

Influence of Reagent Residues and Catalysts on Formaldehyde Release from DMDHEU-Treated Cotton*

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Synopsis

Observations and conclusions drawn from a model *N*-methylol reactant system have been used to study formaldehyde release from cotton fabric treated with *N,N'*-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). Reagent residues produced by DMDHEU in the presence of sodium bisulfate or zinc nitrate were found to be more complex than those formed from the *N*-methylolpyrrolidone (NMP) reactant system, and the exact nature of some of the residues from DMDHEU could not be established. Zinc nitrate produces higher fixation of DMDHEU on cotton as compared to sodium bisulfate and also reduces formaldehyde release. As is the case with the NMP system, the lower amount of formaldehyde release with zinc nitrate catalyst is believed to be at least partially due to the formation of a complex between the *N*-methylol reactant, DMDHEU, and zinc nitrate. The C—OCell bonds in both finishes resist acid-catalyzed cleavage but cleavage of the N—C bonds in *N*-methylol groups (to release formaldehyde) in the presence of acid is greater for the DMDHEU system than for the NMP system. Results with the DMDHEU and NMP systems are similar, but because of the complex nature of the products formed in the DMDHEU system it is very difficult to correlate formaldehyde release with specific chemical structures of residues or reactants.

INTRODUCTION

The release of formaldehyde from cellulosic fabrics treated with *N*-methylol agents has been the subject of many publications. Because of the complex nature of most reactant systems used for durable press finishing, our efforts to precisely determine the source of formaldehyde from these treatments have involved the study of a model reactant system based on *N*-methylolpyrrolidone (NMP).¹⁻⁴ The NMP reactant system produced a "pure" finish,³ i.e., a cellulose derivative of known structure, and reagent residues on the fabric were extracted, identified, and their influence on the extent of formaldehyde release determined.^{1,2,4}

In a continuation of this work, *N,N'*-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) was applied to cotton fabric in exactly the same manner as the NMP. Both NMP and DMDHEU were applied to cotton fabric in presence of

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two different catalysts: (a) sodium bisulfate (a Brønsted acid) and (b) zinc nitrate (a Lewis acid). The reagent residues and formaldehyde release from these treated fabrics were investigated.

EXPERIMENTAL

Materials

Materials. Cotton printcloth (Testfabrics #400, 113 g/m², bleached) was scoured with 2 g/L AATCC detergent, rinsed with water, washed with 0.3% acetic acid, rinsed thoroughly, and dried. Deionized, ultrapure water was used in this study. Paraformaldehyde contained 95% formaldehyde and was used without purification. Sodium bisulfate monohydrate and zinc nitrate hexahydrate were analytical reagent grade.

HPLC Analysis

An Adsorbosphere C₁₈, 5 μm column (250 × 4.6 mm ID) was used with a C₁₈ pellicular guard column. Mobile phase was pure water pumped at a flow rate of 1.0 mL/min. Solutions were injected using a 20 μL loop. The differential refractometer was thermostated by circulating water at 31°C.

DMDHEU (0.5M, for the calibration curve) solution was prepared as follows: paraformaldehyde (95%) (0.395 g, 12.5 mM) was mixed with 2–3 mL of deionized water in a 10 mL vial. Two drops of saturated sodium carbonate solution were added and the mixture stirred for 10–15 min at 35–40°C until a clear solution was obtained (the vial was covered with a clean spherical glass marble to prevent the escape of free formaldehyde). The solution was cooled to room temperature, and 0.59 g (5 mM) of dihydroxyethyleneurea (DHEU), recrystallized twice from methanol, was added to the vial. The pH of the solution was 8.5 10 min after complete dissolution of DHEU. The solution was stirred at room temperature for about 2 h at which time the methylation was complete (as indicated by the absence of DHEU and its monomethylated derivative, MMDHEU, in the HPLC analysis). The pH of the solution was reduced to 5.0 using 2% HCl because it was previously determined that DMDHEU is more stable under mildly acidic conditions than neutral or alkaline conditions.⁵ The solution was then transferred to a 10-mL volumetric flask with a disposable pipet. The vial was rinsed 3 times with 0.2–0.3 mL of deionized water, and the rinses were transferred to the volumetric flask. The solution in the volumetric flask was diluted to volume using deionized water. This solution was stable up to 2 weeks. Aliquots of this stock solution were used to obtain a calibration curve by HPLC. Regression analysis of these data gave equations from which unknown concentrations of DMDHEU could be determined.

