

Common Thermoanalytical Characteristics of Durable Press Reactants Based on Cyclic Ureas*

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Synopsis

Thermal analyses, including differential scanning calorimetry (DSC), thermogravimetry (TG), and differential thermogravimetry (DTG), were performed on a series of derivatives of cyclic ureas under nitrogen. Such compounds are used extensively for durable press finishing of cotton textiles. Three common features were discovered in 15 compounds analyzed. Two features related to the presence of an oxygen-containing substituent on the ring carbons or the ring nitrogens. The former substitution was expressed as an exothermic response between 200 and 300°C and the latter as an endotherm between 300 and 400°C. Specific substituent modifications that changed these responses are described. A final feature was identified. The presence of *N*-methylol groups was recognized. This represented the first evidence that compounds capable of releasing formaldehyde have a thermoanalytical marker. The amount of residue produced in TG analyses was related to structure and indicated that thermally induced polycondensations were occurring.

INTRODUCTION

There are a large variety of crosslinking agents capable of producing durable press (DP) properties in cotton fabrics. Those most often used are adducts of cyclic ureas and formaldehyde (methylol derivatives). The cross-linked products of the reaction between the cotton cellulose and these methylol derivatives are amidomethyl ethers of cellulose. Because these reactions are reversible^{1,2} finish breakdown can occur.

Finish breakdown is ordinarily investigated using nitrogen analyses, total formaldehyde content, or formaldehyde release as the parameters measured. The information obtained is limited and relates only to those bonds involving formaldehyde in formulations.^{3,4} The goal of the present research was to achieve a basic understanding of the relationship between the structure of DP agents and their thermal stability. There is little research reported in this area. Vail and Pierce⁵ investigated the thermal decomposition of some *N*-methylol agents using capillary tubes in an oil bath and made visual observations of decomposition gases evolved. Reinhardt and Andrews⁶ recently studied thermal responses of DP cottons in a laboratory oven and concluded that

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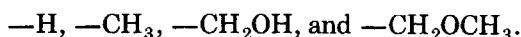
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thermal effects were neither hydrolytic nor reversible. Results indicated that heat broke bonds that were relatively stable to hydrolysis.

In the current investigation, we performed a systematic study of the effects of thermal stress on durable press reactants. The influence of structure on the thermoanalytical properties of selected cyclic ureas and their derivatives was measured by differential scanning calorimetry, thermogravimetry, and differential thermogravimetry techniques.

EXPERIMENTAL AND RESULTS

The chemicals used in this research are based on cyclic ethyleneurea (EU) or cyclic propyleneurea (PU). The structures of the initial agents examined are shown in Figure 1. Substituents on the ring nitrogens included:



Substituents on the ring carbons included:

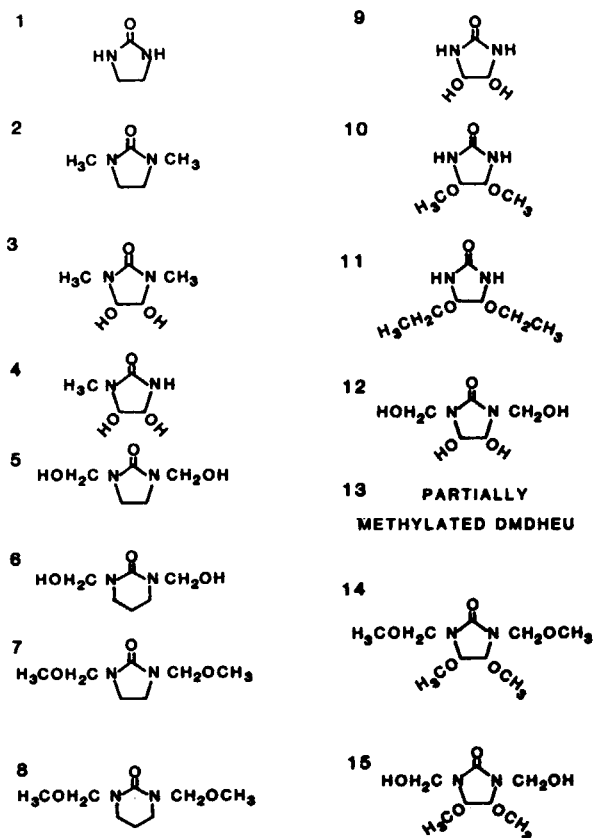


Fig. 1. Identification code number and chemical structures of the compounds based on cyclic ethyleneurea and cyclic propyleneurea used in this study.

TABLE I
Description of Compounds

| Sample code | Substituents ^a | | Source ^b code | Physical state |
|----------------|-----------------------------------|-----------------------------------|--------------------------|----------------|
| | Ring nitrogens | Ring carbons | | |
| 1 | —H | —H | A | Solid |
| 2 | —CH ₃ | —H | A | Liquid |
| 3 | —CH ₃ | —OH | B | Solid |
| 4 | —CH ₃ (MONO) | —OH | B | Solid |
| 5 | —CH ₂ OH | —H | C | Solid |
| 6 ^c | —CH ₂ OH | —H | C | Solid |
| 7 | —CH ₂ OCH ₃ | —H | C | Solid |
| 8 ^c | —CH ₂ OCH ₃ | —H | C | Liquid |
| 9 | —H | —OH | B | Solid |
| 10 | —H | —OCH ₃ | B | Solid |
| 11 | —H | —OCH ₂ CH ₃ | B | Solid |
| 12 | —CH ₂ OH | —OH | C | Solid/solution |
| 13 | Partially methylated #12 | | B | Solution |
| 14 | —CH ₂ OCH ₃ | —OCH ₃ | C | Liquid |
| 15 | —CH ₂ OH | —OCH ₃ | B | Solution |
| Urea | | | A | Solid |
| Propyleneurea | | | A | Solid |

^aSubstitution is symmetrical unless stated otherwise.

^bA = reagent-grade chemical; B = synthesized at SRRC (References 7, 8); C = synthesized at BASF Ammonia Laboratory.

^cPropyleneureas.

A description of each chemical is given in Table I. Agents were prepared earlier by published procedures,^{7,8} or obtained from commercial* sources as indicated in the table. Most isolated samples were solids, some were liquids; other samples were solutions of unisolated derivatives. The samples from BASF were synthesized in their laboratories. A commercial solution of the most common durable press finishing agent, *N,N'*-dimethyloldihydroxyethyl-eneurea (DMDHEU, #12), was also analyzed.

