Formaldehyde Liberation and Cure Behavior of Urea-Formaldehyde Resins

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Summary
The cure behavior of several urea-formaldehyde resins containing different catalyst systems and potential acid-neutralizing additives was followed by differential scanning calorimetry (DSC). Catalysts included ammonium chloride, ammonium sulfate, zinc nitrate, and an amine hydrochloride. Additives included powdered aluminum, glass, and magnesium oxide. The DSC results were employed to guide and interpret formaldehyde liberation testing of the cured systems. Large differences in both cure and formaldehyde liberation behavior were seen among the various resins cured with a given catalyst and as a consequence of using different catalysts and different potential acid neutralizers. In general, for a given resin the more acidic catalyst-additive systems cure the resins more completely and at lower temperature. However, the more acidic systems also exhibit greater postcure formaldehyde liberation. Assuming the observed formaldehyde liberation arises from resin hydrolysis, the results confirm the desirability of neutralizing an acidic cure catalyst after wood bonding to reduce formaldehyde liberation and increase bonded product durability.

Introduction
The primary goal of this research was to determine the influence of several structural and compositional variables on the hydrolytic stability of cured urea-formaldehyde (UF) resins, with emphasis on effects of resin acidity. The variables included formaldehyde to urea (F/U) molar ratio, degree of cure, concentration and type of acidic cure catalysts, pH, and the presence of potential acid-neutralizing additives. For this purpose, we employed a recently reported method for measuring the time-dependent formaldehyde liberation from solid samples (Myers and Koutsky 1987). To aid in interpreting the formaldehyde liberation data, we also examined resin cure behavior using differential scanning calorimetry (DSC).

Two limitations to the use of UF adhesives for wood bonding have been relatively poor durability of and formaldehyde emission from products made using this adhesive system. Available evidence indicates that both of these undesirable properties are, at least in part, a consequence of the hydrolytic instability of cured UF resins (Meyer 1979; Myers 1986). As indicated by Myers and Koutsky (1987), the formaldehyde emission may arise as a result of hydrolysis. Consequently, efforts to reduce the tendency of a cured UF resin to liberate formaldehyde should provide guidelines as to the potential of that resin for manufacturing wood products with acceptable formaldehyde emission and durability.

Except for the carbonyl C=O bond and the relatively stable amide C─N bond, hydrolysis of all bonds in a UF resin will ultimately lead to liberation of formaldehyde. In the absence of significant adsorbed formaldehyde, therefore, measurement of formaldehyde liberation from a cured UF resin should yield an approximate measure of its resistance to hydrolytic degradation. Thus, properly obtained information about the tendency of a cured resin to liberate formaldehyde should provide guidelines as to the potential of that resin for manufacturing wood products with acceptable formaldehyde emission and durability.

We recently described a procedure for measuring the time-dependent formaldehyde liberation from cured resins as a function of numerous variables (Myers and Koutsky 1987). The method was used to illustrate the strong increase in formaldehyde liberation from cured UF resins with increasing F/U ratio, as well as the strong increase in formaldehyde liberation from both cured UF and phenol-formaldehyde resins with increasing relative humidity (RH) (Myers 1986). One virtue of this method is its ability to determine the formaldehyde liberation behavior of solid samples at controlled humidity without leaching ingredients from the sample. Absence of leaching was particularly important for the present study, which examined sam-
ple acidity effects, among others. Note that our experimental method is in principle a version of the WKI bottle method, which has become widely used in Europe for characterizing the release of formaldehyde from particleboards and other commercial products (Roffael 1982, 1988) and has also been applied to UF precursors (Roffael and Schriever 1985).

Results from this and previous (Roffael 1975; Myers 1982, 1986) investigations also demonstrate a significant decrease in formaldehyde liberation as degree of cure increases. Consequently, to interpret the differences in liberation behavior observed on changing other variables, we felt it important to understand qualitatively how those other variables influenced resin cure. For that purpose, we employed DSC with sealed capsules. Sealed capsules preclude vaporization endotherms and therefore give a clearer picture of cure exotherms in the usual range for UF cure, i.e., approximately 70 to 160°C. All but one (Sebenik et al. 1982) of the relevant publications on UF thermal analysis appear to have used unsealed sample holders (Chow and Steiner 1975; Denisov 1978; Matsuda and Goto 1984; Nabiev et al. 1984; Tarakhtunov 1968).

