

Upgrading Melamine–Urea–Formaldehyde Polycondensation Resins with Buffering Additives.

I. The Effect of Hexamine Sulfate and Its Limits

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ABSTRACT: Iminoamino methylene base intermediates obtained by the decomposition of hexamethylenetetramine (hexamine) stabilized by the presence of strong anions such as SO_4^{2-} and HSO_4^- , or hexamine sulfate, were shown to markedly improve the water and weather resistance of hardened melamine–urea–formaldehyde (MUF) resins used as wood adhesives and of the wet internal bond strength performance of wood boards bonded with them. The effect was shown to be induced by very small amounts, between 1 and 5 wt % of this material on resin solid content. This strong

effect allowed the use of MUF resins of much lower melamine content and also provided good performance of the bonded joints. Because the main effect was also present at the smaller proportion of hexamine as hexamine sulfate, it was not due at all to any increase in the molar ratio of the resin as a consequence of hexamine sulfate addition. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 203–214, 2003

Key words: resins; strength; adhesives; polycondensation

INTRODUCTION

The wood panel industry relies heavily on the use of synthetic resins and adhesives, adhesively bonded products of some kind or other constituting about 80% of the wood products on the market today: in short, without adhesives and resins, this industry would not exist.¹ The consumption of panels and their respective adhesives increased, just in western Europe, 13% during the last 4 years and 30% in 10 years. The adhesives used for these panels in 1998 (as shown by data from the European Panels Federation) were 3.2 million tons of resin solids, of which 2.6 million tons were urea–formaldehyde (UF) resins used for interior-grade applications; for exterior-grade applications, 350 thousand tons of melamine–urea–formaldehyde (MUF) resins and 260 thousand tons of phenol–formaldehyde resins were used.

The wood panel industry thus relies on polycondensation resins, including MUF resins. Because performance standards have been established throughout the world for wood composite boards, the percentages on wood of adhesives/resins used for the manufacture of these products to satisfy the requirements of such standards varies little around a typical percentage value characteristic for each type of resin and process used. The resin binder, which constitutes the

more expensive material cost component, is one of the parameters of which it is not possible to markedly change the percentage because this would cause a decrease in performance and, hence, a failure to satisfy the relevant standard specifications. In MUF resins, the high cost of the resin is due to the high cost of melamine. In the past, research on these resins has focused on the effort to decrease the weight proportion of melamine in relation to the proportion of urea in the resin while maintaining the MUF adhesive exterior performance. Thus, from the pure melamine–formaldehyde (MF) resins of 40 years ago, the industry passed to melamine:urea (M:U) weight ratios of 70:30 and, finally, 50:50 and 40:60 for the top-performance range of MUF resins used today. Resins of lower melamine content also exist, where, for example, the M:U weight ratio is 30:70 or even lower, but their exterior-grade performance is noticeably worse, and they are not used for the same target applications.

Attempts to change this situation have led to the proposal of several different approaches to maintain or improve the performance of MUF resins at much lower proportions of melamine. Most of these are based on either resin engineering modifications during resin manufacture or the use of additives during resin application. Among such systems are (1) the use of melamine salts, such as melamine acetates just added in the glue mix to upgrade UF resins to MUF performance^{2–7} or to upgrade low melamine content MUF resins;⁸ (2) the use of small proportions of isocyanates in the glue mix or in the resin to upgrade UF and MUF resin performance;^{6,9–11} (3) the use of ac-

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etals, such as methylal, ethylal, and others, as more effective solvents for melamine and higher molecular weight melamine resin fractions and, hence, as facilitators of homogeneous-phase reactions;^{12,13} (4) the adaptation to this purpose of the use of linear long-chain aliphatic diamines and triamines^{6,14-16} or of aldehydes with long aliphatic pendant chains;¹⁷ and (5) the special use of resin engineering techniques during the manufacture of the resin.¹⁸ All these systems work rather well, but there is also a system that presents exceptional performance but that has not been explicitly reported^{6,18-20} as yet because the reasons why it causes a considerable improvement in performance while decreasing melamine content in MUF resins were not known.

Any additive capable of markedly decreasing the percentages of adhesive needed must also be economically viable and easy to use and produce by industry, for instance, just by the addition to a glue mix.

This article then deals with the development of a totally novel low-cost additive, the use of which just by addition into the adhesive glue mix is capable of more than doubling the exterior-grade performance of MUF resins and, conversely, of allowing the use of MUF resins containing less than half the proportion of melamine while maintaining exterior grade performance unaltered. Our second article deals with some of the underlying principles of its functioning mechanism.

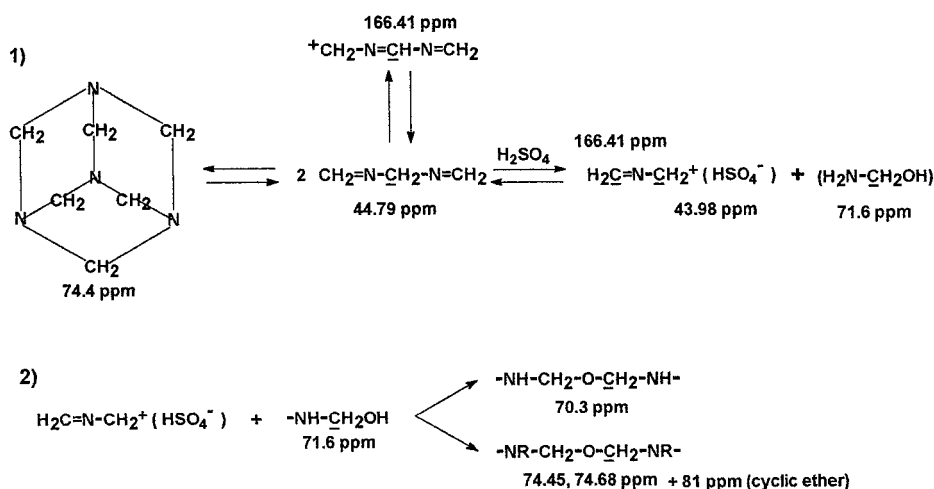
BACKGROUND

Hexamine decomposes readily to formaldehyde and ammonia in an acid environment and slightly less readily to formaldehyde and trimethylamine in an alkaline environment.^{21,22}

