

Evaluation of Some Side Effects from the Use of Formaldehyde Scavengers

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Synopsis

Concentrations of methylol carbamates in several crosslinking formulations prepared from methyl carbamate and formaldehyde and with and without urea or ethyleneurea as scavengers were determined by nuclear magnetic resonance spectroscopy. The scavengers were effective in reducing the free formaldehyde in the solution, but the dimethylol methyl carbamate concentration was reduced by about 25%. Selected chemical and physical properties were obtained from cotton fabrics finished with five different formulations of known composition. Fabric strengths were improved by use of a scavenger, but some undesirable side effects were observed.

INTRODUCTION

Efforts to reduce formaldehyde in *N*-methylol crosslinking systems for durable press fabrics and garments have resulted in many changes in the formulations used for the finishing of cellulose-containing fabrics. Crosslinking agents used in the 1950s and mid-1960s were replaced by less reactive agents, and more durable finishes with less odor of formaldehyde were produced. However, additional improvements were needed and processing techniques with the new agents, dimethyloldihydroxyethyleneurea (DMDHEU) and the methylol carbamates, were further optimized to meet requirements for reducing the formaldehyde content in the atmosphere of the finishing plant and for reducing the formaldehyde released from the finished fabrics and garments. Many approaches were taken to obtain these results and comprehensive reviews of this work are available.¹⁻³

In one of the approaches formaldehyde scavengers or acceptors have been used to reduce the free formaldehyde⁴⁻⁷ content of *N*-methylol crosslinking formulations and pad baths.⁸⁻¹¹ However, more research effort has been applied to the releasable formaldehyde in finished fabrics as measured by the AATCC sealed jar method¹² as noted by literature reviews in recent articles.^{13,14} Scavengers, such as ethyleneurea and urea, on addition to an *N*-methylol formulation combine with some of the free formaldehyde in the solution. The odor of formaldehyde around the pad bath is reduced, but the reduced formaldehyde content in the pad bath can upset the chemical equilibrium and reduce the amount of the original crosslinking agent in the solution.¹

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The final composition is dependent upon a number of factors, including pH, time, temperature, and concentrations of the chemical components in the solution. Quantification of these changes in pad bath composition because of the use of scavengers has received little or no attention. However, it should be obvious that the nature of the chemical composition of the crosslinking system can be altered considerably by conditions selected during formulation.

Although several instrumental methods of analysis for determining the chemical composition of *N*-methylol crosslinking systems are available and have been used previously,¹⁵⁻¹⁸ many of the methods are not well adapted for following rapidly changing chemical compositions in aqueous solution. The methyl carbamate system was selected for study in this work because the various primary components in solution can be rapidly determined^{19,20} using proton nuclear magnetic resonance (NMR). Urea and ethyleneurea were used as scavengers under reaction conditions capable of producing varied compositions in the pad bath. Changes in composition were followed closely, and selected physical and chemical properties of the finishes produced by these crosslinking agents on cotton fabric were evaluated. Particular emphasis was placed on comparisons of durable press and strength properties of the treated fabrics and differences in the chemical composition of the finishes as noted by mild acidic hydrolysis of the finished fabrics.

EXPERIMENTAL

Chemicals

Methyl carbamate (MC) and ethyleneurea (EU) were obtained from commercial sources and all other chemicals used were reagent grade. EU was recrystallized from ethyl alcohol before use.

Instrumental and Wet Analytical Procedures for Solutions

The procedures used in this work to follow reactions by NMR and high performance liquid chromatography (HPLC) have been described previously.¹⁹⁻²¹ Briefly, reactions of MC with formaldehyde (HCHO) in the presence or absence of EU or urea (U) scavengers were followed with emphasis placed on the molar ratio of dimethylol methyl carbamate (DMMC) to the sum of the concentrations of DMMC plus monomethylol methyl carbamate (MMMC). Partial NMR spectra of undiluted, aqueous solutions were obtained from 3.0-4.0 ppm and peak heights of DMMC and MMMC were measured until the solution reached equilibrium.