One of the compounds generated during the finishing process with DMDHEU could not be synthesized and isolated in a pure form, as all attempts to do so failed. However, the retention time for this compound matched perfectly (as determined by coinjection) with that of one of the components (dimer) in commercial samples of DMDHEU. NMR data (C¹³ decoupled and off-resonance spectra) for this component (collected from preparative HPLC) show features that partially support the structure of a

dimer of DMDHEU. The nature of the linkage between the two dihydroxyimidazolidinone rings may be an oxydimethylene group, but the data are inconclusive. However, this structure will be assumed in the present study for determination of molar concentrations. DMDHEU and MMDHEU (as indicated by HPLC) were the other compounds obtained on the finished fabrics.

From HPLC analysis, the amounts of these compounds on fabrics were determined using the following equation:

$$\mu M \text{ of compound/g of fabric} = a \times s \times \text{RF}/w$$

where a is the peak area of the compound being quantitated,⁵ s is the slope (from regression analysis) of the concentration ($\mu M/10 \text{ mL}$) (y -axis) vs. peak area (x -axis) calibration curve for DMDHEU, RF is the molar response factor for the compound relative to DMDHEU, and w is the weight of the conditioned sample.

The molar response factor (RF) for MMDHEU relative to DMDHEU was shown to be equal to the molecular weight ratio of DMDHEU to MMDHEU. The molar response factor for the dimer relative to DMDHEU was obtained using the following equation:

$$(\text{RF})_{\text{molar}} = (\text{RF})_{\text{weight}} \times 178/M$$

where, $(\text{RF})_{\text{weight}}$ is the weight response factor (determined on a sample collected by preparative HPLC from a commercial sample of DMDHEU) for the dimer relative to DMDHEU (1.59), 178 is the molecular weight of DMDHEU, and M is the molecular weight of the dimer (338, assuming the above-mentioned structure). Thus, the molar response factor for the dimer was 0.84.

The total amount of extracted residues (A) as analyzed by HPLC and expressed in terms of μM of DMDHEU/g of fabric was calculated as follows:

$$A = (\text{MMDHEU}) + (\text{DMDHEU}) + 2(\text{dimer})$$

where the concentrations of the residues analyzed by HPLC are shown by the residues in parenthesis. Since the dimer is composed of two molecules of DMDHEU, its concentration was multiplied by 2 to obtain the correct value of A .

Fabric Treatment

DMDHEU for fabric treatment was prepared as follows: Paraformaldehyde (4.2 g) (133 mM) and 2 drops of 20% w/v sodium hydroxide were added to about 45 mL water and the mixture warmed slightly until the paraformaldehyde completely dissolved (about 15–20 min). The solution was cooled to room temperature. The pH of this solution was 9.5. DHEU (5.9 g) (50 mM) was added to this solution, and the solution allowed to stir for about 90 min for complete methylation. The pH of the solution was 8.2 at this stage. It was adjusted to pH 5.0 with 0.5N HCl and diluted with water to 67 mL in a 100-mL graduated cylinder. This solution was 13.28% w/v DMDHEU. Using 15 mL of this solution (which contained 2 g DMDHEU), 25 g pad-baths

containing 8% DMDHEU and 0.4% sodium bisulfate (100 mg) or 0.5% zinc nitrate hexahydrate (125 mg) were prepared. Two sets of fabric samples were padded from each of these pad-baths at about 83% wet pick-up and then dried at 60°C for 7 min. One of the two sets was cured in a convection oven at 160°C for 3 min. A portion of this set was washed after curing. The second set was analyzed as the dried but uncured sample. All samples were conditioned at 65% RH and 21°C for 18 h and then extracted⁵ for analysis by HPLC. Nitrogen content of extracts and extracted fabrics was determined by micro Kjeldahl method. For extracts, 5 mL (out of a 10 mL extract) was taken for nitrogen determination. The titer obtained was multiplied by 2 to get the reading for the entire extract (10 mL).

Thus, the amount of extractable residues was obtained not only from HPLC analysis, but also from nitrogen analysis of extracts. From nitrogen contents, (% N), the amount of residues in extracts (*B*) and extracted fabrics (*C*), expressed in terms of μM of DMDHEU/g of fabric, were obtained as follows:

$$\mu M \text{ residues as DMDHEU/g of fabric} = \% N \times 10,000/28$$

where 10,000 is a conversion factor and 28 is 2 times the atomic weight of nitrogen.