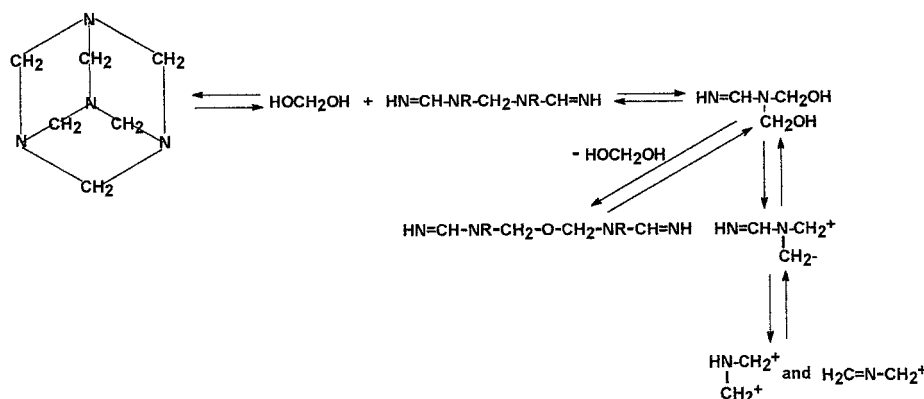
Work on fast-reacting synthetic resorcinol-formaldehyde novolacs (thus deficient in formaldehyde)²³ and other equally reactive species, such as MF resins equally deficient in formaldehyde,²⁴ used as models showed faster high-temperature curing and gelling with hexamine rather than formaldehyde. These experiments gave the first clue as to what happens in the hexamine curing of melamine resin or other highly reactive species. Cross-polarization/magic-angle spinning ¹³C-NMR solid-phase spectra of the hardened resins showed that the hardened resin networks presented a very high proportion of dibenzylamine and tribenzylamine bridges [—CH₂—NH—CH₂— and —CH₂—N(—CH₂—)—CH₂—], rather than only methylene bridges, connecting phenolic or melamine nuclei. Benzylamine (or aminomethylene in the MF case) bridges dominated the interconnections of the resorcinol and melamine nuclei and were much more evident than in Sojka's²⁵ experiments because of the much greater reactivity of the species used in our experiments (resorcinol and melamine).

These spectra explained why curing with hexamine was faster than with paraformaldehyde, for example, as mechanisms founded on the formation of the so-called methylene bases without previous decomposition to ammonia and formaldehyde were proposed.^{23,24}

The concept of methylene bases is not new, having been advanced in 1949 by Hultzs²⁶⁻²⁸ for phenolic resins made with hexamine, a concept difficult to prove because the methylene bases could not be isolated as the instability and reactivity of a species such as ⁺CH₂—NH—CH₂⁺ is so high that if a very reactive, negatively charged species (e.g., resorcinol, melamine, or a tannin) is not present at the time it is formed, it will rather rapidly decompose to formaldehyde and ammonia. In short, methylene bases, because of their



Scheme 1



Scheme 2

high reactivity could not be and have not previously been isolated, with the consequent, expected skepticism that greeted the proposed methylene bases mechanism when this was published.^{23,24} The findings in refs. 29–32 definitely showed the clear existence of $-\text{CH}_2-\text{NH}_2$, $-\text{CH}_2-\text{NH}-\text{CH}_2-$ and $-\text{CH}_2-\text{N}(-\text{CH}_2-)-\text{CH}_2-$ bridges connecting resorcinol and melamine groups. It was finally shown by ^{13}C -NMR spectra of solid hexamine, which had been dissolved in strong acid and then diluted in water solution, that a series of imino-methylene bases (more stable than just the methylene base itself) and even diimino methylene bases formed. This allowed us to clarify the mechanism of hexamine decomposition in the presence of fast-reacting chemical species such as melamine. The mechanisms proposed for hexamine decomposition are shown in Schemes 1 and 2.^{30–32} The NMR shifts of the imines and iminomethylene bases formed are shown in Table I. A typical ^{13}C -NMR spectrum of the stabilized decomposition products of hexamine is shown in Figure 1.^{30–33}

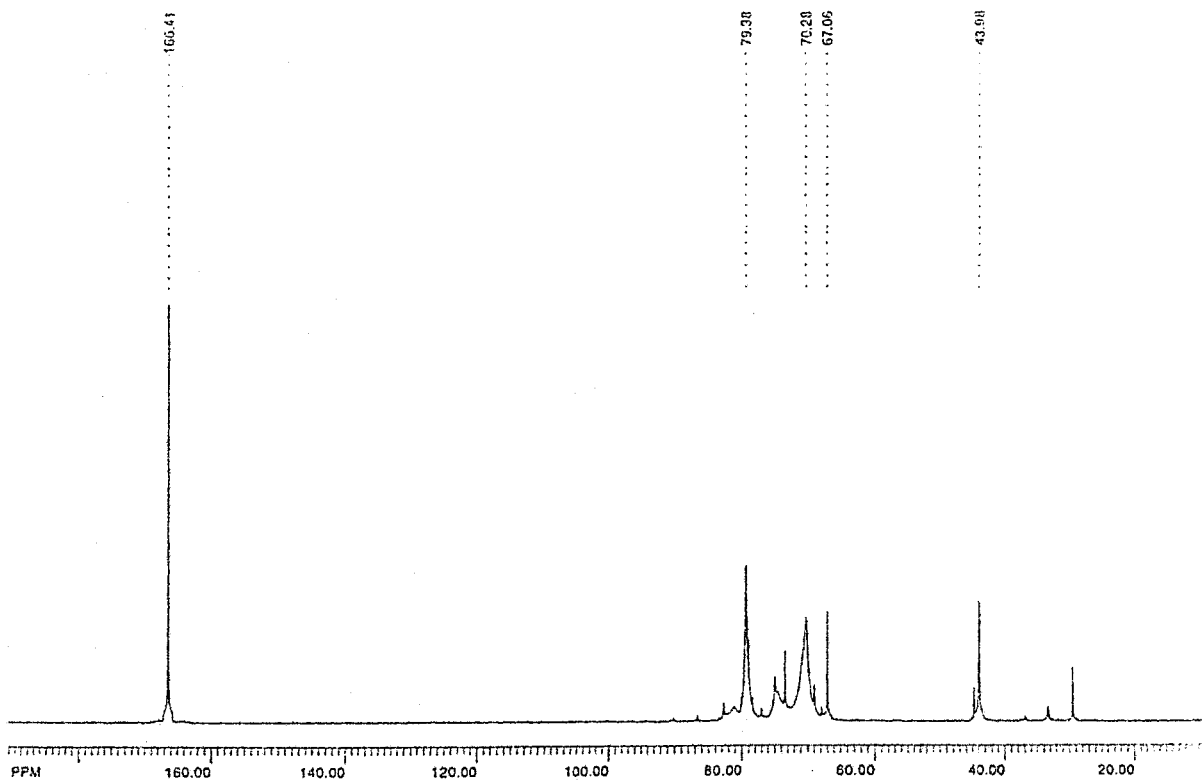
The same compounds can be prepared the inverse way.³³ Because the reactive species are the iminomethylene bases and not hexamine, the latter is not strictly needed. One can prepare the same by reacting an ammonium salt and formaldehyde.³³ This approach proved to be interesting and worked for some adhesives. The results of panels without any system optimization were comparable to the best optimized results obtained with hexamine.³³ Thus, ammonium sulfate and formalin at ambient temperature, or even better after heating, were used to form the same compounds.