The methyl groups in MC, MMMC, and DMMC produce single peaks at 3.65, 3.70, and 3.77 ppm, respectively.^{19,20} Peaks from the methyl group in methanol, from the ring protons in EU, and from water are visible but do not interfere with the analysis. However, the MC and MMMC peaks are too close to consistently obtain reliable quantitative data when the MC content is less than 10% of the total carbamates present. Often the signal from MC becomes a shoulder on the MMMC peak. Therefore, a ratio of the DMMC peak height to the sum of the peak heights of DMMC and MMMC was used to establish the effects of EU and U scavengers on the compositions of the formulations evaluated. The DMMC content (or ratio) calculated in this manner from a

single equilibrated sample and several partial spectra will vary only ± 0.01 units assuming the instrument is well tuned and stable. Base line separation of peaks from the carbamates was not obtained, and therefore quantitative data could not be obtained by integration.

The signals from the CH_2 group in the *N*-methylol products are hidden by the large water peak. Paraformaldehyde was used instead of formalin in some procedures and the conclusions were almost identical. HPLC was used to check carbamate concentrations in selected instances and to obtain reliable MC contents at equilibrium.

Compositions of samples in Table I were calculated from the % MC contents determined by HPLC (and verified by NMR) and the DMMC content (or ratio) calculated from peak heights of DMMC and MMMC using the following two equations:

$$x + y = 100 - z$$

$$x/[x + y] = \text{DMMC content (or ratio)}$$

where x , y , and z are the DMMC, MMMC, and MC concentrations (%), resp.

Errors of considerable magnitude may be introduced into this work if pH levels are not maintained properly or if solutions are diluted at certain pHs. In other words, methylolations of carbamates at room temperature at pH of 10 will reach equilibrium in about 24 h. However, if the solution is originally adjusted to 10.0, it is likely that the pH will fall below 10; and the solution will not reach equilibrium in 24 h. Also, dilution of a DMMC solution at pH 10 results in demethylolation. Therefore, the pH must be adjusted to 6 to prevent demethylolation before any substantial dilution occurs.

TABLE I
Effects of Scavengers on Formulation Compositions
Composition of Samples^a

System ^b	Free formaldehyde	%MC	%MMMC	%DMMC	DMMC/[DMMC + MMMC]
#1, DMMC	3.6%	3	39	58	0.60
#2, MC + HCHO + EU	2.2%	7	50	43	0.46
#3, MC + HCHO + U	1.5%	7	52	41	0.44
#4, DMMC + EU	1.6%	3	39	58	0.60
#5, DMMC + U	1.1%	3	39	58	0.60

^aData obtained from partial NMR spectra. Results represent averages of at least two experiments wherein partial spectra were obtained and measured over the course of the reaction.

^bThe systems studied include:

1. DMMC = conventional equilibrated reactant prepared with a 1:2 molar ratio of MC to HCHO at pH = 10 and then adjusted to pH = 6.
2. MC + HCHO + EU = a 1:2:0.2 molar ratio of these components allowed to reach equilibrium under basic conditions before being adjusted to pH = 6.
3. MC + HCHO + U = same as #2 except urea used as scavenger.
4. DMMC + EU = system #1 adjusted to pH = 6 and 0.2 mol EU added.
5. DMMC + U = same as #4 except U used as scavenger.

Free and total formaldehyde contents in solution were obtained using methods at room temperature and at 4°C.^{4,5} These methods involve the reaction of sodium sulfite with free formaldehyde to liberate base.

Preparation of Crosslinking Formulations at Room Temperature

DMMC. Methyl carbamate was added to undiluted formalin (or a 17.8% formaldehyde solution prepared from paraformaldehyde) to give a 1:2 ratio of methyl carbamate to formaldehyde. The pH was adjusted to 10 with aqueous sodium hydroxide. As in the previous study,²⁰ partial NMR spectra were obtained until equilibrium was established. After equilibrium had been established the pH was adjusted to 6 with dilute hydrochloric acid.

DMMC + EU or U. DMMC was prepared as described above, adjusted to pH = 6, and either ethyleneurea or urea added to give a molar ratio of 1:2:0.2 for methyl carbamate:formaldehyde:ethyleneurea or urea. Solution was kept at room temperature and partial NMR spectra obtained as desired.

MC + HCHO + EU or U. Methyl carbamate, formaldehyde, and ethyleneurea or urea were combined in a molar ratio of 1:2:0.2 and the pH adjusted to 10 with aqueous sodium hydroxide. After it appeared from partial NMR spectra that equilibrium was established, usually between 24 and 48 h at room temperature, the solution was adjusted to pH 6 with dilute hydrochloric acid.