Formaldehyde release from these DMDHEU treated samples was measured by the AATCC Sealed Jar Method 112-1978 using Nash reagent.

RESULTS AND DISCUSSION

Formaldehyde Release. The fabrics that were given a pad-dry-cure treatment with 8% DMDHEU in presence of either 0.4% sodium bisulfate or 0.5% zinc nitrate were conditioned and then tested for formaldehyde release. The data obtained are given in Table 1. The data include formaldehyde release values for both unwashed and washed samples. When these data are compared with similar data from NMP,¹ three inferences can be drawn:

(i) For all samples, DMDHEU gives much higher formaldehyde release than NMP. Considering that there are 2 mol formaldehyde/mol DMDHEU as compared to 1 mol formaldehyde/mol NMP and taking into account the pad-bath concentration (8% for DMDHEU and 9% for NMP) and the wet pick-up (83% for DMDHEU and 80% for NMP) for these two compounds, the amount of total available formaldehyde calculates to 22,380 ppm for DMDHEU and 20,580 ppm for NMP. Thus, the difference (1800 ppm) in the

TABLE I
Formaldehyde Release from Fabrics Cured with NMP and DMDHEU

Catalyst	Formaldehyde release (ppm)			
	DMDHEU		NMP ^a	
	Unwashed	Washed	Unwashed	Washed
0.4% NaHSO ₄	1996	1170	332	38
0.5% Zn(NO ₃) ₂ · 6H ₂ O	841	509	197	34

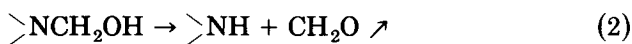
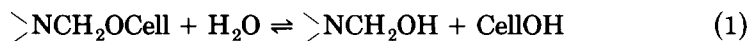
^aData reproduced from Ref. 1.

amount of total available formaldehyde between these two compounds is relatively small.

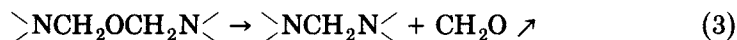
(ii) The difference in formaldehyde release caused by the two catalysts in the study on NMP is also very clearly apparent with DMDHEU. Thus, sodium bisulfate causes a significantly higher formaldehyde release (1996 ppm) than zinc nitrate (841) on unwashed samples.

(iii) In the case of washed samples, where the catalyst and the extractable residues have been removed before the formaldehyde release measurement, the formaldehyde release values are reduced as compared to the unwashed samples, but they are still much higher for DMDHEU than the values obtained for comparable NMP treated samples (1170 vs. 38 ppm) for sodium bisulfate and (509 vs. 34) for zinc nitrate. These results are understandable because the washed DMDHEU-treated fabric is expected to contain some free NCH_2OH groups, whereas the washed NMP-treated fabric is not. There also seems to be some difference between the two catalysts regarding their influence on the stability of these linkages of DMDHEU and its residues to cellulose. The washed sodium bisulfate sample gives a much higher formaldehyde release value (1170 ppm) as compared to the washed zinc nitrate sample (509 ppm). It is not clear how a Brønsted acid catalyst (sodium bisulfate) would give a less stable system for DMDHEU and residues bound to cellulose than the Lewis acid catalyst (zinc nitrate). Reinhardt⁶ found that during rinsing of zinc nitrate treated fabric with distilled water, 50% of zinc nitrate remains on the rinsed fabric. Obviously, if some zinc nitrate remains on the fabric after washing, a reduction in formaldehyde release is expected.¹ On the other hand, the exact composition or nature of these catalyst residues is not known.⁷

The AATCC formaldehyde release test is performed under conditions which allow for N—C bond cleavage of *N*-methylol groups in reagent residues and cellulose derivatives by hydrolysis and thermal decomposition. As indicated in the above discussion, the possibilities for formaldehyde release from various finished substrates are fairly complex. The reactions involved include hydrolysis of the finish [eq. (1)] and release of formaldehyde from the *N*-methylol compound by either hydrolytic or thermal decomposition [eq. (2)]:



There is no evidence that formaldehyde can be released directly from a $\text{>NCH}_2\text{OCe}$ linkage, but we have previously shown that formaldehyde can be released directly from *N,N'*-oxydimethylene linkages in a finish^{1,2}:



Many variables represented by eqs. (1) and (2) have been evaluated, and this extensive research has been summarized in a recent review.⁸

Reagent Residues. Table II contains the data for HPLC-analyzed extractable residues on fabric given the pad-dry cure as well as the pad-dry treatments with DMDHEU in the presence of sodium bisulfate and zinc nitrate.