**Experimental**

**Materials**

Nine UF resins were examined; seven were prepared at the Forest Products Laboratory, and two were obtained from commercial sources. Table 1 summarizes their methods of synthesis and properties. The resins cover a range of F/U ratios and synthesis procedures.

Catalysts included solid ammonium chloride; ammonium sulfate in the form of a solution containing 20% ammonium hydroxide (by weight), 20% ammonium sulfate, and 60% water; solid zinc nitrate; and the hydrochloride of 1-hydroxy-3-aminopropane (AMP-HCl) as a 20% solution in water. Quoted catalyst levels used in resins refer to weight percentage of catalyst solids per weight of resin solids.

Potential acid neutralizers examined were aluminium powder (less than 5 µm average diameter), magnesium oxide (less than 74 µm average diameter), and soda-lime glass (less than 60 µm average diameter). Quoted levels used in resins refer to weight percentage of scavenger per weight of resin solids.

**Methods**

**Formaldehyde liberation**

The procedure for formaldehyde liberation has been described in detail elsewhere (Myers and Koutsky 1987). Briefly, thin films of resin solution were heated under nitrogen in shallow pans between hot press platens for specified times and temperatures. After heating, the resin was vacuum (ca. 0.5 Torr) dried at 25°C to minimize hydrolysis or further cure and to facilitate grinding. It was then ground, sieved to a particle size less than 80 mesh (approximately 180 µm), and further vacuum dried at 25°C. A resin sample of about 10 mg was weighed into a weighing bottle, a glass cross placed on the bottom of the bottle, and the sample subjected to vacuum pumping at 25°C for at least 16 h to ensure removal of any adsorbed formaldehyde. Immediately before starting the liberation experiment, the vacuum was broken, a small beaker containing sulfuric acid placed on the cross, and the bottle scaled and placed in an insulated box within a temperature-controlled room (23°C). At selected intervals, the small beaker was removed, and the formaldehyde concentration in the sulfuric acid was determined using a chromotropic acid procedure (Myers and Koutsky 1987).

**Differential scanning calorimetry**

Scans were performed on 10- to 15-mg samples contained in scaled large volume capsules, at a scan rate of 10°C per minute. Both the temperature scale and the heat flow scale were calibrated with indium. Reaction heats were obtained by integrating exotherm peak areas and are reported as joules per gram of resin solids. For some of the resins, replicate scans allowed calculation of standard deviations in the heat values.

**Carbon-13 nuclear magnetic resonance**

Spectra were obtained on solutions of resins A and B (Table 1) containing about 3 parts of resin solution, 1 part deuterated dimethylsulfoxide, and 100 µg/mL disodium (diethylenetriaminepentaaacetato) Fe(III) as a relaxation agent (Wenzel et al. 1982). A 62.89-MHz instrument was used with the following parameters: 37°C, 30-KHz sweep width, 7.8-µs (45°) pulse width, 30-s pulse delay, inverse

**Table 1. Methods of synthesis and properties of urea-formaldehyde resins**

<table>
<thead>
<tr>
<th>Resin</th>
<th>F/U ratio</th>
<th>Synthesis procedure</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH (7.6)</td>
</tr>
<tr>
<td>A</td>
<td>1.6</td>
<td>50 % formaldehyde; 3-stage urea addition</td>
<td>60</td>
</tr>
<tr>
<td>B</td>
<td>1.2</td>
<td>50 % formaldehyde; 3-stage urea addition</td>
<td>60</td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>UF concentrate; 3-stage urea addition</td>
<td>60</td>
</tr>
<tr>
<td>D</td>
<td>1.4</td>
<td>37 % formalin; 3-stage urea addition</td>
<td>50</td>
</tr>
<tr>
<td>E</td>
<td>1.3</td>
<td>37 % formalin; 2-stage urea addition</td>
<td>60</td>
</tr>
<tr>
<td>F</td>
<td>1.7</td>
<td>37 % formalin; 1-stage urea addition</td>
<td>63</td>
</tr>
<tr>
<td>G</td>
<td>1.3</td>
<td>Resin F + urea at room temperature</td>
<td>NA</td>
</tr>
<tr>
<td>H</td>
<td>1.4</td>
<td>Commercial</td>
<td>60</td>
</tr>
<tr>
<td>I</td>
<td>NA</td>
<td>Commercial</td>
<td>65</td>
</tr>
</tbody>
</table>

1) Formaldehyde to urea molar ratio.
2) Free formaldehyde.
3) Not available.