The above formulations were diluted and a curing catalyst added for fabric treatments. The *calculated* methyl carbamate content was 3.9% (or 7% DMMC) with 4% magnesium chloride hexahydrate as catalyst.

Additional solutions were evaluated for final composition wherein DMMC was prepared as above, but EU was added and the pH maintained at 10. The products were allowed to come to equilibrium and the contents determined by NMR and HPLC. These solutions were not used for fabric treatments.

Fabric Treatment and Testing

The fabric used in this work was a desized, boiled, and bleached, 80 × 80 cotton printcloth (3.2 oz/yd²). Fabric samples were padded to about 80% pickup with the solutions described above, placed on pin frames at original dimensions, dried at 70°C for 5 min, and cured 160°C for 3 min. All the fabrics were given an alkaline afterwash except those submitted for formaldehyde release.

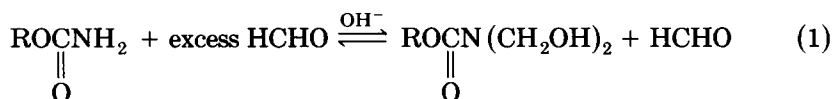
The cured fabrics (after the alkaline afterwash) were hydrolyzed at 40°C for 15 min in excess 0.1 normal hydrochloric acid. After the hydrolysis fabrics were given another alkaline afterwash and were tumble dried.

Nitrogen contents of the fabric samples were determined by the Kjeldahl method. Formaldehyde release was determined on unwashed, cured samples by the sealed jar method in AATCC Test Method 112-1982. Wrinkle recovery of fabrics was obtained using AATCC Test Method 66-1975 recovery-angle method, and durable press ratings were determined by AATCC Test Method 128-1974 appearance method. The Elmendorf method, ASTM designation D1424-63(B) was used for tearing strength determinations.²²

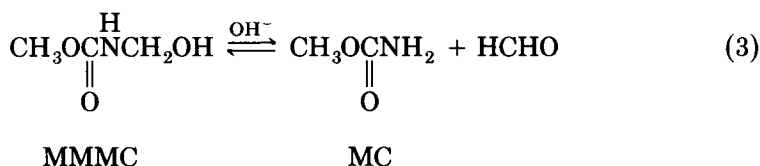
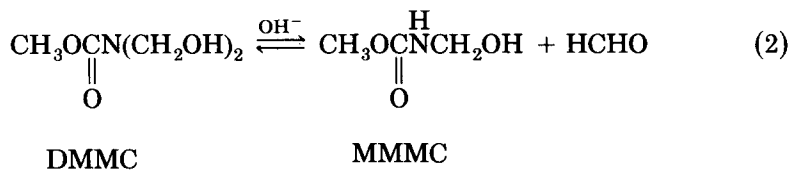
RESULTS AND DISCUSSION

Composition of Crosslinking Formulations

Most prior studies of the general chemistry of the formation of methylol carbamates are concerned with the rates and extents of reaction of formaldehyde with carbamates under alkaline conditions.^{1, 3, 8, 14, 20, 23, 24} Excess formaldehyde was added to force complete methylation of the carbamate [eq. (1)] and to assure optimized properties of the finished fabric^{8, 23}:



Disturbing this equilibrium by removal of some of the uncombined or free formaldehyde can result in reversal of the reaction, partial demethylation of the carbamates [as noted for methyl carbamate in eqs. (2) and (3)], and a substantial reduction in the amount of carbamate capable of crosslinking cellulose. As the DMMC content is decreased, the amount of MC will increase to an extent determined by the reaction (or pad bath) conditions. In an NMR spectrum, peaks from the methyl groups in MC, MMMC, and DMMC are free of interference from water or the scavengers.



If the total concentration of reactants, pH, and the temperature are held constant, useful quantitative data on MC, MMMC, and DMMC contents are obtained in the absence or the presence of EU or U and their methylol derivatives.