Solid samples were dried overnight in a vacuum oven at 60°C and then desiccated to remove any residual water. Under those conditions, compound #8 liquified in the oven and remained so until it cooled to room temperature. No other cleanup procedures were carried out.

Differential scanning calorimetric (DSC), thermogravimetric (TG), and differential thermogravimetric (DTG) analyses were performed with the DuPont 1090 Thermal Analyzer. The DSC 910 and TGA 951 modules were employed. The instrument was equipped with temperature programming and computerized data acquisition capabilities, software for data analyses, and a printer/plotter. The dynamic purge gas was nitrogen flowing at 300 mL/min. Both DSC and TG curves were obtained at a 15°C/min heating rate.

DSC curves were plotted initially using the most sensitive scale possible. Samples were weighed accurately but not exactly to 5.0 mg. Sample size was difficult to control with some specimens, especially the liquids. With the use of

*Names of companies or commercial products are given solely for providing scientific information and do not imply endorsement by the U.S. Department of Agriculture over others not mentioned.

TABLE II
Thermoanalytical Results of Cyclic Urea Compounds

| Sample code | Substituents ^a | | Ring nitrogens | Ring carbons | DSC peak temperatures (°C) ^b | | TGA peak temperatures (°C) ^c | | | | |
|----------------|-----------------------------------|------------------------------------|----------------|--------------|---|----------|---|----------|----------|----------|----------|
| | Ring nitrogens | Ring carbons | | | 79 | 133 | 208, 258 | 78 | 154 | 240 | 338 |
| 1 | -H | -H | | | 79 | 133 | 208, 258 | 78 | 154 | 240 | 338 |
| 2 | -CH ₃ | -H | | | | 138 | | | | | |
| 3 | -CH ₃ | -OH | | | | 150 | 215 | | | 208 | |
| 4 | -CH ₃ (MONO) | -OH | | | | 107, 141 | ×261 | | | 225, 260 | |
| 5 | -CH ₂ OH | -H | | | 90 | 146 | | 384 | 192 | 271 | 389 |
| 6 ^d | -CH ₂ OH | -H | | | | 176 | 232 | 375 | 176 | 238 | 380 |
| 7 | -CH ₂ OCH ₃ | -H | | | | 176 | | | | | |
| 8 ^d | -CH ₂ OCH ₃ | -H | | | 49 | 154 | | 369 | 185 | | |
| 9 | -H | -OH | | | | 139 | ×248 | | 147, 154 | 230, 244 | |
| 10 | -H | -OCH ₃ | | | | 114 | 202, ×283 | | | 202, 278 | |
| 11 | -H | -OCH ₂ OCH ₃ | | | | 124, 164 | 217, ×295 | | | 224 | 308 |
| 12 | -CH ₂ OH | -OH | | | 76 | 135 | ×245 | 348 | 140 | 245 | 363 |
| 13 | Partially methylated #12 | -OH | | | | 160, 180 | 230 | 343 | | 205, 236 | 336 |
| 14 | -CH ₂ OCH ₃ | -OCH ₃ | | | | 174 | | | 188 | | |
| 15 | -CH ₂ OH | -OCH ₃ | | | | 194 | ×275 | 328 | | 207, 288 | 329 |
| Urea | | | | | | 137 | 205, 236 | 322, 387 | | 242 | 348, 356 |
| Propyleneurea | | | | | | | 270 | | | 285 | |

^aSubstitution is symmetrical unless otherwise stated.

^bExothermic peak denoted by ×.

^cTemperatures of maximum weight loss.

^dPropyleneureas.

additional software for normalization of all DSC curves to 5.0 mg sample size, the curves were replotted on the same heat flow scale to allow for direct comparisons.

Thermogravimetric analyses (TGA) were performed with samples that weighed approximately 10 mg. Percent weight loss was monitored and residues were measured at 575°C. TG peak temperature is the term employed to represent the temperature at which the maximum rate of weight loss occurred.

The derivative of each TG curve was also calculated. These thermograms were used to calculate the TG peak temperatures and to identify melting point peaks in DSC analyses.

The results of the DSC and TG analyses are tabulated in Table II. The peak temperature data are arranged so that some general similarities could be readily observed.

The DSC thermograms of urea, ethyleneurea, and propyleneurea are shown in Figure 2. The top curve is the DSC curve of urea; the first peak was the melting peak followed by decomposition peaks. There are some similarities in the urea and EU curves. The second peak of the EU thermogram was the melting of the compound and the subsequent peaks were associated with decomposition that was completed at a lower temperature than for urea.

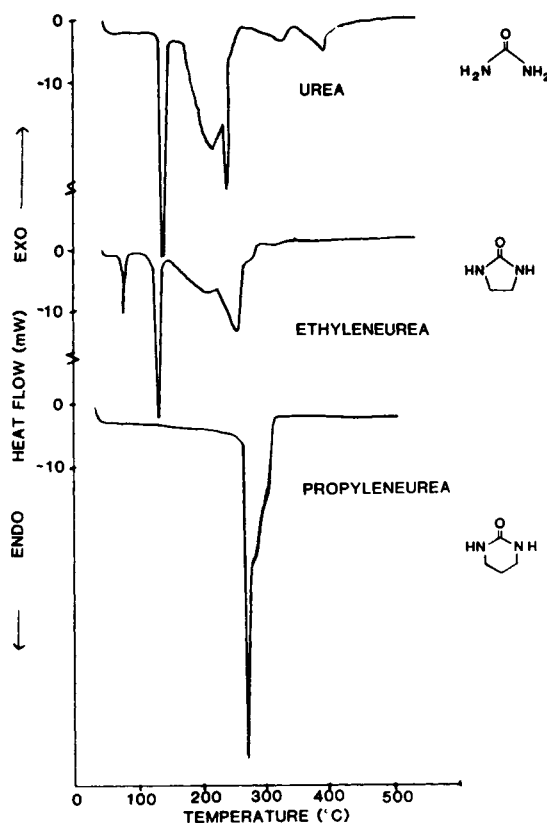


Fig. 2. Differential scanning calorimetric (DSC) thermograms of urea, ethyleneurea, and propyleneurea.