Ammonium sulfate is just an example. It was, however, sufficient to show that at ambient temperature, very few iminomethylene bases were formed, whereas as soon as one used an acid anion as a stabilizer or heated up the system, a mass of very reactive iminomethylene bases were formed.^{30–32}

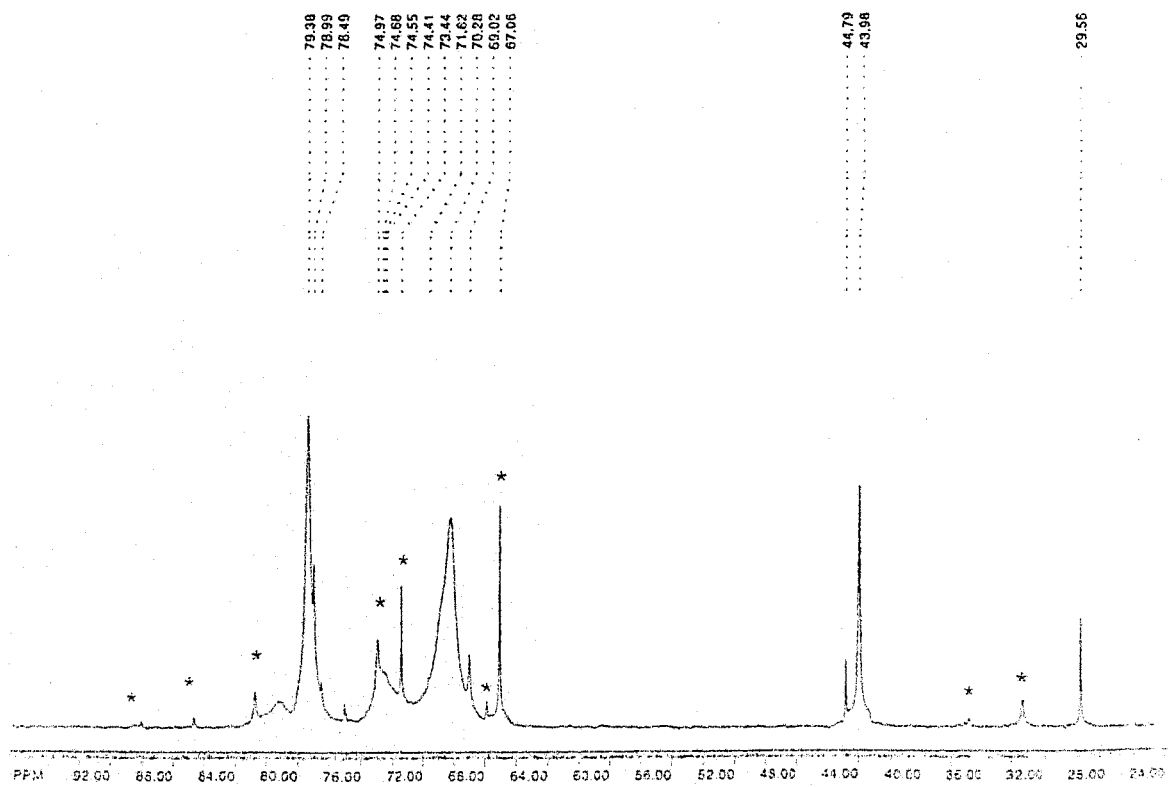
This is why these compounds considerably improve, under certain application conditions, the performance of these MUF resins.

TABLE I
Hexamethylenetetramine Decomposition Products Liquid ^{13}C -NMR Peak Shift Assignments