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gating, and 250 scans. Rammon (1985) reports the urea carbonyl relaxation time to be greater than 20 s. For that reason, we used 30-s pulse delay in addition to the iron relaxation agent. Nevertheless, we found the ratios of total \(CH_2\) to total carbonyl intensities to be 15% to 20% above the \(F/U\) feed ratios, indicating that the carbonyl transition did not have sufficient time for complete relaxation. The reported intensities, calculated relative to that of the carbonyl in the respective spectrum, must therefore be inspected with this 15% to 20% difference in mind.

Free formaldehyde of resins

Free formaldehyde of resins was determined using a standard sodium sulfite method modified by being conducted at approximately 5 to 10°C and by adding sodium lignosulfonate (approximately 2:1 ratio with resin solids) to maintain the resin in solution (Gollob 1987).

Cured resin pH

The apparent pH of the cured resin samples was determined on slurries in water (1 part resin to 10 parts water) after shaking overnight.

Results and Discussion

**Differential scanning calorimetry**

In the following, we present the DSC data and briefly comment on their meaning with reference to resin cure; the significance of these data for formaldehyde liberation is discussed after the liberation data are presented.

Resin comparisons

Figure 1 compares DSC scans for several resins with ammonium chloride catalyst, either at 1% catalyst (by weight) or at 0.7% (resins A and B). Points to be noted are as follows:

1. Exotherm peak temperatures differed significantly, ranging from 75 to 100°C (348 to 373 K). Nevertheless, no overall correlation was apparent between peak temperatures and resin \(F/U\) ratio, presumably because of the different synthesis procedures. However, in the pairs A—Band F—G, the resins B and G are daughters of A and F, respectively, differing from their parent only by addition of more urea in a final synthesis step that leads to lowered \(F/U\) ratio of B relative to A and G relative to F (Table 1). For these closely related resins, one result of lowered \(F/U\) ratio was an increase in peak temperature. This is consistent with data from differential thermal analysis (DTA) experiments at higher ammonium chloride contents and somewhat lower temperatures (Chow and Steiner 1975). It is also consistent with the expectation that the lower free formaldehyde content (Table 1) at lower \(F/U\) ratio will liberate less hydrochloric acid by reaction with the ammonium chloride catalyst; this in turn will produce a less reactive system.

2. Exotherm reaction heats also differed greatly among the seven resins, ranging from 26 to 154 J/g. (Rescans of all samples indicated little or no residual exotherm.) As with the peak temperatures, the only apparent relationship between reaction heat and resin variables is an increase in the exotherm heat after adding urea to a particular resin. For example, the reaction heat of resin A (87 J/g) increased 77% after urea was added to bring the \(F/U\) ratio down from 1.6 to that of 1.2 for resin B (154 J/g), and the reaction heat of resin F (26 J/g) increased 130% when the \(F/U\) ratio decreased from 1.7 to that of 1.3 for resin G (60 J/g). This result, too, is qualitatively consistent with data reported earlier from DTA (Chow and Steiner 1975), although those earlier heat data were measured only as peak heights, not the more quantitative peak areas.

![Fig. 1. The DSC exotherms for several resins. Bracketed numbers are \(F/U\) ratio and percentage of free formaldehyde: values in parentheses are measured heats in joules per gram resin solids. Ammonium chloride catalyst concentration was 1% by weight of resin solids, except for 0.7% for resins A and B. NA, not available. (ML88 5652)](image-url)
Table 2. C¹³ nuclear magnetic resonance for resins A and B