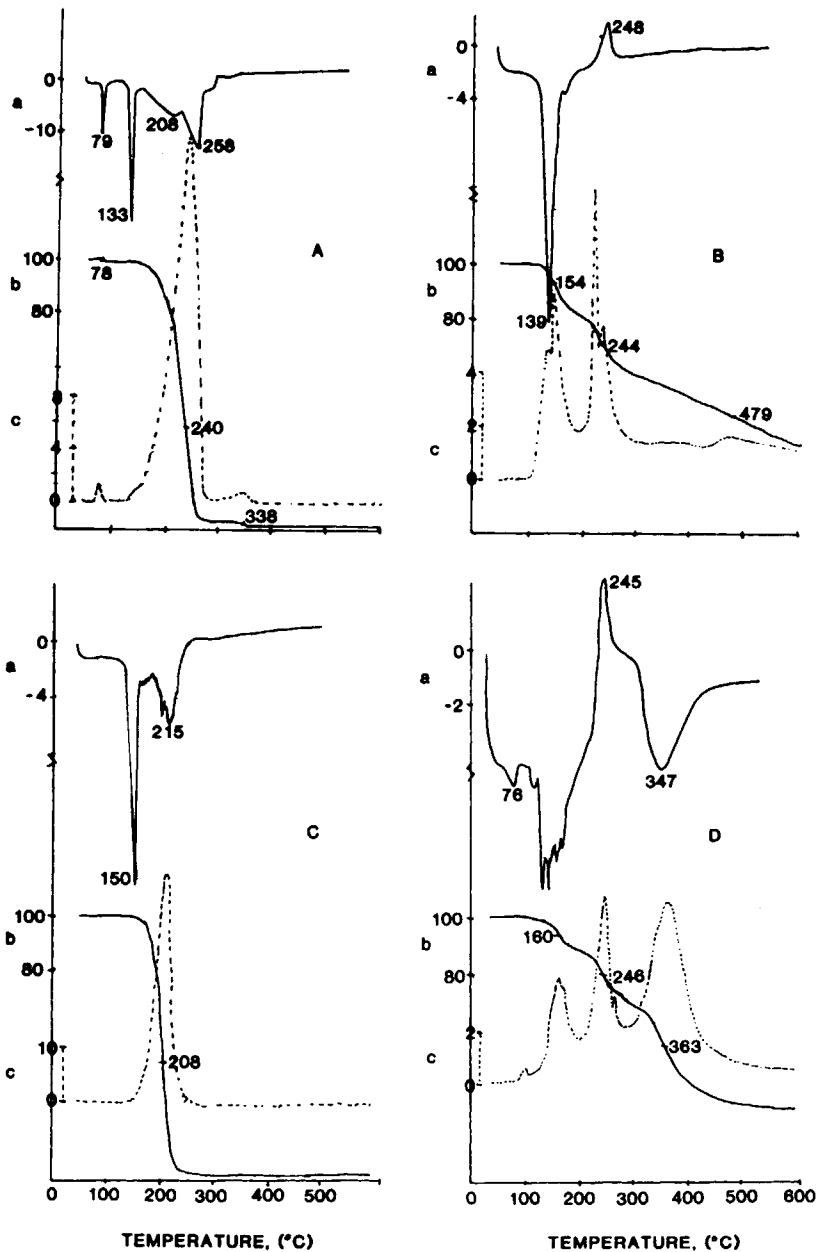


Fig. 3. Differential scanning calorimetric (DSC), thermogravimetric (TG), and differential thermogravimetric (DTG) thermograms of: (A) ethyleneurea; (B) dihydroxyethyleneurea; (C) *N,N'*-dimethyldihydroxyethyleneurea; (D) *N,N'*-dimethyloldihydroxyethyleneurea. Measurement unit for DSC curves (a) = heat flow in (mW), TG curves (b) = weight percent, and DTG curves (c) = percent weight loss/minute.

Propyleneurea melted at a much higher temperature and then decomposed rapidly, reached complete decomposition at approximately the same temperature as EU.

The DSC, TG, and DTG thermograms of four compounds contained in composite Figure 3 illustrate the variety of thermoanalytical features encountered in this research. The TG and DTG curves are plotted beneath the DSC curves. Thermograms of ethyleneurea (EU, compound #1) are contained in Figure 3A. The DSC curve for EU contained a small endothermic peak at 79°C, another at 133°C and a large area of endothermic decomposition activity between 150–350°C with the major peak at 258°C. There was only 0.7% weight loss associated with the first endothermic peak and no weight loss with the second. The 133°C peak represented the melting point of ethyleneurea. Major weight loss (96%) was associated with the large endothermic, decomposition area. The corresponding TG peak temperature was 240°C. At 575°C only 1.5% residue was present. There was virtually no change in residue after 400°C.

Figure 3B illustrates the thermoanalytical results from —OH substitution on the ring carbons. Dihydroxyethyleneurea (DHEU, #9) was reported to melt at 133–135°C.⁹ With DSC analysis, we found the agent melted, but immediate decomposition/volatilization followed. The largest peak, an endotherm, occurred at 139°C and corresponded to this process. Also, a new feature was present in this thermogram. There was an exothermic peak at 248°C. The corresponding TG curve showed two distinct weight-loss regions and a continuous, gradual loss until at 575°C there was 35.4% residue. The DTG curve showed that more than one peak was present in each of the two major weight loss regions. Between 100–200°C, 19% of the sample was lost, and between 200–300, 21% was lost.

Figure 3C shows the thermograms of cyclic ethyleneurea with methyl groups present on the ring nitrogens and hydroxyls on the ring carbons. After melting, which peaked at 150°C, *N,N'*-dimethyldihydroxyethyleneurea (#3) rapidly began to decompose with jagged, endothermic activity. By 300°C all thermal activity had ceased. The TG curve revealed that 96% of the sample was lost by 300°C. At 575°C only 3.1% of the material remained.