TABLE II
Extracted Residues Determined by HPLC and Nitrogen Analyses

cat. ^a	D/C ^b	$\mu\text{M/g}$ of fabric					
		HPLC analysis			Nitrogen analysis		
		MMDHEU	DMDHEU	Dimer	Residues extracted (A) ^c	Residues extracted (B) ^d	$B - A$
SB	D	2	90	34	160	220	60
SB	C	0	12	0	12	58	46
ZN	D	6	294	23	346	377	31
ZN	C	0	0	0	0	36	36

^aSB = 0.4% NaHSO₄ and ZN = 0.5% Zn(NO₃)₂ · 6 H₂O.

^bD = Pad-dry-treated, C = pad-dry-cure treated.

^cResidues extracted and analyzed by HPLC, expressed as DMDHEU $\mu\text{M/g}$ of fabric, $A = (\text{MMDHEU}) + (\text{DMDHEU}) + 2(\text{dimer})$.

^dResidues extracted and determined from nitrogen analysis, expressed as DMDHEU $\mu\text{M/g}$ of fabric, $B = \%N \times 10,000/28$.

MMDHEU, DMDHEU, and the dimer are the three extractable residues found on both the pad-dry-treated samples (sodium bisulfate and zinc nitrate). However, after curing, the sodium bisulfate treated sample shows only DMDHEU left on the fabric and the zinc-nitrate-treated sample does not show any extractable residue. Thus, it is evident that during the curing step, not only DMDHEU, but also MMDHEU and the dimer have reacted with cellulose.

Table II also shows the total extractable residues (A) expressed in terms of DMDHEU $\mu\text{M/g}$ of fabric. These values are significantly different for the two pad-dry-treated samples (160 for sodium bisulfate and 346 for zinc nitrate). This indicates that a significant amount of residues must have reacted with cellulose in the presence of sodium bisulfate during the pad-dry treatment, thus reducing the amount of extractable residues.

A part of the water extract used for HPLC analysis was also used for nitrogen analysis. This was done to determine if there were any residues in the extract that could not be determined by HPLC. Table II contains the data on extracted residues (B) determined from nitrogen analysis and clearly show that the nitrogen-analyzed residues (B) in the water extract are greater than the HPLC-analyzed residues (A) in the same extract. This indicates that some residues, although extracted from the samples by water, may have long retention times in HPLC and their peaks may have merged with the baseline noise making them unidentifiable by HPLC. These residues are likely to be oligomers of DMDHEU. Similar observations were made in a recent study⁹ on quantitative analysis of commercial DMDHEU finishes. The difference between A and B values (both expressed in terms of DMDHEU) would give the amount of DMDHEU that is converted into oligomeric residues not identifiable by HPLC. These amounts are shown as $B - A$. Sodium bisulfate gives a relatively larger amount of such residues than zinc nitrate, the difference being greater on the pad-dry-treated samples than on the pad-dry-cure

TABLE III
Residues Fixed on Cellulose as Determined by Nitrogen Analysis^a

Catalyst	Treatment	DMDHEU fixed	NMP fixed
0.4% NaHSO ₄	D	150	78
0.4% NaHSO ₄	C	312	475
0.5% Zn(NO ₃) ₂ · 6H ₂ O	D	20	7
0.5% Zn(NO ₃) ₂ · 6H ₂ O	C	361	464

^a Residues fixed determined from nitrogen analysis of fabric after extraction with water and expressed as DMDHEU $\mu M/g$ of fabric = %N \times 10,000/28 or as NMP $\mu M/g$ of fabric = %N \times 10,000/14. See Table II for abbreviations.

treated samples, which indicates that some of these residues may have reacted with cellulose during curing.

All the residues that were not extracted by water were assumed to have reacted with cellulose. Since DMDHEU is not known to give large polymers and because, it is a highly polar compound, it is not likely to give water-insoluble residues. The amount of residues fixed on cellulose was determined by nitrogen analysis of each sample after extraction with water, drying and conditioning. The data obtained are shown in Table III. Comparison of the two pad-dry-treated samples shows that significantly larger amounts of residues have reacted with cellulose in the presence of sodium bisulfate than in presence of zinc nitrate. A similar trend was also seen in the studies with NMP (Table III). This confirms the previous conclusion¹ that sodium bisulfate, being a Brønsted acid, lowers the energy of activation sufficiently to catalyze the reaction between cellulose and an *N*-methylol compound at 60°C. In the case of pad-dry-cure treated samples, zinc nitrate gives higher fixation of DMDHEU residues on cellulose than does sodium bisulfate. This marked increase in the amount of residues fixed on cellulose during the additional curing step indicates that zinc nitrate is a more efficient catalyst than sodium bisulfate for catalyzing the reaction between cellulose and DMDHEU residues at 160°C. Such a marked difference between the two catalysts was not found in the studies on NMP.

