using high performance liquid chromatography is reported in the accompanying paper.[4] Other chemicals used were reagent grade.

Fabric Treatment and Methods

The fabric was an all-cotton, 80 × 80 printcloth that had been desized, scoured, and bleached. One roll of fabric was used for the entire study, and it was stored in a formaldehyde-free area. Fabrics were treated by immersing precut samples in the pad bath, passing through a squeeze roller, drying, and curing on pin frames. As noted in the text, the curing step was occasionally omitted. Drying conditions were 5–7 min at 60°C; curing was performed at 160°C for 3 min. Some fabrics were washed immediately after curing, while others were used in experiments prior to washing. Washing was done in a domestic machine.

$CellOCH_2Py$ was prepared by padding (immersion followed by squeeze roll treatment) the cotton fabric with a solution (pad bath) containing 9% $PyCH_2OH$ and 0.4% sodium bisulfate (pH = 2.1), followed by drying and curing. Fabrics were laundered to remove reactant and catalyst residues and the ratio of total formaldehyde to nitrogen was 1:1. Nitrogen content, by the traditional macro-Kjeldahl method, of laundered fabrics varied slightly, but was generally 0.66–0.68%. This is considered to be a "pure" $CellOCH_2Py$ finish [see eq. (1)].

Free formaldehyde contents of randomly selected fabrics were obtained in the early phases of the work. Untreated fabrics and the fabric with the "pure" $CellOCH_2Py$ finish were found to possess about 10 ppm free formaldehyde by the cold sodium sulfite–iodine method. The method is not accurate for a value this low.[3] However, these data indicate that free formaldehyde is not contributing significantly to the formaldehyde that is released. Formaldehyde-release values were determined by AATCC Test Method 112-1978 (Sealed Jar Method). Values obtained from this method are subject to a number of variables that are difficult to control.[7] All percentages are by weight. Additional details are provided in the tables or as needed in this article.

RESULTS AND DISCUSSION

Tables II–VI provide results from experiments designed to establish trends developed in formaldehyde release from a model reactant system based on *N*-methylolpyrrolidone. The pyrrolidone moiety was used because it is a monofunctional reagent that should result in the formation of

TABLE II
Formaldehyde Release from Fabrics Cured with $PyCH_2OH$

	Formaldehyde release (ppm)	
Cure catalyst	Unwashed	Washed
1. 0.4% $NaHSO_4$	332	38
2. 0.5% $Zn(NO_3)_2 \cdot 6H_2O$	197	34

TABLE III

Formaldehyde Release for Cotton Fabrics with Selected Additives[a]

Formaldehyde source	Catalyst		
	None	$Zn(NO_3)_2$	$NaHSO_4$
1. 2% $PyCH_2OH$	—	—	104
2. 4% $PyCH_2OH$	—	—	146
3. 6% $PyCH_2OH$	229	102	214
4. 6.8% $PyCH_2OCH_3$	22	32	[b]
5. 8.2% $PyCH_2OCH(CH_3)_2$	14	2	[b]
6. 9.5% $PyCH_2Py$	15	29	10

[a] Pyrrolidone derivative and catalyst padded on cotton fabric and dried only. Catalyst concentrations were 0.5% $Zn(NO_3)_2 \cdot 6H_2O$ and 0.4% sodium bisulfate. Similar concentrations of additives were used for experiments discussed in Table V.

[b] These alkoxymethylpyrrolidones hydrolyzed (pH 2) in the presence of sodium bisulfate during padding and drying of the fabric. Therefore, the data were not recorded.

a smaller number of reaction products than a di- or polyfunctional finish. In addition, the pyrrolidone finish possesses a resistance to acid hydrolysis that is similar to currently used durable press finishes[8,9] and, as a result, should be a suitable model for investigating variables that influence formaldehyde release. Therefore, it is expected that the results in this work will be applicable to similar reactant systems involving carbamates and urea–glyoxal finishes.

Cure catalysts were limited to sodium bisulfate (a Brønsted acid) and zinc nitrate (a Lewis acid). Table II demonstrates that sodium bisulfate develops a higher level of formaldehyde release as compared to zinc nitrate. Part of the formaldehyde released from the unwashed fabrics is also due to deposits of $PyCH_2OCH_2Py$ and $PyCH_2OH$ on the fabric.[4] Washing the fabric reduces the level to a low 34–38 ppm formaldehyde release.