The most common agent used commercially in durable press finishing of cotton textiles is *N,N'*-dimethyloldihydroxyethyleneurea (DMDHEU, #12). The thermograms for this compound are contained in Figure 3D. The DSC curve was complex. A small endotherm appeared. This represented the melting point of DMDHEU (reported by Gonzales et al.¹⁰ to be 76.5°C). The DSC curve next showed a region of jagged, endothermic activity between 100–200°C. This activity was followed by the appearance of an exotherm peaking at 245°C. The DSC curve ended with a broad endotherm peaking at 347°C. The thermogravimetric curves were also complicated. Three major weight loss regions were identified and represented 12%, 18%, and 36% weight loss respectively. DMDHEU had 28.3% residue at 575°C.

DISCUSSION

Common thermoanalytical characteristics among cellulose finishing agents were sought. DSC thermograms of the first compounds illustrated above

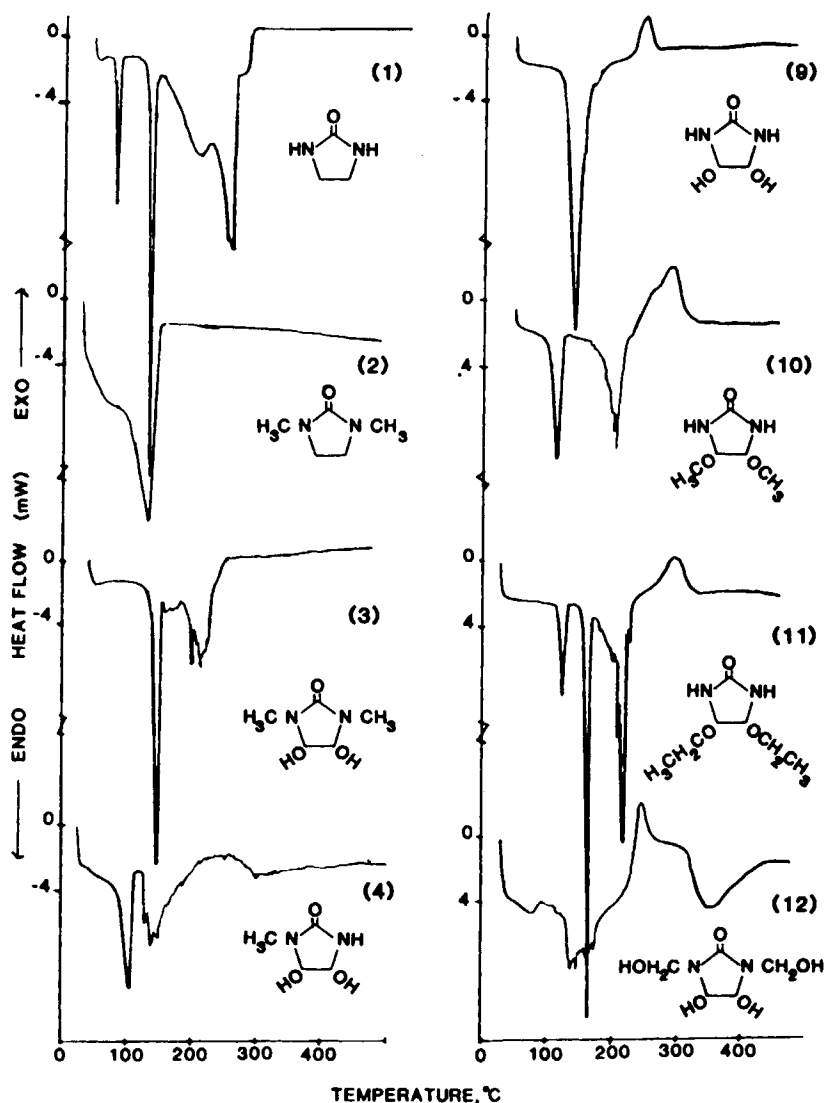


Fig. 4. Comparison of DSC thermograms of compounds shown to illustrate the structures that produce an exothermic response between 200–300°C.

presented one notable feature. Two of the materials showed an exotherm between 200–300°C. This was the first characteristic investigated. Figure 4 presents the DSC thermograms of 8 compounds that illustrate the structural features observed to be necessary to produce the exotherm.

The exotherm in the range 200–300°C was present in the DSC curve of DHEU (#9). It was not seen in the curves of *N,N*-dimethylethyleneurea (#2) or *N,N*-dimethyldihydroxyethyleneurea (#3) which contained methyl substituents on the nitrogens. However, when the ring nitrogens remained unsubstituted and the ring carbon's hydroxyl groups were replaced with methoxy (#10) or ethoxy substituents (#11), the exotherm was still present.

Therefore, the initial hypothesis was that an exotherm was produced when the ring carbons were substituted with an —OH or an —OR group and the ring nitrogens remained unsubstituted.

Additional support for the theory that unsubstituted ring nitrogens are necessary to produce an exotherm was found in the DSC curve for *N*-methyl-dihydroxyethyleneurea (#4). The DSC thermogram showed an indistinct exothermic portion that could be attributed to the presence of the single unsubstituted nitrogen.

The DSC curve for *N,N'*-dimethyloldihydroxyethyleneurea, DMDHEU (#12), forced the final modification of the hypothesis. This compound, with its methylol group present on the ring nitrogens, also exhibited the exotherm. The final hypothesis states that an exotherm in the 200–300°C range is