Table IV shows the overall mass balance and the % distribution of various residues. The sum (T_1) of the extractable residues as analyzed by HPLC (A) and the residues fixed on cellulose (C) is smaller than the sum (T_2) of the extractable residues as analyzed by nitrogen (B) and the residues fixed on cellulose (C). The difference $T_2 - T_1$ is the same as the difference $B - A$ shown in Table II and represents the residues not identifiable by HPLC. Since T_2 includes all possible residues originating from DMDHEU, it represents the initial amount of DMDHEU applied. Residues A , B , and C (all expressed in terms of DMDHEU) were calculated as a percent of this initial amount of DMDHEU applied for each sample. Comparison of the two pad-dry-cure treated samples shows that in presence of sodium bisulfate, 3% DMDHEU remains as unreacted residue, 13% (16-3%) DMDHEU is converted into water-extractable residues (oligomers) that are not identifiable by HPLC, and 84% DMDHEU is fixed on cellulose either by itself or more than likely, in the form of a mixture of MMDHEU, DMDHEU, and their oligomers. The

TABLE IV
 Mass Balance of Residues^a

Catalyst	D/C	Residues extracted ^b (HPLC data)		Residues extracted ^b (N% data)		Residues fixed ^c (N% data)		A + C (T ₁)	B + C (T ₂)
		(A)	% of T ₂	(B)	% of T ₂	(C)	% of T ₂		
SB	D	160	43	220	59	150	41	310	370
SB	C	12	3	58	16	312	84	324	370
ZN	D	346	87	377	95	20	5	366	397
ZN	C	0	0	36	9	361	91	361	397

^aAll residues are expressed as DMDHEU $\mu\text{M}/\text{g}$ of fabric. See Table II for abbreviations.

^bData reproduced from Table II.

^cData reproduced from Table III.

corresponding values in the case of zinc nitrate are 0, 9, and 91%, respectively. Thus, zinc nitrate fixes a greater % (91 vs. 84) of DMDHEU on cellulose, whereas sodium bisulfate leaves a greater % (16 vs. 9) of water-extractable residues of DMDHEU on the cured fabric.

To determine the contribution of all these residues to the formaldehyde release process, it is necessary to know the extent of residues having the free *N*-methylol groups and the residues having the ether linkages. This information is very difficult to obtain from the results of this study since (i) the nature of residues not identifiable by HPLC is not known and (ii) it is not known to what extent DMDHEU and some of its residues are crosslinked to cellulose (thus giving only the ether linkages with cellulose and no free *N*-methylol groups) and to what extent these residues have undergone mono-substitution with cellulose (thus giving a mixture of free methylol groups and ether linkages to cellulose). Hence, no definite conclusions can be drawn regarding the contribution of reagent residues of DMDHEU to the formaldehyde release process from DMDHEU treated fabrics. However, since the sodium-bisulfate-treated sample contains more unreacted DMDHEU (3%) and more extractable residues (16%) than the zinc-nitrate-treated sample (which contains 0 and 9% of these residues, respectively), it appears that formaldehyde release should be more facile from the former than the latter.

Catalysts. Since it was found in the studies with NMP¹ that, in addition to the nature and amount of reagent residues, the nature and amount of catalyst used in the finishing process contribute to formaldehyde release, it was decided to extend this study to DMDHEU. Thus, a fabric was given a pad-dry-cure treatment with a solution containing 8% DMDHEU (prepared in the laboratory) and 0.4% sodium bisulfate followed by thorough washing and rinsing to remove all the extractable residues and the catalyst. This fabric was divided into five parts and each part was given a pad-dry treatment with DMDHEU and/or zinc nitrate solutions (similar to the treatments with NMP). The concentrations used for DMDHEU and zinc nitrate and the pH of the pad-bath from which they were applied to the fabric are shown in Table V. The formaldehyde release was measured on these samples after conditioning, and the results obtained are given in Table V. It is evident from the data that increasing the concentration of zinc nitrate decreases the formaldehyde

TABLE V
Effect of Pad-Bath pH and Zinc Nitrate Concentration on
Formaldehyde Release from Cellulose Treated with DMDHEU

% DMDHEU ^a	% Zinc nitrate hexahydrate ^a	Pad-bath pH	Formaldehyde release (ppm)
6	0	7.10	8113
6	0.25	7.00	4330
6	0.50	7.00	3000
0	0.50	2.00 ^b	1871
0	0.50	6.20	24

^aA pad bath containing DMDHEU and/or zinc nitrate was applied to a laundered fabric finished with DMDHEU. The padded fabrics were dried at 60°C for 7 min and conditioned for 24 h before measuring formaldehyde release.