Tables I and II provide quantitative data on the effects of reaction conditions on the composition of crosslinking systems as influenced by pH and the order of addition of the scavengers. Results are summarized as follows:

- (1) The addition of urea or ethyleneurea to a DMMC solution prepared at pH 10 and adjusted to pH 6 before addition of the scavengers (Table I, systems 4 and 5) results only in the reduction of the formaldehyde concentration. The DMMC concentration is not affected in a 24-h period.
- (2) The formulations were prepared by addition of the scavengers to a solution of methyl carbamate and formaldehyde with adjustment of the pH to 10 (Table I, systems 2 and 3). The examination of NMR partial

TABLE II
Effect of EU on DMMC Composition^a

Sample description	Composition of samples			
	%MC	%MMMC	%DMMC	DMMC/[DMMC + MMMC]
DMMC	2.9	35.7	61.4	.63
DMMC + EU at pH 10	6.6	46.9	46.5	.50

^aData obtained by HPLC. Data obtained from partial NMR spectra are similar but quantitative data from NMR spectra for low %MC concentrations were not considered reliable. Compare DMMC/[DMMC + MMMC] ratios in Table II with those in Table I.

spectra over a 24–48-h period indicated that once the reaction products were equilibrated, the final composition was essentially identical to another situation (Table II) wherein the scavenger was added to DMMC at pH 10. The addition of ethyleneurea to a DMMC solution at pH 10 caused a rapid reduction in the DMMC and formaldehyde concentrations. At room temperature an equilibrium was established within about 48 h and the MC content was more than doubled. The reduction in DMMC concentration in solutions at pH 10 by addition of 0.2 mol scavenger/mol carbamate is substantial. HPLC data (Table II) indicate that with ethyleneurea the DMMC concentration is reduced from 61.4 to 46.5 or 24%. NMR data (Table I) suggest the DMMC concentration is reduced 26% by addition of ethyleneurea and 29% by the addition of urea. Thus, about a fourth of the DMCC is lost by the addition of 0.2 mol scavenger/mol carbamate.

- (3) The HPLC analysis in Table II of some carbamate solutions provided an accurate determination of low MC contents at equilibrium. The addition of 0.2 mol EU to DMCC at pH 10 increased the MC concentration from about 3 to 7%. These data were used with the DMMC content (or ratio) obtained by NMR experiments to calculate DMMC and MMMC concentrations in Table I for similar formulations at equilibrium.
- (4) As expected, the free formaldehyde concentrations (Table I) in the solutions of methylolated carbamates are reduced in solutions at pH 6 and at pH 10 by addition of the formaldehyde scavengers. The concentrations were determined about 24 h after the formulations were mixed and at roughly the same time as the formulations were used in the fabric treatments.

The partial NMR spectra did not furnish useful information on the chemical structure or the amount of methylolureas or methylolethyleneureas in the formulation. Only the ring protons of the ethyleneureas produce peaks that are visible, but separate, distinct peaks were not produced by the ring protons of the methylolethyleneureas and ethyleneurea. Mixtures of known compounds only broadened the single peak. Further, prior literature^{1,3,8} provides additional evidence that ethyleneurea and urea add to formaldehyde under the experimental conditions used in this study.

TABLE III
Fabric Properties from Carbamate Formulations^a

Pad bath, system	Durable press rating	Wrinkle recovery	Tear strength ^b	Formaldehyde Release ^c ($\mu\text{g/g}$)
		angle ^b $W + F$ (deg)	W (g)	
#1, DMMC	3.5	262 (-13)	486 (+44)	899
#2, MC + HCHO + EU	3.0	264 (-26)	524 (+116)	1104
#3, MC + HCHO + U	3.5	260 (-25)	537 (+53)	915
#4, DMMC + EU	3.0	260 (-33)	549 (+61)	1086
#5, DMMC + U	3.0	264 (-29)	494 (+106)	805
Untreated fabric	1.0	187	1027	—

^aCalculated methyl carbamate concentration in the pad baths was 3.9%. Samples were cured at 160°C for 3 min with 4% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as catalyst. No additives other than the scavengers were used.

^bFigures in parenthesis refer to loss in WRA or gain in tear strength after cured fabrics were hydrolyzed in 0.1N HCl for 15 min at 40°C.

^cFabrics stored four months before these values were determined ($1 \mu\text{g/g} = 1 \text{ ppm}$).

Properties of Finished Cotton Fabrics

The five pad baths prepared for this study have been shown to possess significantly different chemical compositions. Systems 1, 4, and 5 contain the highest DMMC concentration and systems 2 and 3 contain about three-fourths this amount. However, the wrinkle recovery values and durable press rating in Table III for the finished fabrics provide conflicting evidence of the level of crosslinking. The wrinkle recovery angles ($W + F$) are essentially the same and range from 260° to 264°. On the other hand, fabrics finished with methylolated carbamate, DMMC only, produced a durable press rating of 3.5, whereas only one of four fabrics finished with methylolated carbamates plus methylolated scavenger had more than a rating of 3.0. In general, the competition of mono- and difunctional reactants for reaction sites in cellulose and the possible coreaction of these reactants with themselves or the nonmethylolated nitrogenous compounds present in the formulation appears to reduce the efficiency of the crosslinking reactions.

