

Upgrading of MUF Polycondensation Resins by Buffering Additives. II. Hexamine Sulfate Mechanisms and Alternate Buffers

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ABSTRACT: Iminoamino methylene bases intermediates are obtained by the decomposition of hexamethylenetetramine (hexamine). These are stabilized by the presence of strong anions such as SO_4^{2-} and HSO_4^- , that is, "hexamine sulfate." The effect of hexamine sulfate was closely linked to the strong buffering action it has on MUF resins. Its role is mainly to induce regularity of the reaction and the stability of conditions during resin networking, due to the buffer. Shifting of the polycondensation \rightleftharpoons degradation equilibrium to the left appeared to be the determinant factor. This was a consequence of maintaining a higher, constant pH during curing, due to the buffer action. The modulus of elasticity (MOE) increases the curves of hexamine sulfate-catalyzed MUF resins, confirming this trend. The resins are faster curing than when catalyzed by ammonium sulfate. The effect is valid within the narrow buffering range of pH's used

for resin hardening. Polycondensation is far too slow to occur at a much higher pH, and degradation is, instead, more predominant at much lower pH's. The network formed is then more crosslinked and less tainted by degradation when curing occurs within the correct pH range. The result is a much better performance of the wood board after water attack. The effects induced by hexamine sulfate effects are of longer duration than those of other potential buffers. This is due to the hexamine sulfate heat stability under standard hot curing conditions of the resin. Alternate systems were found and shown to have a comparable effect.

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INTRODUCTION

Reactive iminoamino methylene bases (so-called because their formulae, namely, $\text{HN}=\text{CH}-\text{NH}-\text{CH}_2-\text{NH}-\text{CH}=\text{NH}$, and $\text{H}_2\text{C}=\text{N}-\text{CH}_2^+$, contain both imino and amino groups) were obtained as SO_4^{2-} stabilized intermediates of the decomposition of hexamethylenetetramine (hexamine).¹ This material is called "hexamine sulfate" for the sake of brevity. Hexamine sulfate was also shown to markedly improve the water and weather resistance of hardened melamine/urea/formaldehyde (MUF) resins used as wood adhesives. It also improved the wet internal bond (IB) strength performance of wood boards. Small amounts of this material, between 1 and 5% by weight on MUF resin solids content, induced these improvements. Thus, it allowed the use of MUF resins with a much lower melamine content while maintaining good performance of the bonded joints. The main effect is also present at lower levels of hexamine sulfate. This has been shown not to be due to any increase in molar ratio of the resin, as a consequence of hexamine sulfate addition.

This system was reported^{1,2–5} only recently. The reasons why hexamine sulfate causes a considerable improvement of performance in MUF resins were not known in previous studies.^{2–5}

As with any other additive capable of markedly decreasing the percentages of adhesive needed, this additive is commercially very viable. It is also easy to use and produce in industry, simply by its addition to a glue mix. There is no need for any investment or other technical modification. This article deals with the underlying principles and mechanisms which led hexamine sulfate to upgrade the performance of MUF resins to the level outlined in the preceding article.

EXPERIMENTAL

Preparation of hexamine sulfate

Hexamine sulfate was prepared starting from sulfuric acid of a 60% concentration in water. Thus, 100 g of hexamine sulfate contains 30 g of hexamine crystals; a 60% sulfuric acid solution, 70 g (equivalent to 42 g of H_2SO_4 at 100%); and water, 28 g. It was also prepared using sulfuric acid at a 52% concentration by adding 80 g of it to 20 g hexamine crystals. The inverse hexamine sulfate was prepared by premixing 3 g ammonium sulfate with 7.35 g of a formalin solution at a

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37% HCHO concentration. This solution was heated to the boiling point and then immediately cooled. The other solutions of hexamine sulfate were prepared by the same method but in the proportions indicated in Table III.