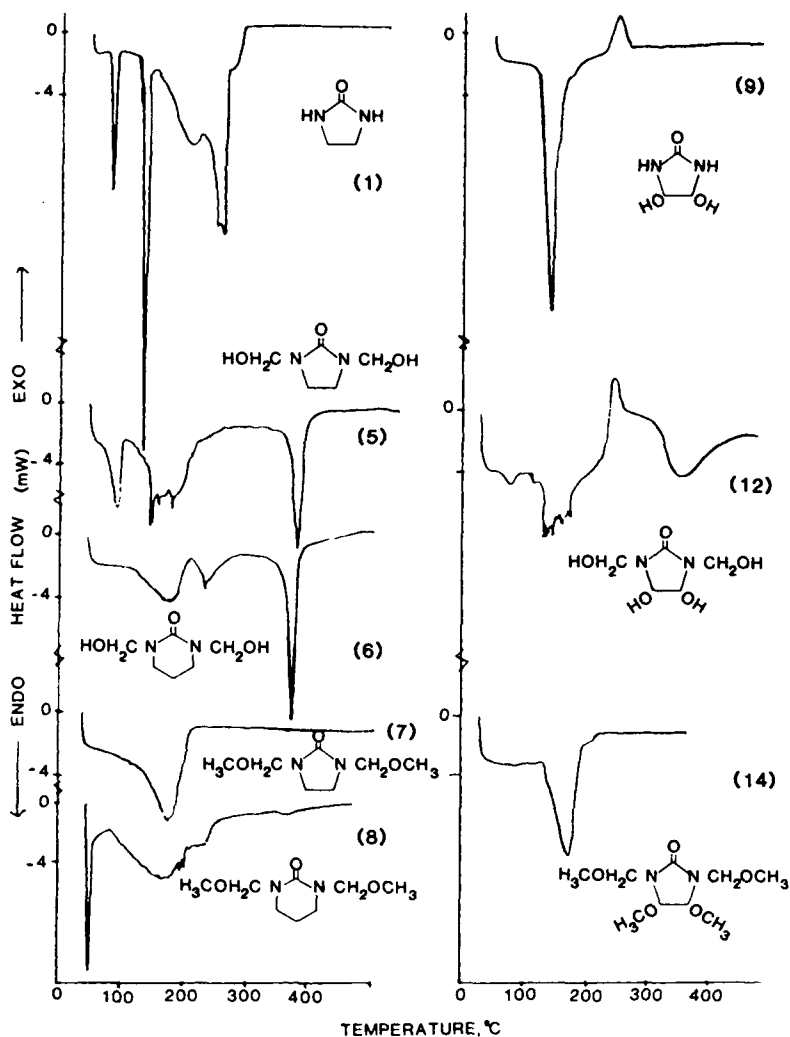


Fig. 5. Comparison of DSC thermograms of compounds shown to illustrate the structures that produce an endothermic response between 300–400°C.

produced in ethyleneurea derivatives when the ring carbons are substituted with pendant oxygen-containing groups ($-\text{OH}$ or $-\text{OR}$), and the ring nitrogens remain unsubstituted or are substituted with groups containing terminal hydroxyls.

Figure 5 shows the DSC thermograms of additional cyclic ureas that illustrate a second common feature discovered. The upper two thermograms are the same compounds as in Figure 4. The next lower curves illustrate the behavior of *N,N'*-dimethylolethyleneurea (#5) and DMDHEU (#12). Both compounds produced an endothermic response between 300–400°C. A similar endotherm was produced by *N,N'*-dimethylolpropyleneurea (#6).

When DMDHEU was fully etherified with methanol, the product was an isolated liquid. This compound (#14) produced a simple DSC thermogram that is illustrated at the lower right of Figure 5. As predicted by the first hypothesis, no exotherm was produced. Nor did this material give an endotherm between 300–400°C. Similarly, when *N,N'*-dimethoxymethylated eth-

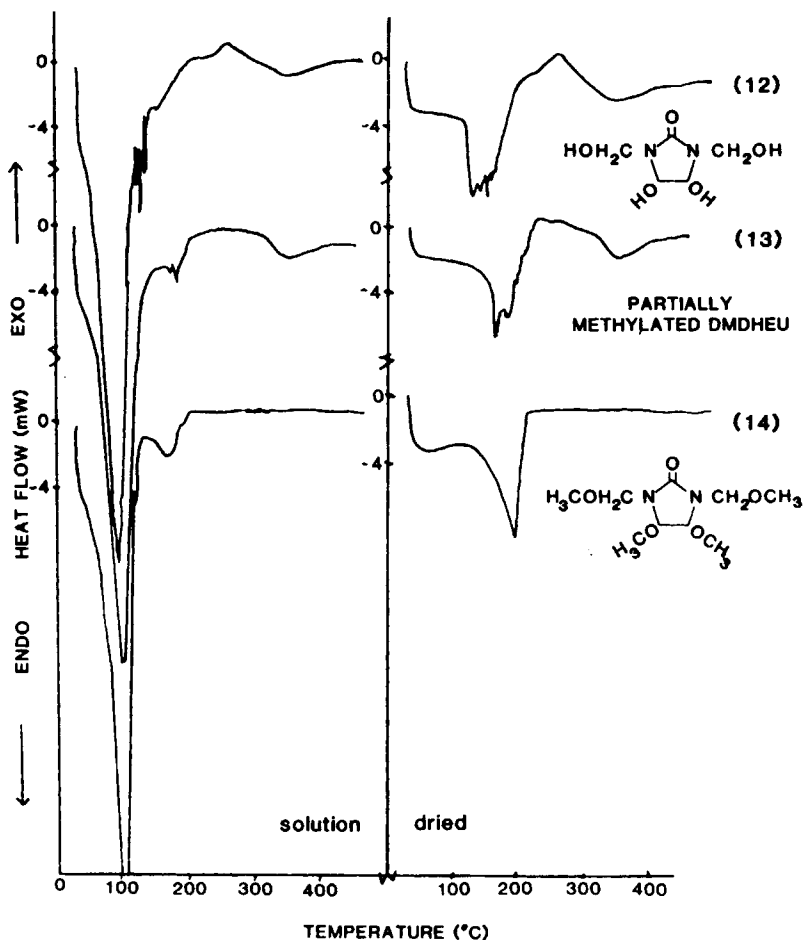


Fig. 6. Comparison of DSC thermograms of compounds shown to illustrate solution masking of DSC features and the increased resolution of features after drying a solution for 2 h at 60°C.

ylene and propylene ureas (#7, 8) were analyzed, their DSC thermograms showed no significant endothermic activity between 300–400°C.

From the above observations, the presence of an endotherm between 300–400°C in the DSC curves of cyclic ureas can be predicted by a second hypothesis based on agent structure. Because *N,N'*-dimethylethyleneurea produced no such endotherm, we can state that, for an endotherm to occur between 300–400°C, the ring nitrogens must be substituted with —CH₂OH, and that the ring carbons must be either unsubstituted or have free hydroxyls.

A partially methylated DMDHEU was prepared as a 50% solution, and was neither isolated nor purified. The DSC thermograms of this solution, as well as 50% solutions of DMDHEU and tetramethylated DMDHEU, are illustrated on the left side of Figure 6. The water endotherm was so large that it effectively masked the low temperature features of the thermograms. The exotherm of DMDHEU was still visible as was the higher temperature endotherm. The partially methylated sample showed only a hint of an exotherm between 200–300°C, however, the endotherm was still recognizable. This indicated the presence of some free hydroxyl groups in the molecule.