The lowered efficiency for crosslinking by DMMC is substantiated by the higher tearing strengths found for all the fabrics treated with a scavenger-containing formulation. These values (warp only) range from 494 to 549 g compared to the methylol carbamate (system #1, DMCC) treated fabric with a tearing strength of 486 g. The formaldehyde release values on the unwashed, treated fabrics provide little information of value to this discussion. The values are somewhat higher than those normally encountered, but stored fabrics are known to increase in amounts of formaldehyde released.^{11, 25, 26}

The results of the mild acidic hydrolysis reported in Table III confirm the presence of urea or ethyleneurea moieties in some crosslinks from scavenger-containing formulations. The higher loss of wrinkle recovery and higher gain in tearing strength for these fabrics reflect the known susceptibility of urea- and ethyleneurea-based finishes to acidic hydrolysis when compared to carbamate-based finishes.^{3, 8, 23} EU-modified DMMC finishes have been shown

previously⁸ to display a susceptibility to milder acidic hydrolysis conditions than used in this work.

Further Considerations

Factors other than addition of a scavenger and direct uptake of formaldehyde can cause an alteration of the expected content of methylolated carbamates. Methanol, present in formalin solution, can methylate MMMC and methylolureas under alkaline conditions.²⁷ Also, formaldehyde is simultaneously oxidized and reduced with base catalysis in the Cannizzaro reaction to form methanol and formic acid. Neither of these reactions is expected to cause a substantial alteration in the content of the carbamates unless the formulation is kept at alkaline conditions for long periods of time or heated for short periods. Once a formulation has achieved equilibrium and is neutralized, the contents should not change substantially.

At least seven reactants are present in a carbamate formulation containing urea or ethyleneurea as scavenger. DMMC, MMMC, MC, dimethylolated scavenger, monomethylated scavenger, the scavenger, and formaldehyde are all capable of reaction during drying or curing of the cellulose-containing fabric. These reactants coreact and/or compete with each other for sites in cellulose. The chemical composition and physical properties of the treated fabrics are therefore expected to vary and are dependent upon the composition of the pad bath and the processing conditions.

In prior work⁸ it was shown that scavenger-modified (ethyleneurea) carbamate finish was destabilized after mild acid hydrolysis or after five alkaline launderings. In the present work fabrics with the scavenger-modified finish possessed better original strength properties than those that contained no scavenger. Removal of labile crosslinks by mild acid hydrolysis reduced the wrinkle recovery angles of the treated fabrics but did not result in an exceptional recovery of strength properties.

The methylolated scavengers or their coreactants appear to be very successful in the competition with DMMC for sites in cellulose. The susceptibility to acid hydrolysis of scavenger-modified finishes from reactant systems 4 and 5 as compared to reactant system 1 substantiates this belief. The DMMC content in the pad bath was identical in these three systems, yet the presence of 20 mol % of the methylolated scavenger produced a finish similar to the DMMC deficient systems 2 and 3.

The general findings in this work are expected to apply to scavengers used with DMDHEU. Again, the equilibrium is upset by the compound that removes formaldehyde from solution, and a new reactant system containing numerous components results. Attempts to follow these reactions by NMR were not successful.

CONCLUSIONS

Proton nuclear magnetic resonance spectroscopy (NMR) is an effective method to determine the concentrations of carbamates in formulations containing urea or ethyleneurea for durable press finishing of cotton-containing fabrics. Under alkaline conditions the carbamate-formaldehyde equilibrium is upset and the concentration of dimethylol methyl carbamate (DMMC) is

reduced about 25% in 24–48 h by the addition of only 20 mol % of either formaldehyde scavenger. DMMC content was not altered over the same period if the scavenger was added to the prepared DMMC agent at pH 6. The scavengers reduce the free formaldehyde content in these formulations, and the resulting addition product has a substantial effect upon the chemical and physical properties of the treated fabric. Crosslinking of cellulose by DMMC is reduced when these scavengers are used in the formulation.

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