Group	Shift (ppm)
$\text{HN}=\text{CH}-\text{N}(\text{CH}_2-)\text{CH}_2\text{OCH}_3$	29.56
$=\text{N}-\text{CH}_2^+$	43.98
$\text{HN}=\text{CH}-\text{NH}-\text{CH}_2-\text{NH}-\text{CH}=\text{NH}$	44.79
$\text{HN}=\text{CH}-\text{NH}-\text{CH}_2\text{OCH}_2-\text{N}(\text{CH}_2-)-\text{CH}=\text{NH}$	69.02
$\text{HN}=\text{CH}-\text{NH}-\text{CH}_2\text{OCH}_2-\text{NH}-\text{CH}=\text{NH}$	70.28
$\text{HN}=\text{CH}-\text{N}(\text{CH}_2-)\text{CH}_2\text{OH}$ and $\text{HN}=\text{CH}-\text{N}(\text{CH}_2\text{OH})_2$	71.62 shoulder
$-\text{CH}_2-$ of hexamethylenetetramine	74.41
$\text{HN}=\text{CH}-\text{NH}-\text{CH}_2\text{OCH}_2-\text{N}(\text{CH}_2-)-\text{CH}=\text{NH}$	74.45
$\text{HN}=\text{CH}-\text{N}(\text{CH}_2-)\text{CH}_2\text{OCH}_2-\text{N}(\text{CH}_2-)-\text{CH}=\text{NH}$	74.68
$\text{HN}=\text{CH}-\text{N}(\text{CH}_2-)\text{CH}_2\text{OCH}_3$	79.38
$\begin{array}{c} \text{N}-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HC} \quad \quad \text{O or HOCH}_2\text{OH} \\ \diagdown \quad \diagup \\ \text{NH}-\text{CH}_2 \end{array}$	81.0 broad and very small
$\text{H}_2\text{C}=\text{N}-\text{CH}_2^+$ or $-\text{N}=\text{CH}-$	166.41



(a)



(b)

Figure 1 (a) ^{13}C -NMR spectrum of the decomposition products of hexamethylenetetramine stabilized by HSO_4^- . (b) Magnification of the 22–96-ppm region of the ^{13}C -NMR spectrum of the decomposition products of hexamethylenetetramine stabilized by HSO_4^- . Spinning sidebands are indicated by an asterisk.

TABLE II
Composition of the Historical Sequence of Hexamine Sulfate Hardeners

	Type of hexamine sulfate hardener				
	SH1	SH2	SH3	SH4	SH5
Weight concentration (%) of H ₂ SO ₄ used to make the hexamine sulfate hardener	48	75	60	52	52
Composition by weight percentage of the reactives used for the making of hexamine sulfate					
Hexamine powder	39.06	21.6	30	27.1	20
H ₂ SO ₄ expressed as 100% pure	29.25	58.8	42	38.0	24.0
Water	31.69	19.6	28	34.9	56

EXPERIMENTAL

Preparation of hexamine sulfate

We prepared hexamine sulfate starting from 60% sulfuric acid in water. Thus, 100 g of hexamine sulfate contained 30 g of hexamine crystals, 70 g of a 60% sulfuric acid solution (equivalent to 42 g of H₂SO₄ at 100%), and 28 g of water. The same was prepared by the addition of 80 g of 52% sulfuric acid to 20 g of hexamine crystals. The inverse hexamine sulfate was prepared by the premixture of 3 g of ammonium sulfate with 7.35 g of formalin solution at a concentration of 37% HCHO. This solution was heated to boiling and then immediately cooled.

Other solutions of hexamine sulfate were prepared by the same method but in the proportions indicated in Table II. We used the emission from panels (discussed later) with the perforator method for the HCHO measurement, and the solution formaldehyde content was determined by the iodometric method.^{34,35}

Preparation of MUF resins

Two basically different MUF resin formulations were used for the experiments. One was a resin formulation in which the addition of melamine and urea are performed according to their respective reactivities with formaldehyde according to known sequential manufacturing procedures.² This was done to ensure the maximum extent of the copolymerization of melamine and urea. This type of formulation generally gives very strong bonds. The second formulation was instead an almost pure MF formulation where a relatively low proportion of urea, in defect, too much less reactive in relation to melamine to participate to the reaction, was added at the beginning of the reaction. This MF resins with unreacted urea in relatively high proportion was then drowned at the end of the reaction period in a further, considerable excess of urea. This approach was the same that has been used in some present-day commercial PUF resins.³⁶ For amino-plastic resins, it gives much weaker bonds but better formaldehyde emission because of the very high amount of urea that is left free and noncopolymerized

with melamine. For ease of understanding, we call this second resin a nonsequential MUF resin.

For the first formulation approach, MUF resins with melamine + urea/formaldehyde [(M+U):F] molar ratios of 1:1.9, 1:1.5, and 1:1.2 and with M:U weight ratios of 47:53, 40:60, 30:70, and 20:80, respectively, and a UF with a molar ratio of only 1:1.5 were prepared according to known sequential manufacturing procedures.² Here, we give an example for a resin with a 1:1.9 molar ratio, an M:U of 47:53: to 269.6 parts of formurea (a precondensate of 23% urea, 54% formaldehyde, and 23% water), we added 57.9 parts of urea and 71.1 parts of water. The pH was set at 10–10.4, and the temperature was brought to 92–93°C under mechanical stirring. The pH was then lowered to 7.8, and the reaction continued at the same temperature, which allowed the pH to fall by itself over a period of 1 h 30 min to 6.5–7 (the pH must never fall below 5). To bring the pH to 9.5 or higher, a 22% NaOH solution was added; then, 71.1 parts of melamine premixed with 37.2 parts of water were added. Two parts of dimethylformamide were then added to the reaction mixture, while the temperature was maintained at 93°C. The percentage water tolerance of the resin was checked every 10 min, and the pH was allowed to fall by itself. When the *water tolerance* (the percentage of water that is possible to add to the liquid resin) reached a value of 180–200% (the pH reached was around 7.2), 35.5 parts of urea were added, and the pH was again brought up to 9.5. The reaction was continued until the water tolerance was lower than 150% (the pH had reached 7.7 at this stage).

The pH was then corrected to 10.0–10.2 by the addition of a NaOH solution, and the resin was cooled and stored.