$PyCH_2OH$ is relatively stable and resists demethylolation (loss of formaldehyde) under thermal conditions used to cure *N*-methylol reagents.[10] No kinetic data are available on the demethylolation of $PyCH_2OH$, and studies[11,12] on other *N*-methylol compounds generally indicate that the reaction is catalyzed by acid or base. As noted previously, the hydrolysis of $CellOCH_2Py$ to $PyCH_2OH$ [see eq. (1)—reverse reaction] is acid-catalyzed. Thus, it is not unexpected that the more acidic catalyst (sodium bisulfate) developed the higher level of formaldehyde release. Similar results have

TABLE IV

Effect of Addition of $PyCH_2OH$ to $CellOCH_2Py$ on Formaldehyde Release

Additive[a]	Formaldehyde release (ppm)
1. 2% $PyCH_2OH$	100
2. 4% $PyCH_2OH$	161
3. 6% $PyCH_2OH$	201
4. 0.4% $NaHSO_4$	283
5. 2% $PyCH_2OH$ + 0.4% $NaHSO_4$	320
6. 4% $PyCH_2OH$ + 0.4% $NaHSO_4$	336
7. 6% $PyCH_2OH$ + 0.4% $NaHSO_4$	332

[a] These additives were padded on pure $CellOCH_2Py$ and the fabrics were dried prior to determination of formaldehyde release.

TABLE V
Formaldehyde Release from Pure CellOCH$_2$Py Plus Various Additives

Pad bath properties			
Additive[a]	Amount, (%)[b]	pH	Formaldehyde release (ppm)
1. Water only	—	5.6	29
2. NaHSO$_4$(A)	0.4	2.0	283
3. Zn(NO$_3$)$_2$ · 6H$_2$O(B)	0.5	5.5	23
4. PyCH$_2$OH	6.0	6.3	149
5. PyCH$_2$OH + A		2.1	316
6. PyCH$_2$OH + B		6.1	56
7. PyCH$_2$OCH$_3$	6.8	6.0	26
8. PyCH$_2$OCH$_3$ + B		5.0	24
9. PyCH$_2$OCH(CH$_3$)$_2$	8.2	4.8	0
10. PyCH$_2$OCH(CH$_3$)$_2$ + B		4.8	0
11. PyCH$_2$Py	9.5	3.4[c]	0
12. PyCH$_2$Py + A		2.1	120
13. PyCH$_2$Py + B		3.4	0

[a] A pad bath containing the following additives applied to a laundered fabric finished with PyCH$_2$OH. See Experimental for details.

[b] Amounts correspond to additives listed in the first column, e.g., pad bath contained 9.5% PyCH$_2$Py and 0.5% Zn(NO$_3$)$_2$ · 6H$_2$O for run No. 13. The pyrrolidones are present in equimolar amounts.

[c] The pH of the solution of PyCH$_2$Py indicates that some acid has been carried along with this compound during its purification by distillation. This attraction for acids by PyCH$_2$Py supports the acid scavenging effect suggested in the paper. This type of acid entrainment has been previously observed in our laboratories.

been obtained from other studies[13-15] involving various catalyst systems with conventional crosslinking agents, but the nature of the catalyst residues was essentially ignored.

The additives used in this part of the study were applied, by padding and drying only, to untreated cotton fabric to determine their formaldehyde release properties in the absence of a finish, i.e., CellOCH$_2$Py. The data in Table III show that in the presence of NaHSO$_4$ the amount of released formaldehyde increased as the level of PyCH$_2$OH increased. Further, at the application level of 6% PyCH$_2$OH, the amount of formaldehyde release is about the same in the presence of NaHSO$_4$ as in the absence of catalyst, but a reduction in the amount of formaldehyde release is noted when zinc nitrate is present. There is little or no formaldehyde release from PyCH$_2$OCH$_3$ and PyCH$_2$OCH(CH$_3$)$_2$ in the absence of catalyst or in the presence of zinc nitrate. The alkoxy derivatives hydrolyzed under the conditions of sample preparation with sodium bisulfate (pH 2), and no data are recorded. There is little or no formaldehyde release from PyCH$_2$Py under any of the conditions studied.