^bpH adjusted with 0.2N HCl.

release from the finished fabrics. These results confirm the suggestion in the similar studies with NMP¹ that zinc nitrate forms a complex with the *N*-methylol groups and that this complex is fairly stable during the test conditions used for measurement of formaldehyde release. The greater the amount of zinc nitrate used, the larger the number of *N*-methylol groups tied up and the lower the formaldehyde release. Thus, complexation of zinc nitrate with *N*-methylol groups seems to be an important factor responsible for the lower formaldehyde release from fabrics given the pad-dry-cure treatment with DMDHEU in the presence of zinc nitrate as compared to that in presence of sodium bisulfate. It is also possible that zinc nitrate may tie up formaldehyde released from the finish, but this occurrence has not been established.

Another important factor is the acidity of the catalyst. The data in Table V show that the zinc nitrate solution acidified to pH 2.00 (the pH obtained with sodium bisulfate solution) causes greater formaldehyde release (1871 ppm) as compared to the zinc nitrate solution at its normal pH of 6.20 (24 ppm). This indicates that at higher hydrogen ion concentration, there is greater hydrolysis of C—O linkages of DMDHEU and its residues with cellulose and also greater rupture of N—C linkages of the *N*-methylol groups resulting in greater release of formaldehyde. Thus, the pad-bath pH is another important factor contributing to the formaldehyde release process from the finished fabrics.

CONCLUSIONS

The studies with a monofunctional model compound, *N*-methylolpyrrolidone, indicate that the nature of the catalyst (whether Brønsted acid or Lewis acid) used in the finishing process determines the nature and amount of residues generated during this process. The nature and amount of these residues, in turn, have a significant contribution to the formaldehyde release process from the finished fabrics. Also, the nature and amount of catalyst used affects the extent of formaldehyde release from the finished fabrics.

These model studies were extended to DMDHEU, a commonly used durable-press finish. Since the exact nature of some of the residues from DMDHEU could not be established, the role of specific reagent residues from DMDHEU

on formaldehyde release from finished fabrics could not be determined. The influence of the nature and amount of catalyst used on formaldehyde release from DMDHEU finished fabrics was similar to that found in case of *N*-methylolpyrrolidone; however, formaldehyde release is greater for DMDHEU-treated fabrics than for fabrics treated in a comparable manner with NMP. Because of the presence of $\text{>NCH}_2\text{OH}$ groups in the DMDHEU finish, the acidity in this system will have a greater influence on the amount of formaldehyde release than in the NMP finish. This is because the demethylolation of DMDHEU is strongly catalyzed by the presence of acid whereas demethylolation of NMP is not.

References

1. S. L. Vail, X. Zhou, K. R. Beck, and D. M. Pasad, *J. Appl. Polym. Sci.*, **29**, 3569 (1984).
2. K. R. Beck, D. M. Pasad, S. L. Vail, and X. Zhou, *J. Appl. Polym. Sci.*, **29**, 3579 (1984).
3. S. L. Vail and X. Zhou, *Text. Res. J.*, **54**, 783 (1984).
4. K. R. Beck, D. M. Pasad, and S. L. Vail, to appear.
5. K. R. Beck and D. M. Pasad, *Text. Res. J.*, **52**, 269 (1982).
6. R. M. Reinhardt, *Text. Res. J.*, **53**, 493 (1983).
7. H. M. Ziifle, R. J. Berni, and R. R. Benerito, *J. Appl. Polym. Sci.*, **7**, 1041 (1963).
8. S. L. Vail, in *Cellulose Chemistry and Its Applications*, T. P. Nevell and S. H. Zeronian, Eds., Ellis Horwood, Chichester, U.K., 1985, pp. 384-422.
9. D. M. Pasad, Ph.D. dissertation, Purdue University, 1984, pp. 18-46.

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