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency (ppm)</th>
<th>Relative intensity</th>
<th>Resin A</th>
<th>Resin B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC¹³H₂N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between 2 secondary N</td>
<td>47.3 - 7.5</td>
<td>0.19 (0.0018)</td>
<td>0.15 (0.0016)</td>
<td></td>
</tr>
<tr>
<td>Between 1 secondary</td>
<td>54.0 - 57.1</td>
<td>0.36 (0.0035)</td>
<td>0.34 (0.0035)</td>
<td></td>
</tr>
<tr>
<td>and 1 tertiary N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between 2 tertiary N(¹)</td>
<td>57.6 - 58.3</td>
<td>0.05 (0.0005)</td>
<td>0.05 (0.0005)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.62 (0.0057)</td>
<td>0.54 (0.0056)</td>
<td></td>
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</tr>
<tr>
<td>NC¹³H₂OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>On secondary N</td>
<td>65.1 - 65.4</td>
<td>0.52 (0.0048)</td>
<td>0.41 (0.0033)</td>
<td></td>
</tr>
<tr>
<td>On tertiary N</td>
<td>71.7 - 71.9</td>
<td>0.22 (0.002)</td>
<td>0.15 (0.0016)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.74 (0.0069)</td>
<td>0.56 (0.0058)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃C¹³H₂OCH₂OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and/or</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃C¹³H₂OCH₂NH</td>
<td>69.6 - 69.7</td>
<td>0.18 (0.0017)</td>
<td>0.11 (0.0011)</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂C¹³H₂OCH₂NH</td>
<td>76</td>
<td>0.07 (0.006)</td>
<td>0.04 (0.0024)</td>
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<tr>
<td>Total</td>
<td>0.25 (0.0023)</td>
<td>0.15 (0.0016)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>83.4</td>
<td>0.01</td>
<td>tracc</td>
<td></td>
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<tr>
<td>Dimer</td>
<td>87</td>
<td>0.01</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>87</td>
<td>0.02</td>
<td>tracc</td>
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</tr>
<tr>
<td>Carbonyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between 2 secondary N</td>
<td>159.8 - 160.6</td>
<td>0.74 (0.00069)</td>
<td>0.56 (0.0058)</td>
<td></td>
</tr>
<tr>
<td>and tertiary N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>or 2 tertiary N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between 2 secondary N</td>
<td>161.2 - 161.7</td>
<td>0.23 (0.0021)</td>
<td>0.22 (0.0023)</td>
<td></td>
</tr>
<tr>
<td>or secondary and</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tertiary N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unsaturated urea</td>
<td>163.2 - 163.3</td>
<td>0.04 (0.0004)</td>
<td>0.22 (0.0023)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1.01 (0.0004)</td>
<td>1.00 (0.004)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹) Based on assignments in the literature (de Breet et al., 1977; Pratt, 1980; Rammon, 1985; Slomini et al., 1977; Tomita and Hatano, 1978).
²) Values outside parentheses are expressed in moles per mole carbonyl. Values within parentheses are expressed in moles per gram resin, normalized for F/U differences.

(1) Observed effects differed with resin type. Resin G thermograms changed little if any, in peak temperature or reaction heat on increasing the ammonium chloride content from 1% to 5%. However, over the same catalyst range, resin G’s parent resin F (with lower urea and higher F/U ratio) showed a 12°C decrease in peak temperature, with an apparent 35% increase in reaction heat between 1% and 3% catalyst. Resin I (data not shown) showed no significant change in peak temperature or reaction heat with 1% and 3% ammonium chloride. From DTA measurements, others report no change in exotherm peak temperature but a 30% increase in reaction heat (peak height) for a resin with 1.3 F/U over this same ammonium chloride concentration range (Chow and Steiner, 1975).

(2) Between 0.2% and 0.6% ammonium sulfate, resin E decreased its peak temperature about 12°C and increased its exothermic reaction heat over 40% (55 to 70 J/g). Only minor changes occurred on further increasing catalyst to 1.0%.

Fig. 2. Effect of ammonium salt catalysts on DSC exotherms of three resins. Catalyst contents are in percentage by weight of resin solids; values in parentheses are heats in joules per gram resin solids. (ML85653)
Moisture

Figure 3 illustrates another, totally different factor of potential importance to the cure of UF resins, that is, the retardation of cure at low moisture content. Water is actually a product of the curing reactions between methylols and urea, and, according to mass action considerations, its presence should hinder the reaction rate. As Figure 3 shows, however, very low moisture content hindered the reaction, especially in the presence of ammonium sulfate catalyst. This effect could be due to decreased polymer chain and catalyst mobility and to decreased acid production. Implications may exist for curing products such as particleboard when the resin-coated flakes are overdried.