The additives examined in Table III are examined further in Tables IV–VI wherein they are added to the "pure" CellOCH$_2$Py finish. However, in the studies based on application of the additives to pure cotton fabric (Table III) several important trends are noted. The acidic conditions developed by sodium bisulfate readily hydrolyzed the alkoxymethylpyrrolidones, but the acid conditions developed by sodium bisulfate did not accelerate the release of formaldehyde from PyCH$_2$OH (see experiment 3, Table III). Further, zinc

TABLE VI
Effect of pH and Zinc Nitrate Concentration on Formaldehyde Release from Pure $CellOCH_2Py$[a]

% $PyCH_2OH$[b]	% Zinc nitrate[b]	pH	Formaldehyde release (ppm)[c]
6	0	7.4	491
6	0.25	6.4	263
6	0.50	6.45	231
0	0.50	2.15[d]	445
0	0.50	6.2	10

[a] This portion of the study was conducted at Purdue University. Water used in these experiments was deionized and ultrapure, whereas the water used in the SRRC studies was distilled and gave a slightly lower pH.

[b] A pad bath containing $PyCH_2OH$ and/or Zinc nitrate was applied to a laundered fabric finished with $PyCH_2OH$. The padded fabrics were dried at 60°C for 7 min and conditioned for 24 h before measuring formaldehyde release.

[c] These values are higher than the corresponding data from SRRC (Table V). Previous studies (Ref. 7) have shown that interlaboratory variations in formaldehyde release values may be large. One significant contributor to these variations may be the oven used in the test. A direct comparison of data from this table to the other tables cannot be made.

[d] pH adjusted with 0.2*N* HCl.

nitrate did not accelerate formaldehyde release; its presence reduced formaldehyde release.

Since we are concerned with establishing trends for formaldehyde release due to several selected factors, trials were made to determine levels of additives on $CellOCH_2Py$ needed to obtain meaningful results. Data in Table IV show the formaldehyde released by treatment of the base fabric ($CellOCH_2Py$) with 2%, 4%, and 6% $PyCH_2OH$ and 2%, 4%, and 6% $PyCH_2OH$ plus 0.4% sodium bisulfate. In the absence of catalyst, the amount of released formaldehyde increased as the level of $PyCH_2OH$ increased, and the rate of increase was not directly proportional to the concentration of the added $PyCH_2OH$. In the presence of bisulfate the amount of formaldehyde release increased (relative to experiments 1–3) but was similar for all levels of added $PyCH_2OH$. With only $NaHSO_4$ (experiment 4) present, the only source of formaldehyde release is the finish ($CellOCH_2Py$). As $PyCH_2OH$ is added to the $NaHSO_4$ + $CellOCH_2Py$ system (experiments 5–7), the formaldehyde release from the $PyCH_2OH$ should increase (see Table III, experiments 1–3) while formaldehyde release from the $CellOCH_2Py$ should decrease proportionately giving the observed leveling effect. Apparently, $NaHSO_4$, with either $CellOCH_2Py$ or $CellOCH_2Py$ + $PyCH_2OH$, is capable of catalyzing the release of only about 330 ppm of formaldehyde. The reasons for this puzzling leveling effect are not immediately apparent, but the effect is reproducible (see also experiment 1, Table II and experiments 2 and 5, Table V).

Data in Table V are similar to those shown in Table IV, except additional variables are included. In Table V, experiments 1–3, a fabric containing the pure $CellOCH_2Py$ finish was padded (and then dried) in deionized water, bisulfate catalyst, and zinc nitrate catalyst solutions, respectively. The bisulfate catalyst produced a large increase in formaldehyde release whereas the zinc nitrate produced no increase. The large increase in formaldehyde release with bisulfate is due to its greater acidity (pH 2 with bisulfate as against 5.5 with zinc nitrate). The larger the H^+ ion concentration, the greater is the hydrolysis of the ether linkage in $CellOCH_2Py$ generating $PyCH_2OH$. The acid-catalyzed rupture of the N—C linkage in $PyCH_2OH$ to give PyH and formaldehyde does not appear to be a significant factor. This hypothesis was confirmed in a separate experiment in which the pH of the zinc nitrate bath was brought down from 6.2 to 2.15 with 0.2*N* HCl. $CellOCH_2Py$ was padded with this solution, dried, and conditioned. A similar treatment was given with the zinc nitrate solution at pH 6.2. Formaldehyde release on both these samples was measured and the data obtained as shown in Table VI. The sample treated with zinc nitrate solution at pH 2.15 gives a formaldehyde release of 445 ppm compared to a release of 10 ppm from the sample treated with zinc nitrate solution at pH 6.2. This shows that pH of the pad bath has a very strong influence on formaldehyde release from $CellOCH_2Py$.