The second MUF adhesive formulation was prepared as follows. To 390 parts of formurea were added 190 parts of water, and the pH of the mixture was adjusted to 9 by the addition of a few drops of a 33% NaOH solution. The temperature was brought to 30°C, and then, 175 parts of melamine powder were added. The reaction was conducted in a glass reactor equipped with a reflux condenser and was always under mechanical stirring. The temperature of the re-

action mixture was brought to 94°C over a period of 1 h, and the pH generally went down to 8.5. The reaction was kept at 94°C for 30 min, and the pH decreased to 8.5. The turbidity point, measured at 30°C, was generally reached at this stage. The pH was adjusted to 8.95 by the addition of a 33% NaOH solution, and then, a second amount of 46 parts of melamine was added to the reaction mixture. Small amounts of the 33% NaOH solution were added continuously to keep the pH from decreasing too much. The reaction was continued for 15 min, and then, 155 parts of urea were added. The reaction mix was kept at 74°C for 3–5 min, and the pH was maintained at 9. The reaction mix was then cooled slowly and reached a temperature of 45°C after approximately 1 h of cooling. The pH was then 9.3. Monoethanolamine (7.7 parts), used as a buffer to maintain the long-time shelf life of the resin, was added, and the pH was 9.65. About 15–20 min later, after the resin had cooled down to 30°C, the resin is stored. The MUF obtained had a final (M+U):F molar ratio of 1:1.2 and an M:U weight ratio of 47:53. In reality, if one calculated according to the relative reactivities of melamine and urea with formaldehyde, the (M+U):F molar ratio would be 1:2.15 and the M:U weight ratio would be 70:30, drowned in urea. This was done to reduce the high formaldehyde emission that would be expected by such a high-molar-ratio resin when applied to wood panels.³⁵

Thermomechanical analysis (TMA)

These resins were tested dynamically by TMA on a Mettler 40 apparatus (Switzerland). Triplicate samples of beech wood alone and of two beech wood plys, each 0.6 mm thick bonded with each system, for a total sample dimensions of 21 × 6 × 1.2 mm, were tested in the nonisothermal mode between 40 and 220°C at heating rates of 10, 20, and 40°C/min with the Mettler

40 TMA apparatus in three-points bending on a span of 18 mm with a force cycle of 0.1/0.5 N on the specimens for 12 s (6 s/6 s). The classical mechanics relation between force and deflection, $E = [L^3 / (4bh^3)][\Delta F / (\Delta f)]$, allowed us to calculate Young's modulus (E) and to follow its rise as function of both temperature and time.^{37,38} The deflections (Δf) obtained and the values of E obtained from them were proven to be constant and reproducible.^{37,38}

Glue mixes and wood particleboard preparation and testing

We prepared the glue mixes of the panels by adding to the relevant resin (as indicated in the tables) 1, 2, and 5% hexamine sulfate on resin solids, taking care wherever possible to compare the amounts of hexamine sulfate corresponding to the same proportion of SO_4^{2-} ions, as in the 3% ammonium sulfate used as a control.

Duplicate one-layer laboratory particleboards with dimensions of 350 × 310 × 14 mm were then produced from industrial wood chips composed of 70 wt % beech and 30 wt % spruce by the addition of 10% total MUF + salt resin solids content on dry wood particles pressed at a maximum pressure of 28 kg/cm² (2 min from platen contact to high pressure and the maintenance of the high pressure) followed by a descending pressure cycle of 1 min at 12–14 kg/cm² and 2 min at 5–7 kg/cm² at 190–195°C for a total pressing time of 5 min. The moisture content of the resinated chips was 12%. All of the panels had densities between 0.695 and 0.704 g/cm³. The panels, after light surface sanding, were tested for internal bond (IB) strength after 2 h of boiling and 16 h of drying at 105°C. Specimens from the pressed panels were tested for formaldehyde emission by the perforator method;³⁵ the results are expressed in milligrams of formaldehyde per 100 g of panel.

TABLE III
Effect of Hexamine Sulfate (SH5) on a Nonsequential MUF Adhesive Resin for Particleboard

Ethanolamine	Control panel		Hexamine sulfate experimental panel		
	Without	With	Without	With	
Resin molar ratio		1.2		1.2	
Hardener type		NH ₄ Cl		SH5	
Dry hardener/dry resin (%) ^a		3		1	
Pressing time (s/mm of panel thickness)		13		13	
Dry resin content/dry wood (%)		12		12	
Dry IB strength (MPa)		0.73		0.87	
Density (kg/m ³) of dry IB samples		664		665	
2-h boil thickness swelling (%)		41		28	
2-h boil IB strength (MPa)	0.00		0.0		0.32
Density (kg/m ³) of 2-h boil IB samples		699		696	

^a In pure hexamine equivalents and in pure NH₄Cl.

TABLE IV
Increase of Formaldehyde Emission Compared to Theoretical Increase in Formaldehyde Proportion in the (M+U):F Molar Ratio Nonsequential MUF Resins as a Function of the Percentage of Hexamine added in the Form of Hexamine Sulfate

	Initial resin molar ratio (M+U):F								
	1:1.1			1:1.2					
Dry hexamine ^a /dry resin (wt %)	0	1	2	4	6	10	0	1	2
Theoretical total molar ratio of resin to which hexamine sulfate was added (if hexamine all went to HCHO)									
EN 717	1.10	1.14	1.18	1.26	1.34	1.51	1.20	1.24	1.28
Experimental formaldehyde emission (mg/100 g of panel)	7.4	7.6	7.9	8.1	8.9	9.5	9.7	10.3	12

^a Added as hexamine sulfate SH3.

Liquid-phase ¹³C-NMR analysis

The samples for NMR analysis were prepared as mixtures of 30:42:28 w/w hexamethylenetetramine/H₂SO₄/distilled water. The temperature of the solution maintained under cooling water rose by itself to 65°C, thus above the temperature of decomposition of the hexamine before it was cooled down to ambient temperature. The liquid ¹³C-NMR spectrum of this solution was obtained on a Brüker MSL 300 Fourier transform NMR spectrometer (Ettlingen, Germany). Chemical shifts were calculated relative to (CH₃)₃Si(CH₂)₃SO₃Na dissolved in D₂O for NMR shift control.³⁹ The spectra were done at 62.90 MHz for approximately 1000 transients. The spectra were run with a relaxation delay of 5 s, and the chemical shifts were accurate to 1 ppm. The assignments of the different peak shifts observed (Table I) were both obtained from the relevant literature and calculated.^{30–32,39–46} Typical spin-lattice relaxation times for the types of compounds analyzed were taken from the literature.³⁹ The samples of iminomethylene bases were obtained by the mixture of ammonium sulfate and a 37% formaldehyde water solution (formalin) in stoichiometric proportions for the formation of hexamine without any addition of acid at ambient temperature and at 90°C but with the addition of diluted sulfuric acid to supply a greater amount of sulfate ion to stabilize the imines and iminomethylene bases formed.