Neutral pH production after cure

Much evidence exists that low pH accelerates not only the rate of cure of UF resins but also their rate of hydrolysis after cure (Allan et al. 1980; de Jong and de Jonge 1953; Higuchi and Sakata 1979; Higuchi et al. 1980; Myers 1982; Troughton 1969), and we provide confirmation of the latter in the section on formaldehyde liberation. It was of interest, therefore, to determine by DSC the curing effectiveness of less acidic catalysts of different chemical types from the ammonium salts. Figs. 3 and 4 compare the DSC scans using zinc nitrate, an amine hydrochloride, and ammonium sulfate (Fig. 3, resin E) or ammonium chloride (Fig. 4, resin I). Clearly, both the zinc salt and the amine hydrochloride were much less effective in curing the UF system than were the ammonium salts; their peak temperatures were 2.5 to 30°C higher than those for the ammonium salts, and their exotherm heats were significantly reduced. This relative ineffectiveness presumably derives from the less acidic nature of the zinc nitrate and amine hydrochloride, as evidenced by the higher pH values of the “cured” resins (data to be shown later in this paper). At the concentrations used here, it seems unlikely that zinc nitrate and amine hydrochloride would be acceptable catalysts for producing wood panels at high production rates.

Another possible way to achieve neutral pH after cure is by using additives that neutralize acid at such a rate that cure is not interfered with (Higuchi et al. 1980; Myers 1983). Figure 5 shows the effects of three additives on the DSC scans of resin E with ammonium sulfate catalyst. Although the glass and aluminum powders did not significantly alter the exotherm peak temperature, they may have marginally decreased the
total exotherm heat. The latter is particularly likely with the aluminum because part of the exotherm heat was contributed by a high temperature shoulder, possibly caused by the aluminum-acid reaction. Magnesium oxide, on the other hand, clearly interfered with cure, causing a major reduction in heat and shifting the reaction to higher temperatures. Figure 6 compares the effects of two levels of glass powder and magnesium oxide on resin G with ammonium chloride catalyst. While the 1% glass powder probably did not hinder cure, the 3% level may have done so. Again, the magnesium oxide clearly interfered with cure, probably even at the 1% level. From the point of view of permitting resin cure, therefore, these particular aluminum and glass powders may be satisfactory additives, but the magnesium oxide is too acid reactive. Perhaps magnesium oxide with a larger particle size (lower surface area) would be more suitable.

**Formaldehyde liberation**

Resin comparisons

Figure 7 compares the formaldehyde liberation behavior of four resins, two of them at two different cure times. The following points are noted:

(1) Resins A and B were identically prepared except for a larger final urea addition to resin B; final F/U ratios were 1.6 for resin A and 1.2 for resin B. Figure 7 demonstrates a dramatic reduction in formaldehyde liberation by lowering the F/U ratio; qualitatively similar results were found using the WKI bottle method on particleboards made with different molar ratio resins (Roffael 1975). On an absolute scale, the reduction in formaldehyde liberation after extended cure (filled compared to open symbols) was much greater for resin A than for the lower F/U resin B, and the reduction was apparently also greater for resin A on a relative scale (approximately 65% reduction for resin A at 30 days compared with 40% for resin B). The greater effect of extended cure on the higher F/U resin A is not too surprising as resin A must contain a higher proportion of labile moieties, such as methylene ether or methylol, at low or moderate cure than does the lower F/U resin B.

(2) The fact that the liberation curves for resins D and H are almost identical is fortuitous in view of the differences in synthesis procedures (Table 1) and in humidities during the liberation test. That their liberation curves fall between resins A and B, however, may reflect their intermediate F/U value of 1.4.