These three solutions were subjected to a drying step in an attempt to remove the water without substantially altering the DSC thermograms. After 2 h at 60°C in a forced draft laboratory oven, a portion of each material (generally a thick syrup) was tested. These thermograms are given in the right side of Figure 6. The major features of both DMDHEU and tetramethylated DMDHEU were present. The partially methylated sample clearly showed a small exothermic peak between 200–300°C. The drying step had substantially improved the distinctiveness of the samples' DSC curves.

From the two hypotheses developed in this research, an experiment was performed to predict the thermoanalytical features of an additional compound. The basis of the predictions is outlined in Table III.

This new compound was expected to produce an exotherm in the range of 200–300°C. An endotherm would be present between 300–400°C if an oxygen-containing group was required, that is, if alkyl substitution on hydroxyls did not destroy the endotherm.

A sample of methylolated dimethoxyethyleneurea was analyzed first as a 50% solution. The thermograms of the four ethyleneurea derivatives listed in Table III and methylolated dimethoxyethyleneurea (#15) are shown in Figure 7. The DSC curve of solution #15 had the large water endotherm; however, it showed both an exotherm and an endotherm as predicted. When a

TABLE III
Prediction of Thermoanalytical Response Based Upon Observed Responses in Cyclic Ureas

| Substituent on ring | | Exotherm 200–300°C | Endotherm 300–400°C |
|-----------------------------------|-------------------|-----------------------|------------------------|
| —N | —C | | |
| —CH ₂ OH | —H | NO | YES |
| —H | —OCH ₃ | YES | NO |
| —CH ₂ OH | —OH | YES | YES |
| —CH ₂ OCH ₃ | —OCH ₃ | NO | NO |
| —CH ₂ OH | —OCH ₃ | ? | ? |

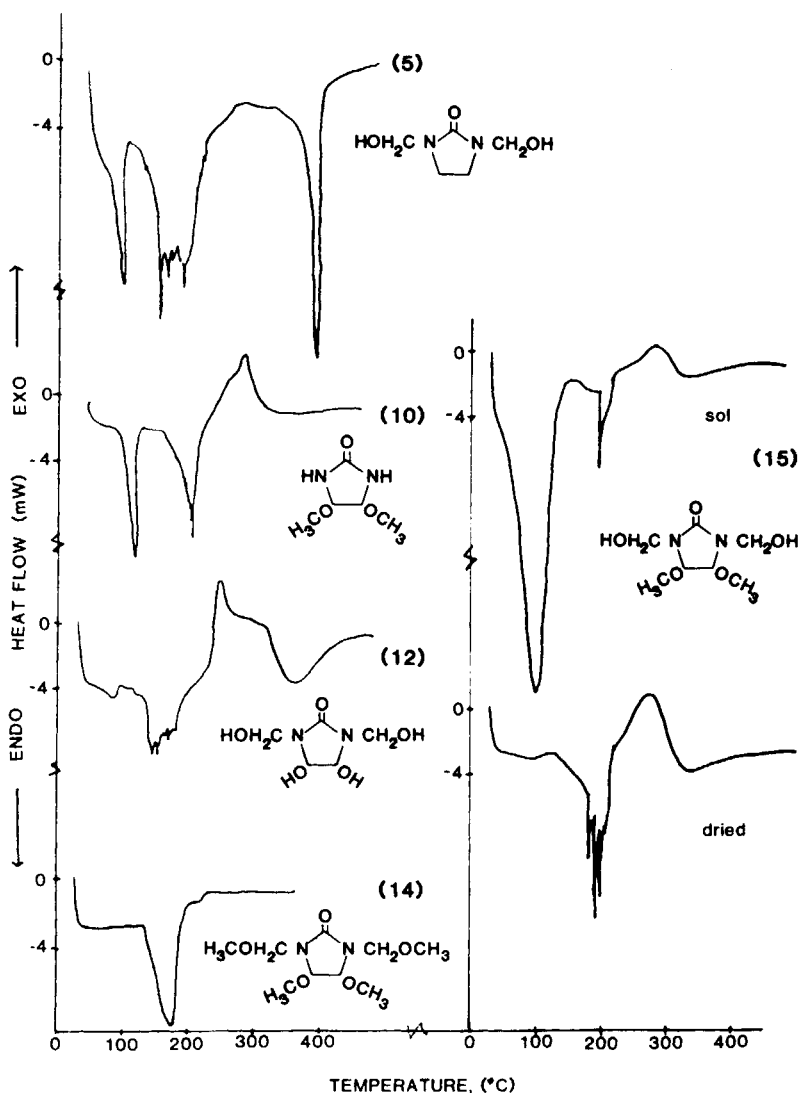


Fig. 7. Comparison of DSC thermograms of compounds listed in Table III and the curves for *N,N'*-dimethyloldimethoxyethyleneurea, in solution and dried. The new compound showed the predicted exothermic and endothermic responses.

portion of solution #15 was dried for 2 h at 60°C and analyzed by DSC, the features of the thermogram were clearer. The exotherm was easily recognizable.

Additional significant information was realized from these thermograms. The dried material (#15) showed jagged endothermic activity between 100–230°C that had been masked by the water endotherm. Previous isolated samples had produced similar activity in this temperature range. All those materials shared a common structural feature, namely, the presence of *N*-methylol groups. Figure 8 illustrates the DSC thermograms of those compounds. The presence of *N*-methylol groups was expressed as a jagged endo-