DISCUSSION

The improvement in the water resistance and strength of MUF resins induced by their hardening in the presence of small amounts of a raw mix of iminoamino methylene base sulfates derived by the stabilization of the decomposition intermediates of hexamine in the presence of sulfuric acid was found by chance. The raw mix of iminoamino methylene bases stabilized by an anion, here the sulfate ion, is defined in the text that

follows as hexamine sulfate for the sake of brevity. In Table III are shown the results of IB strength after 2 h of immersion in boiling water (and 16 h of drying at 100°C) of wood particleboard panels in which a type of hexamine sulfate (SH5; see Table II) was used as the hardener of a MUF resin instead of a traditional MUF resin hardener (ammonium chloride). Table I shows a very marked improvement of IB strength from 0.13 to 0.32 MPa when 1% hexamine in the form of hexamine sulfate was used instead of 3% ammonium chloride.

The wet strength improvement of the panel (Table III) obtained by the hardening of the MUF adhesive by the addition of hexamine sulfate was not caused by any noticeable increase in the proportion of formaldehyde and the F:(M+U) molar ratio, as shown by the calculations in Table IV. The proportion of hexamine sulfate used in this work comprised between 1 and 5% of the total MUF resin solids; thus, the F:(M+U) molar ratio would, at the most, increase between 0.04 and 0.2. This was so, even if all of the hexamine added as hexamine sulfate had decomposed to formaldehyde, and this was already shown not to be the case.^{30–32} Thus, any increase in the F:(M+U) molar ratio from this did not explain the marked improvement in the

TABLE V
TMA Minimum Deflections and pHs of Nonsequential MUF Resin Hardened by SH1 and SH2

Dry hexamine ^a /dry resin (wt %)	SH1		SH2	
	Deflection minimum (μm)	Glue-mix pH	Deflection minimum (μm)	Glue-mix pH
1	23.7	6.32	21.6	6.90
2	21.3	5.81	19.1	6.48
3	22.2	5.28	—	—
4	19.4	5.15	18.6	5.92
5	17.1	4.83	—	—
6	19.9	4.23	19.9	5.62
10	—	—	20.8	5.10

^a Added as hexamine sulfate SH3.

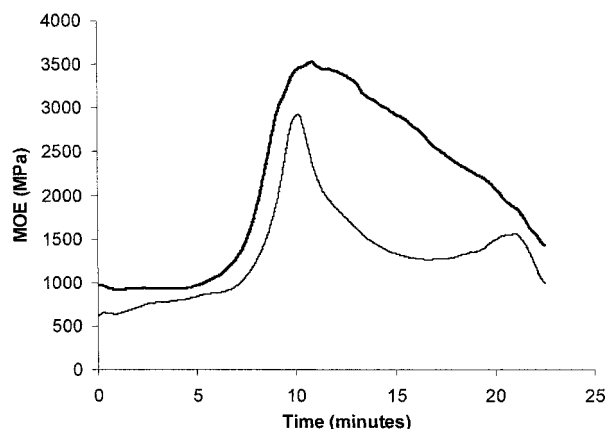


Figure 2 Increase in modulus of elasticity (MOE) as a function of time measured by TMA of the curing on beech wood joints of (—) a 47:53 MUF resin hardened at an equal SO_4^{2-} content with hexamine sulfate and (---) the same resin hardened with ammonium sulfate. The heating rates was constant at $10^\circ\text{C}/\text{min}$.

wet performance of MUF resins.^{1,29} The increase in formaldehyde emission measured experimentally (Table IV) was much lower than would be predicted if hexamine had decomposed completely into formaldehyde. For example, in the case in Table IV in which 10% of hexamine was added to a MUF resin with a F:(M+U) molar ratio of 1.10, the experimental formaldehyde emission measured (9.5 mg of HCHO/100 g of panel) was even slightly lower than that measured for the reference MUF resin with a higher molar ratio [F:(M+U) = 1.2; emission = 9.7 mg/100 g]. If the total decomposition of hexamine to formaldehyde had occurred, the MUF resin would have passed from a F:(M+U) molar ratio of 1.10 to one of 1.51 (Table IV) and, hence, to a type of resin known to yield boards of very much higher formaldehyde emission (in general between 20–30 mg/100 g); instead, its emission behavior was similar to the MUF control resin with a molar ratio of 1.2 (Table IV). The important result was that the marked increase in wet IB strength corresponded to a much smaller increase in formaldehyde emission (in general, the wet IB strength increased

approximately three times faster than the formaldehyde emission). This makes it feasible to restore board emission to that of the original resin and to maintain the strength performance with hexamine sulfate and decreasing board resin content.

The values of the minimum deflection of joints bonded with the MUF resin hardened with hexamine sulfate, as obtained by TMA according to testing systems already developed,^{37,38} are shown in Table V. These indicate that an amount of 4–5% hexamine added as hexamine sulfate yielded the best results (the minimum deflection). An example of the comparison of such TMA curves of a resin hardened at equal SO_4^{2-} contents with hexamine sulfate and the same resin hardened with ammonium sulfate are shown in Figure 2. A constant heating rate of $10^\circ\text{C}/\text{min}$ was used. It must be remembered, however, that TMA tests used in this manner correlate mainly with the dry IB results of panels bonded with MUF resins and are no guarantee that correlation will exist with wet strength results in the case of new, experimental resin systems.^{5,47–49} In this case, it is necessary to prepare wood particleboard to establish if such correlation exists.^{47–49} The laboratory particleboard results presented in Table VI indicate that although variations of IB strength did exist, the addition of hexamine sulfate at lower proportions in the 1–5% range yielded similar results. The results of the wet IB strength were higher at 1 and 2% than at 5%. This led us to two deductions:

1. The main effect was present also with the smaller proportion of hexamine as hexamine sulfate.
2. The decrease in wet IB strength with increasing hexamine sulfate proportion was likely to have been due to the known action of hydrolysis induced by the sulfate ion on any hardened aminoplastic resins.^{1,21}