Catalyst/pH effects

Figure 8 compares the formaldehyde liberation behavior of resins D (filled symbols) and H (open symbols) after heating at 110°C under three conditions:
formaldehyde liberation from the material catalyzed with ammonium chloride may be reduced by reaction of ammonia with formaldehyde to produce hexamethylenetetramine.

uncatalyzed, catalyzed with 1% ammonium chloride, and catalyzed with phosphoric acid at an initial pH 3.0. Several points are of interest:

(1) DSC scans for the catalyzed, cured samples all showed no residual exotherms. However, scans for the uncatalyzed, heated samples showed small, broad residual exotherms. These findings indicate that complete cure was achieved in the catalyzed samples but not in the uncatalyzed. Confirming the DSC, infrared absorbances (normalized by the carbonyl absorbance) in the methylol region (1010 to 1030 cm\(^{-1}\), Myers 1981) for the catalyzed samples were approximately one-half those for the uncatalyzed samples.

(2) Despite their lower degree of cure and higher methylol contents, both uncatalyzed samples exhibited significantly lower formaldehyde liberation than did their catalyzed counterparts. We presume this difference resulted from catalysis of cured resin decomposition by residual acid in the catalyzed samples. For example, the ammonium chloride and phosphoric acid in resin H produced pH levels of 2.3 and 2.8, respectively, after cure, whereas the uncatalyzed, heated resin H had a pH of 7.2. Interestingly, Roffael reported that formaldehyde release (WKI bottle method) from particleboard made with ammonium chloride-catalyzed UF resin was significantly below that from board made with the same uncatalyzed UF resin (Roffael 1975). Although that finding is perhaps more consistent with one’s expectations, a direct comparison between Roffael’s board experiments and our resin experiments is clearly not possible.

(3) The lower formaldehyde liberation from samples catalyzed with ammonium chloride compared to phosphoric acid is inconsistent with the above argument based on acid catalysis of decomposition, because the ammonium chloride sample is more acidic than the phosphoric acid (pH 2.3 compared to 2.8). However, formaldehyde liberation from the material catalyzed with ammonium chloride may be reduced by reaction of ammonia with formaldehyde to produce hexamethylenetetramine.

The strong influence of sample pH on formaldehyde liberation and the secondary influence of cured resin structure are further demonstrated in Figure 9 for resin E with and without ammonium sulfate catalyst. Again, the approximately neutral (pH 8.3), uncatalyzed, dried sample (circles) showed much lower formaldehyde liberation. The pH of the identically catalyzed samples was 2.1, but the formaldehyde liberation increased slightly in the following order: 16 h/air-dried (diamonds), 20 min/100°C (filled triangles), 3 min/100°C (open triangles). The 100°C cure temperature was 10°C above the exotherm peak (Fig. 4), and the resultant samples exhibited little or no residual exotherm. However, as the DSC behavior in Figure 4 attests, the air-dried, catalyzed sample (diamonds) was not fully cured; for that reason, it would be expected to exhibit higher formaldehyde liberation. The lower liberation of the air-dried, catalyzed sample compared to the catalyzed, heated samples may then be the consequence of greater ammonia retention in the absence of heat, with subsequent scavenging of formaldehyde.

We showed earlier (Figs. 3 and 4) that zinc nitrate and
Fig. 9. Effect of ammonium sulfate catalyst and heating time on formaldehyde liberation from resin E at 60% RH. ○ no catalyst, vacuum dried 1 h at ambient temperature. All other samples contained 1% ammonium sulfate: ■ heated 3 min at 100°C; ▲ heated 20 min at 100°C ○ dried 16 h in air. Values in parentheses are pH after heating. (ML88 5660)

an amine hydrochloride (AMP-HCl) do not function as effectively as ammonium chloride or ammonium sulfate in catalyzing resin cure, apparently because the zinc nitrate and amine hydrochloride are not as acidic as the ammonium salts. Figure 10 compares the formaldehyde liberation behavior of resin E catalyzed with zinc nitrate (circles) and amine hydrochloride (diamonds) with that of resin E catalyzed with ammonium sulfate (triangles). In each case, the resin was heated for 3 and 20 min (open and filled symbols, respectively) at temperatures approximately 10°C above the exotherm peak temperatures (Fig. 4). As Figure 4 demonstrates, the 3-min heating was insufficient to achieve complete cure using zinc nitrate and the amine hydrochloride; however, rescans after the 20-min heating (not shown) showed no residual exotherm. The formaldehyde liberation behavior in Figure 10 indicates again that pH has a very strong influence, supplemented by degree of cure, and, possibly, by formaldehyde scavenging by the amine. Thus, these two unconventional catalysts could contribute to reducing formaldehyde emission, but they may not be acceptable catalysts from the point of view of achieving satisfactory cure at acceptable conditions.