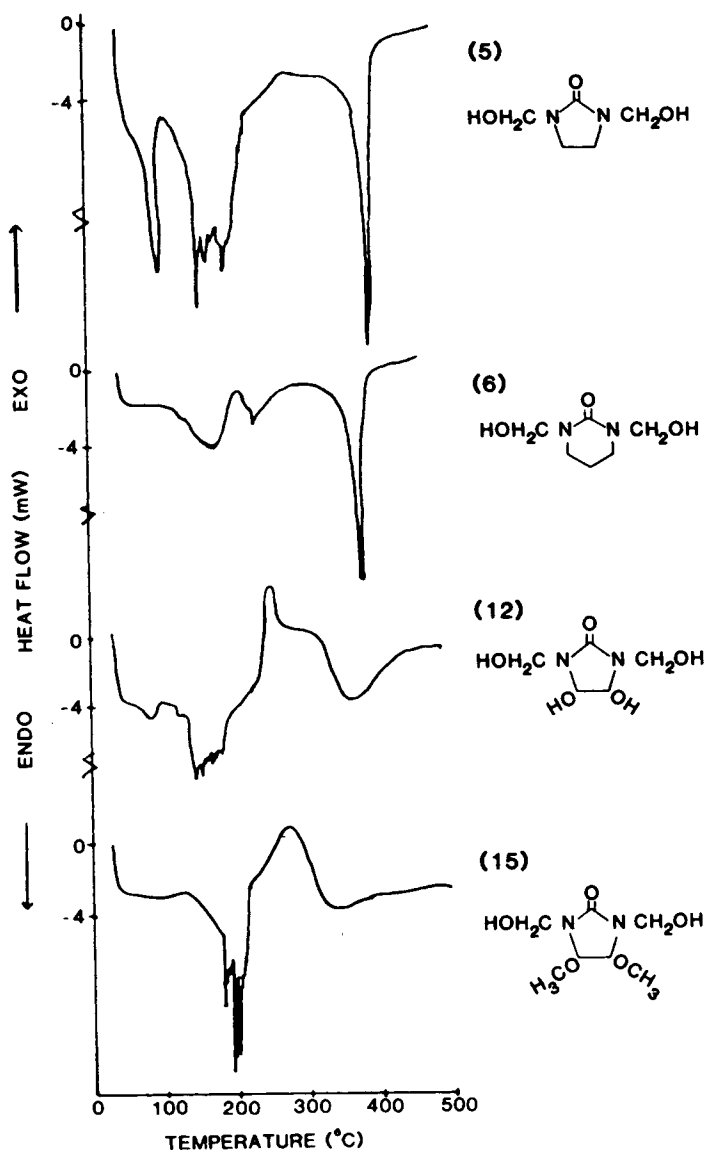


Fig. 8. Comparison of DSC thermograms of compounds shown to illustrate the presence of low temperature, endothermic decomposition (100–230°C) associated with *N*-methylol groups.

thermic activity between 100–230°C in DSC thermoanalysis. This finding represented the first evidence that the compounds that most easily release formaldehyde have a recognizable thermoanalytical feature.

The residue, expressed as percentage of starting material that remained after thermogravimetric analyses, was the final parameter investigated. All the residues were measured at 575°C. Figure 9 presents the compound structure (except for partially methylated DMDHEU) and the corresponding percent residue values. The residue value for ethyleneurea was low; those for urea and propyleneurea (0.05 and 1.1) were lower.

TGA RESIDUE (%)

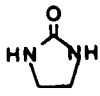
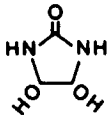
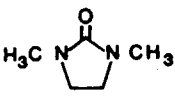
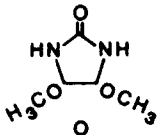
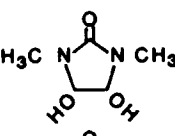
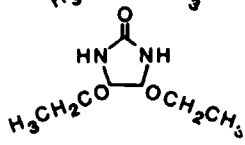
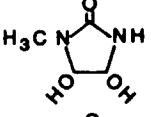
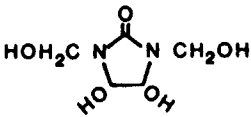
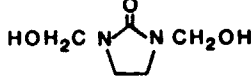
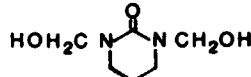
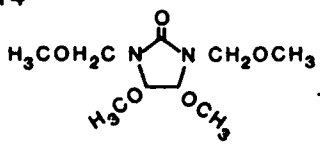
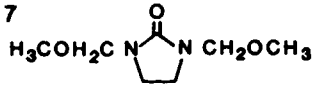
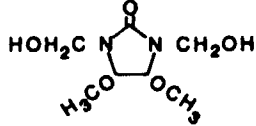
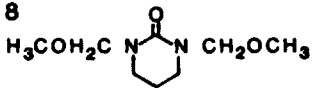
| | | | | | |
|---|---|------|----|---|------|
| 1 |  | 1.5 | 9 |  | 35.4 |
| 2 |  | 0.7 | 10 |  | 34.1 |
| 3 |  | 3.1 | 11 |  | 25.8 |
| 4 |  | 23.9 | 12 |  | 28.3 |
| 5 |  | 12.0 | 13 | PARTIALLY METHYLATED DMDHEU | 29.4 |
| 6 |  | 13.4 | 14 |  | 1.1 |
| 7 |  | 1.3 | 15 |  | 53.2 |
| 8 |  | 1.8 | | | |

Fig. 9. Thermogravimetric analyses (TGA) data on present residue at 575°C of the compounds based on cyclic ethyleneurea and cyclic propyleneurea used in this study.

The first correlation discovered was that the cyclic ureas which produced an exotherm in thermoanalyses also produced high residues. The pure liquids boiled/decomposed early and left small residues. There were substantial differences in residues among *N,N'*-dimethylethyleneurea (#2), *N,N'*-dimethyldihydroxyethyleneurea (#3) and *N*-methyldihydroxyethyleneurea (#4). The presence of a single, unsubstituted nitrogen caused an eightfold increase in residue. All the cyclic ureas studied here that had unsubstituted ring nitrogens produced high residue values. Additionally, those samples that had *N*-methylol substituents also had moderate to high residues.