The second point indicates that the possible improvement observed at 5% addition might have been due to the presence of a second effect. This might have been the greater extent of crosslinking generated by

TABLE VI
Influence on the Performance of Nonsequential MUF-Bonded Particleboard of the Percentage Hexamine Sulfate Hardener Used

Hardener type	Hardener (%)	Dry IB strength (MPa)	IB strength 2-h boil (MPa)	Panel density (kg/m^3)	Formaldehyde emission (mg/100 g)	24-h cold-water swelling (%)
$(\text{NH}_4)_2\text{SO}_4$	5	1.05	0.10	720	3.8	6.5
SH5	1	0.87	0.32	696	5.6	6.0
SH5	2	0.87	0.26	701	5.6	6.1
SH4	3	0.86	0.20	712	5.6	6.4
SH4	4	1.20	0.21	722	7.6	6.3
SH4	5	1.10	0.25	722	5.8	6.2
SH4	7.5	0.96	0.20	716	4.2	6.5

TABLE VII
Gel Times with Different Hardeners and Different Percentage Hardeners of a Sequential MUF Resin with an F:(M+U) Molar Ratio of 1.9 and a M:U Weight Ratio of 47:53

	SO ₄ ²⁻ (%)	Gel time (s)
Ammonium sulfate (%)		
2	1.46	81
4	2.91	65
6	4.37	60
Hexamine sulfate (%)		
4	1.57	60
7.60	3.02	45
11.50	4.54	45

(1) the high reactivity with melamine and MUF resins of the anion-stabilized iminoamino methylene bases or (2) the slight increase in the proportion of formaldehyde and, hence, the F:(M+U) molar ratio generated by the addition of hexamine sulfate. However, this advantage appeared to be lost at higher hexamine sulfate proportions as a consequence of the acid-induced hydrolysis of the hardened resin network (Table VI). The disadvantage induced by acid hydrolysis could perhaps be reduced with anions as stabilizers from weaker acids. However, it is not possible to ascertain from these data whether these would also be able to stabilize the iminoamino methylene bases formed by the decomposition of hexamine.

The first point clearly indicates that it was not any potential increase in the proportion of formaldehyde, and hence, of the F:(M+U) molar ratio, which caused the marked improvement in the wet strength performance of the MUF resin and of the boards bonded with it.

Equally clear is that it was not the higher reactivity with melamine of the iminoamino methylene bases sulfate that was the main cause of the effect, due to the small amount needed to note such an improvement in performance. It is true that the iminoamino methylene base sulfate was slightly more reactive at a parity of SO₄²⁻ ion concentration than a traditional hardener; this is shown in the gel time results in Table VII. However, this slightly higher reactivity was insufficient to explain the marked performance improve-

ment that was observed. The effect was indeed very marked (see Tables I and VI), even at very small proportions of hexamine sulfate. What are then

1. The limits of the improvement induced by such an additive?
2. The causes of such a marked wet performance improvement?
3. How can such an effect be put to best use?

Even without knowing the answer to the second question, it is possible to address the applied limits of the use of such an additive. Thus, in Table VIII is shown the comparison of the performances of the same top-of-the-range MUF resin with a M:U weight ratio of 47:53 with a traditional MUF resin hardener, ammonium sulfate, and the same amount of one type of hexamine sulfate (Table II) at two different pressing times of the wood particleboard. It was evident that the difference in dry IB strength was within experimental error and that there was practically no difference in the performance of the two hardeners when the panel was tested dry. The difference was, however, considerable at both pressing times after the panels were submitted to accelerated aging by a 2-h immersion in boiling water followed by 16 h of drying at 105°C. In both cases, the board bonded with the MUF resin hardened with hexamine sulfate presented a much better 2-h boil IB strength and a lower percentage thickness swelling. Formaldehyde emission was similar in the two cases and well within the limits required by the relevant international standard specifications.^{40,41} Of interest is the fact that the experimental system also worked at the relatively faster press time of 8 s/mm, which is an important consideration for industrial applications.

An alternative way to use the effect observed was to use MUF resins that were less expensive due to lower melamine content, while maintaining the performance of the best formulations by the addition of a small amount of hexamine sulfate. Thus, in Table IX, MUF resins were prepared according to a basic sequential MUF formulation already reported⁵⁰ but in which the relative proportion of melamine was progressively

TABLE VIII
Effect of Pressing Time on the Performance of Particleboard Bonded with a Nonsequential MUF Resin [47:53, (M+U): F = 1:1.2] Made with an Experimental Hexamine Sulfate (SH5) Hardener Compared with the Results of the Same Resin Hardened with a Control Hardener (Ammonium sulfate)

Press time (s/mm)	Hardener type	IB dry (MPa)	IB after 2-h boil (MPa)	Panel density (kg/m ³)	Formaldehyde emission (mg/100 g)	24-h cold-water swelling (%)
8	5% (NH ₄) ₂ SO ₄	0.94	0.17	701	3.5	8.7
8	5% SH5	1.02	0.32	699	3.9	7.3
10	5% (NH ₄) ₂ SO ₄	1.01	0.17	705		8.0
10	5% SH5	1.00	0.30	710		8.2

TABLE IX
Particleboard Results and Performance when the Amount of Melamine in the MUF Resin Was Decreased in a Nonsequential Adhesive Formulation: A Comparison of the Control Hardener and the Experimental Hexamine Sulfate SH5 Hardener