In experiments 4–6 (Table V), $PyCH_2OH$ was added to the pad bath and catalysts were the same as in experiments 1–3. A significant increase of formaldehyde release due to the added $PyCH_2OH$ is noted (compare experiments 1 and 4), but the increase due to added $PyCH_2OH$ in the presence of the catalysts (compare experiments 2 and 5 and also 3 and 6) is surprisingly small. A comparison of the values in experiments 4 and 6 again suggests that zinc nitrate is inhibiting formaldehyde release.

This inhibiting effect of zinc nitrate was further confirmed by data in Table V. $CellOCH_2Py$ samples were padded with solutions containing 6% $PyCH_2OH$ and 0%, 0.25%, and 0.5% zinc nitrate, dried, and conditioned. Formaldehyde release from those samples was measured, and the data obtained are shown in Table VI. Formaldehyde release values of 491, 263, and 231 ppm were obtained at zinc nitrate concentrations of 0%, 0.25%, and 0.5% respectively. Note that only overall trends in the data can be utilized. Single samples in Table VI cannot be compared to single samples in other tables.

This decrease in formaldehyde release with increase in zinc nitrate concentration can be explained by assuming the formation of a complex between $PyCH_2OH$ and zinc nitrate. As the concentration of zinc nitrate is increased, more $PyCH_2OH$ is tied up in the form of this complex and is not readily available as a source of formaldehyde, thus leading to the decrease in formaldehyde release.

The exact chemical composition and structure of this complex is unknown. Previously reported structure determinations of complexes of *N*-methylol compounds and metal salts, usually based on infrared spectral data, have been questioned and found to be subject to error.[16] Indisputable evidence based on single crystal X-ray structure determinations of complexes of *N*-methylol compounds and metals has not been published because of the difficulties in isolating an appropriate crystalline material.

The catalyst residue from the cure of *N*-methylolpyrrolidone and zinc nitrate does not appear to be "pure" zinc nitrate. The formaldehyde release from the sample cured with zinc nitrate (see Table II) is much greater than similar fabrics described in Table III and V. No explanation for this observation can be provided from this work.

Experiments 7–10 in Table V involving the ethers, further confirm the well-established fact that capping of *N*-methylol agents reduced formaldehyde release (compare to experiment 4 and also to data in Table III). These results also support the previous conclusion that zinc nitrate does not enhance formaldehyde release.

Methylenebisamides are generally difficult to hydrolyze, and therefore $PyCH_2Py$ was not expected to release formaldehyde. Examination of formaldehyde release data in experiments 11–13 suggests that the $PyCH_2Py$ is acting as an acid acceptor and the lower release values (compare experiment 12 to experiment 2) are due to this effect. Perhaps this acid scavenging action by *N*-methylol compounds and derivatives is the primary reason that some post-cure and undercured fabrics have unexpected low levels of formaldehyde release when considering the chemical constitution of the system.

Further, it is expected that the interaction of the curing catalysts with the fabric could have an effect upon the level of formaldehyde release. Wool or nylon containing fabrics should have an acid scavenging action which could result in lower formaldehyde release when compared to similar cellulosic or polyester fabrics. We believe that further research of this type with well-defined reactants is desirable. This work has established that even a pure monofunctional, *N*-methylol reactant system in the presence of cotton cellulose undergoes chemical changes during padding, drying, and curing. Thus, studies based on impure polyfunctional reactants are subject to numerous unknown variables involving catalyst and reactants.

CONCLUSIONS

A study of a well-defined, model *N*-methylol reactant system with regard to formaldehyde release has provided strong evidence to support some prior suggestions regarding the source of, or reasons for, the amount of formaldehyde released in the AATCC Sealed Jar Method. In addition, the study demonstrates that unreacted reagent does not release formaldehyde at a rate directly proportional to the concentration of the material. Low release values may be due to an acid scavenging effect from a Lewis base present in the system, e.g., $PyCH_2Py$. Also, increasing the acidity of the treated fabric by lowering the pH of the pad bath increases the formaldehyde release from fabric finished with *N*-methylolpyrrolidone. On the other hand, increases in zinc nitrate concentration on the fabric inhibits the formaldehyde release from such fabrics. Formation of a complex between zinc nitrate and $PyCH_2OH$, the actual formaldehyde donor, may be the reason for this inhibiting effect. Under the test conditions studied release of formaldehyde from $PyCH_2OH$ was not accelerated by lowering the pH of the system.

The observations and conclusions from this model system are now being used to study formaldehyde release from fabric treated with *N,N'*-dimethylol-4,5-dihydroxyethyleneurea.

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