Acid neutralizer effects

Aluminum and glass powders were shown earlier (Figs. 5 and 6) to interfere only marginally in resin cure; they neutralized the acid catalyst at a sufficiently slow rate that they did not prevent good cure. Their influence on the final pH of cured resin and on formaldehyde liberation in resin E catalyzed with ammonium sulfate is compared in Figure 11 with that of the ammonium sulfate control (triangles). Magnesium oxide was not examined here because it clearly interfered with resin cure (Figs. 5 and 6). The glass powder (squares) produced little or no effect on cured resin pH or formaldehyde liberation. In contrast, aluminum powder (diamonds) increased the cured resin pH from 2.1 to about 4, and, as a consequence, significantly reduced formaldehyde liberation.

Fig. 10. Effect of different catalysts and heating time on formaldehyde liberation from resin E at 60%, RH. ○ 1% ammonium sulfate heated at 100°C for 3 and 20 min, respectively; ◆ 2% AMP-HCl heated at 124°C for 3 and 20 min, respectively; ○ 2% Zn(NO₃)₂ heated 130°C for 3 and 20 min, respectively. Values in parentheses are pH after heating. (ML88 5661)

Fig. 11. Effect of potential acid scavengers and heating time on formaldehyde liberation from resin E at 60% RH. All samples contained 1% ammonium sulfate catalyst. Samples heated at 100°C for times indicated. Values in parentheses are pH of resins after heating. A. A no additive; □ glass powder (3%); ◇ aluminum powder (3%). (ML88 5662)
Summary and Conclusions

Using DSC, we examined the cure behavior of several UF resins in the presence of different catalysts and potential acid-neutralizing additives. These data aided in interpreting the measured formaldehyde liberation characteristics of the same systems in the cured (or partially cured) state during exposure to 23°C and 60–80% RH for 2 to 6 weeks. For those conditions, the major findings and conclusions are as follows:

(1) Cure exotherm peak temperatures and heats differ greatly among the resins. A final urea addition during synthesis, in particular, leads to higher reaction heats, probably due to increased amounts of reaction between methylols and primary amide groups during cure.

(2) Formaldehyde liberation also differs greatly among the cured resins. Final urea addition, leading to lower F/U ratio, significantly decreases formaldehyde liberation, as does extended cure. Lower F/U ratio should decrease the methylol and ether contents and thereby decrease formaldehyde liberation. Extended cure will have a similar effect but may also reduce liberation due to diffusional barriers within a more crosslinked sample.

(3) Neither zinc nitrate nor the amine hydrochloride AMP-HCl are as effective as ammonium chloride or sulfate in catalyzing resin cure. However, the ammonium salts produce a lower pH in the cured resin and higher formaldehyde liberation.

(4) Uncatalyzed resin subjected to the same heating cycle as the resin catalyzed with ammonium chloride has higher pH and lower formaldehyde liberation. The latter occurs despite the fact that infrared measurements show much greater methylol content in the heated, uncatalyzed sample.

(5) Powdered magnesium oxide interferes strongly with cure in a resin catalyzed with ammonium chloride. Powdered aluminum shows only marginal cure interference but causes an increase in cured resin pH and lowers formaldehyde liberation. Powdered soda lime glass does not interfere with cure and does not alter cured resin pH or formaldehyde liberation.

(6) Ammonium salts as cure catalysts may provide some benefit over inorganic acid catalysts because of formaldehyde scavenging by ammonia liberated during cure.

Taken altogether, these results show large differences in cure behavior and formaldehyde liberation for the different systems. Perhaps the most important observation, however, is the predominant influence of cured (or partially cured) resin acidity on formaldehyde liberation. Because UF resin hydrolysis is acid catalyzed, we take the observed increase in formaldehyde liberation with lower pH as further evidence that these formaldehyde liberation data directly reflect resin hydrolysis. It then follows that these results confirm the desirability of maintaining neutral pH for minimum formaldehyde emission and maximum durability of UF-bonded wood products. The results also illustrate the usefulness of combining the formaldehyde liberation and DSC techniques to screen UF resin systems.

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