Hardener type	M:U	Dry IB strength (MPa)	IB strength 2-h boil (MPa)	Panel density (kg/m ³)	Formaldehyde emission (mg/100 g)	24-h cold-water swelling (%)
5% (NH ₄) ₂ SO ₄	47:53	1.05	0.10	720	3.8	6.5
5% SH5	47:53	1.10	0.25	722	5.8	6.2
5% (NH ₄) ₂ SO ₄	37:63	1.19	0.21	728	3.5	8.2
5% SH5	37:63	1.13	0.32	716	5.0	9.0
5% (NH ₄) ₂ SO ₄	30:70	1.02	0.12	722	3.6	9.4
5% SH5	30:70	1.13	0.32	765	4.0	7.3
5% (NH ₄) ₂ SO ₄	25:75	0.85	0.12	727	4.3	11.1
5% SH5	25:75	1.02	0.26	727	5.5	9.4
5% (NH ₄) ₂ SO ₄	18:80	0.86	0.05	719	4.0	12.0
5% SH5	18:82	0.99	0.23	728	5.8	9.7

decreased from an M:U weight ratio of 47:53 down to 40:60, 30:70, 25:75, and 20:80, respectively. As expected, no great differences were noticed between the dry IB strength values of boards bonded with MUF resins of different M:U weight ratios, with perhaps a drop in dry IB strength only noticeable at the lowest melamine proportion (M:U = 20:80). However, IB strengths after 2 h of immersion in boiling water showed marked differences between ammonium-sulfate-hardened and hexamine-sulfate-hardened resins. The boards bonded with hexamine-sulfate-hardened MUF resins always had much higher IB strengths after accelerated aging and, except in one case, provided lower percentages of thickness swelling than the boards bonded with ammonium-sulfate-hardened MUF resins. The wet IB strength of the boards bonded with ammonium-sulfate-hardened MUF resins progressively decreased with decreasing proportion of melamine in the resin and decreased in order from the M:U 40:60 ratio down to the 20:80 ratio. The 30:70 and 25:75 M:U ratios furthermore yielded results that did not satisfy the requirements of standard specifications for exterior-grade boards, although this is approximately what would be expected for such a type of resin.^{50,51} The boards bonded with hexamine-sulfate-hardened MUF resins instead showed a much less marked decrease in wet IB strength in the same M:U ratio range (40:60 to 20:80), with a wet IB strength

value for the 30:70 M:U ratio being clearly anomalous (too high) because the density of the panel was too high. All cases, including the one at the lowest proportion of melamine, satisfied the requirements of the relevant standards for exterior-grade, weather-resistant boards. The level of formaldehyde emission did not show any particularly marked trend in relation to melamine content, but the formaldehyde emission was better in all cases for the boards bonded with ammonium-sulfate-hardened MUF resins. However, all cases were within the strict limits imposed for formaldehyde emission by current regulations.³⁵ We conclude, then, that at a parity of performance with these top-of-the-range MUF resin systems, the use of hexamine sulfate additive allows the same performance but with resins containing a much lower proportion of melamine, which provides cost savings.

It was of interest to check if the results obtained by the production of anion-stabilized iminoamino methylene bases by the addition of SO₄²⁻ to hexamine yielded similar results to the mixture of similar compounds obtained by the reaction of ammonium sulfate with formaldehyde. This was of interest because just the combination of ammonium sulfate and formaldehyde with a brief preheat is a very easy way to make the hardener. In Table X are reported the results of boards bonded with the much stronger sequential MUF resins hardened with hexamine sulfate prepared

TABLE X
Use of the (NH₄)₂SO₄ + HCHO Mix as an Alternate Route to the Hexamine Sulfate Intermediates

Hardener type	Hardener (%)	M:U by weight	IB strength 2-h boil (MPa)	Panel density (kg/m ³)	2 h boil swelling wet (%)	2-h boil swelling, dry (%)
3% (NH ₄) ₂ SO ₄		47:53	0.39	723	36	21
3% (NH ₄) ₂ SO ₄	+5% HCHO	47:53	0.45	719	37	22
3% (NH ₄) ₂ SO ₄		20:80	0.05	722	71	49
3% (NH ₄) ₂ SO ₄	+5% HCHO	20:80	0.15	741	52	38

Used as a hardener for high-molar-ratio MUF resins; sequential (M+U):F = 1:1.9.

TABLE XI
Sequential MUFs of Different M:U Weight Ratios and a Low (M+U):F Molar Ratio of 1:1.2: Comparison of Ammonium Sulfate and Inverse Preparation of Hexamine Sulfate (Ammonium Sulfate + HCHO) Hardener

M:U	Hardener type	Panel density (kg/m ³)	2-h boil swelling (%)	IB strength after 2-h boil (MPa)
47:53	3% (NH ₄) ₂ SO ₄	730	31.2	0.15
47:53	5% hexamine sulfate	730	24.6	0.26
40:60	3% (NH ₄) ₂ SO ₄	725	32.9	0.15
40:60	5% hexamine sulfate	723	26.8	0.22
30:70	3% (NH ₄) ₂ SO ₄	705	46.8	0.03
30:70	5% hexamine sulfate	706	40.2	0.08

Amount of dry resin on dry wood content = 10%.

by the premixture of ammonium sulfate with formaldehyde with preheating for a short period at 80°C. The MUF resins used were first top of the range, not only for the high proportion of melamine (M:U = 47:53) but also for their high content of formaldehyde, with a high F:(M+U) molar ratio of 1.9, and also for a lower melamine content (M:U = 20:80) with the F:(M+U) molar ratio still high at 1.9. The results indicate that improvements in wet IB strength were indeed also obtained with this approach. The improvement was less marked for the very strong 47:53 M:U ratio and 1.9 MUF formulation than for the less strong 20:80 M:U formulation. As the difference observed in Table X could be due to the higher molar ratio used for the sequential resin used, a series of boards bonded with sequential MUF resins of lower molar ratio [F:(M+U) = 1.2] and progressively decreasing melamine proportions was also tested (Table XI). The results in Table XI show that a marked improvement still did occur, but that it was less marked than for the cases reported in previous tables where the hexamine sulfate was obtained by the addition of sulfuric acid to hexamine in solution. Thus, even strong sequential formulations benefit considerably by the addition of this hardener; their improvement was still evident but less marked than for the weaker nonsequential formulations. This difference could simply be ascribed to the proportion of compounds that were formed according to one route or the other and to the equilibria involved. In conclusion, this alternative route to anion-stabilized iminoamino methylene bases can be used, but it needs to be, at minimum, optimized to compete with the effectiveness of the original hexamine sulfate preparation route.

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