Figure 10 shows the TG thermograms for all the materials studied including urea and the two cyclic urea controls. The upper portion of the figure contains the curves for those agents that retained less than 5% residue at 575°C. Except for urea and compound #2, all these materials thermally degraded in

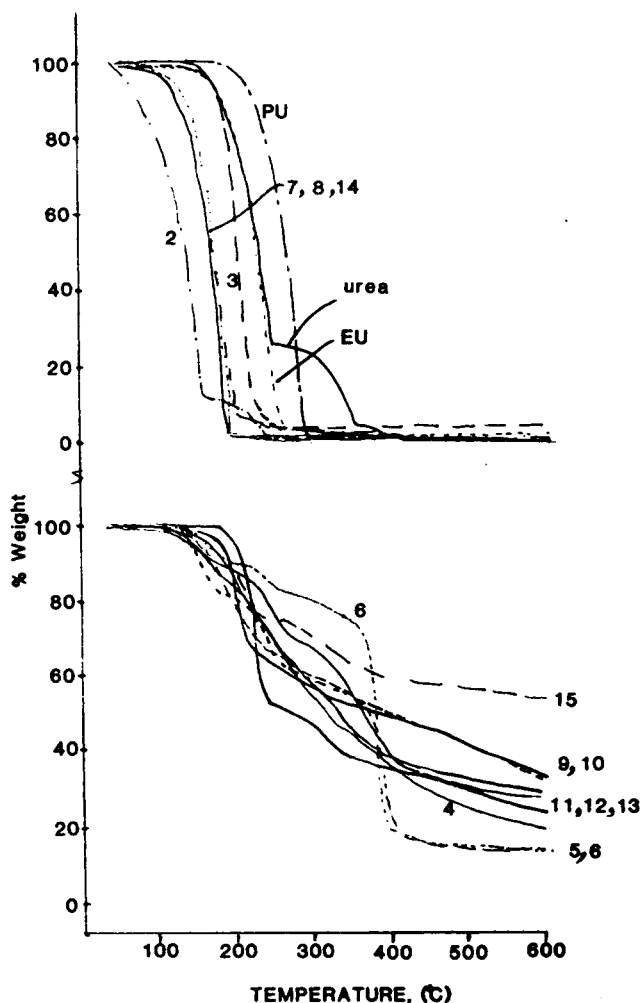


Fig. 10. Thermogravimetric analyses (TGA) curves of all compounds in this study. Upper curves are of samples that left comparatively no residue. Lower curves are from samples that left high residues. Curves for #13 and #15 represent dried solutions.

a single, steep weight loss step. Some materials may have simply volatilized without decomposing; others may have decomposed through ring cleavage. By 300°C, the degradation process of all but urea was completed. As stated earlier, urea was completely decomposed by 400°C.

The lower portion of Figure 10 contains the TG curves for those agents that retained large residues. These compounds apparently responded to heat through more complex mechanisms. Most still retained > 60% of original weight by 230°C, the maximum temperature associated with loss of *N*-methylol groups.

Vail *et al.* claim formation of bisamides under alkaline conditions by linear compounds: $\text{RC}(\text{O})\text{NH}(\text{CH}_2\text{OH})$.^{11,12} Others reported products/contaminants obtained from addition of ureas and glyoxals¹³ including $-\text{CHOH}-\text{CHOH}-$ bridges between cyclic ureas. Compounds with this latter bridge group were

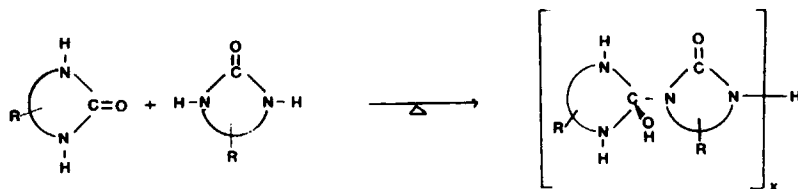


Fig. 11. Generalized reaction showing proposed formation of polycondensation products from cyclic ureas initiated by the extreme heat of thermoanalysis.

TABLE IV
Comparison of *N*-methylol content with Percent Weight loss in TGA of Jagged Endothermic Peak Associated with *N*-methylol Group

| Compound | MW | Percent substituent | | TGA weight loss % |
|----------|-----|---------------------|----|-------------------|
| | | mono | di | |
| 5 | 146 | 20 | 41 | 34 |
| 6 | 160 | 18 | 38 | 11 |
| 12 | 178 | 16 | 34 | 23 |
| 15 | 206 | 14 | 29 | 24 |

Note: Partially methylated DMDHEU (#13) lost 24%

used by Frick and Harper¹⁴ to produce nonformaldehyde textile finishes. Oxydimethylene dimers of DMDHEU have also been reported by Pasad.¹⁵ Formation of these materials could contribute to residue production in the thermal degradation process.

Residue production from the compounds shown in Figures 9 and 10 could also occur by a polycondensation mechanism initiated by the high heat encountered in thermoanalyses. Such a possible condensation is illustrated in Figure 11. A requirement for this mechanism is that a ring nitrogen be unsubstituted.

However, several compounds that produced substantial residues contained substituents on the ring nitrogen. We have postulated that the methylol groups are lost early in the heating process. This can be supported semi-quantitatively by TGA data as seen in Table IV.

For those compounds listed, the weight loss data indicated that a substantial portion of the pendant methylol groups were gone. The loss of the substituent early in the heating process (100–230°C), apparently removed the hindrance to such a polycondensation.

The actual reactions that cause the polymerization/condensation to occur are unknown. They are likely to be combinations of this proposed mechanism and others not mentioned.

SUMMARY AND CONCLUSIONS

Thermoanalytical techniques have been successfully employed to investigate the effects of thermal stress on cyclic ureas. Such compounds are used in the durable press finishing of cotton textiles. DSC and TGA thermograms were studied and several relationships between agent structure and thermal

responses were revealed. The DSC results may be summarized:

DSC Responses as Related to Agent Structure

| Heat flow | Temp Range °C | Substituent on | |
|-----------|------------------|-------------------------|--------------|
| | | Nitrogen | Carbon |
| Endotherm | 100–230 | —CH ₂ OH | —H, —OH, —OR |
| Exotherm | 200–300 | —H, —CH ₂ OH | —OH, —OR |
| Endotherm | 300–400 | —CH ₂ OH | —H, —OH, —OR |

Residue data from TG analyses indicated that, while cyclic ethyleneurea and propyleneurea did not produce significant residue, derivatives of cyclic EU and PU condensed when heated if the ring nitrogens were unsubstituted, or if the substituents (primarily —CH₂OH) were lost at low temperatures. When the ring nitrogens were methyl-substituted, the condensation reaction was blocked and decomposition was rapid.

In addition to the basic knowledge about the thermal characteristics of these durable press agents and how they relate to chemical structure, an important practical application emerged. The recognition of the endothermic loss of *N*-methylol groups at low temperatures by DSC analyses, represents a first direct link between thermoanalytical data and the major substituent known to release formaldehyde.

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