Preparation of MUF resins

Two basically different MUF resin formulations were used for the experiments. One is a resin formulation, in which the addition of melamine and urea were done according to their respective reactivities with formaldehyde using known sequential manufacturing procedures.² This was done to ensure the maximum extent of copolymerization of melamine and urea. This type of formulation generally gives very strong bonds. The second one was an almost pure MF formulation, where a relatively low proportion of urea, with too little reactivity, in relation to melamine, to participate in the reaction, is added at the beginning of the reaction. This MF resin with unreacted urea in a relatively high proportion was then "drowned" at the end of the reaction period in a further, considerable excess of urea. This approach is the same as has been used in some present-day commercial PUF resins. In the case of MUF resins prepared in this way, the high amount of unreacted urea gives a resin of weaker strength but of lower formaldehyde emission. For ease of understanding, we will call this second resin a nonsequential MUF resin.

For the first formulation approach, MUF resins of molar ratios of (M + U):F of 1:1.9, 1:1.5, and 1:1.2 and of M:U weight ratios of, respectively, 47:53, 40:60, 30:70, and 20:80 as well as a UF only of molar ratio 1:1.5 were prepared according to known sequential manufacturing procedures.² Herewith is given an example for a resin of a 1:1.9 molar ratio, M:U of 37:63: To 269.6 g of formurea (precondensate of formaldehyde, 54%; urea, 23%; water, 23%) were added 57.9 g urea and 71.1 g of water. The pH was set at 10–10.4 and the temperature increased to 92–93°C under mechanical stirring. The pH was then decreased to 7.8 and the reaction was continued at the same temperature, allowing the pH to decrease by itself over a period of 1.5 h to a pH of 6.5–7 (the pH must never decrease below 5). To increase the pH to 9.5 or higher, a 22% NaOH solution was added, then 71.1 g of melamine premixed with 37.2 g of water. Dimethylformamide, 2 g, was then added to the reaction mixture, maintaining a temperature of 93°C. The percentage water tolerance of the resin was checked every 10 min while the pH was allowed to decrease 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 was added and the pH was again increased to 9.5. The reaction continued until the water tolerance

reached was lower than 150% (the pH reached 7.7 at this stage). The pH was then corrected to 10.0–10.2 by addition of the NaOH solution and the resin was cooled and stored.

The second MUF adhesive formulation was prepared as follows: To 390 g of formurea (precondensate of formaldehyde, 54%; urea, 23%, water, 23%) were added 190 g water and the pH of the mixture was adjusted to 9 by adding a few drops of a 33% NaOH solution. The temperature was increased to 30°C and 175 g of melamine powder was added. The reaction was conducted throughout in a glass reactor equipped with a reflux condenser and under mechanical stirring. The temperature of the reaction mixture was increased to 94°C over a period of 1 h, the pH generally decreasing to 8.5. The reaction was kept at 94°C for 30 min and the pH decreased to 7.5. The turbidity point, measured at 30°C, was generally reached at this stage. The pH was adjusted to 8.95 by addition of a 33% NaOH solution, and then a second amount of 46 g of melamine was added to the reaction mixture. Small amounts of a 33% NaOH solution were added continuously to prevent the pH from decreasing too much. The reaction was continued for 15 min and then 155 g of urea was added. The reaction mixture was kept at 74°C for 3–5 min and the pH maintained at 9. The reaction mixture was then cooled slowly to reach a temperature of 45°C after approximately 1 h cooling. The pH was then 9.3. Monoethanolamine, 7.7 g, used as a buffer to maintain the long-time shelf life of the resin, was added and the pH obtained was 9.65. About 15–20 min later, once the resin was cooled to 30°C, the resin was stored. The MUF obtained had a final (M + U):F molar ratio of 1:1.2 and an M:U weight ratio = 47:53. In reality, if one calculates according to the relative reactivities of melamine and urea with formaldehyde, this represents an (M + U):F molar ratio of 1:2.15 and an M:U weight ratio = 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.

Preparation of melamine salt (melamine acetate)

The preparation procedures used for the preparation of melamine monoacetate were already reported,⁶ but were partially modified as regards materials concentration.⁷ The melamine monoacetate original preparation and drying procedures were retained.⁶

The procedure used was the following: Melamine, 50 g, was suspended in 1 L water and heated to 100°C while under continuous mechanical stirring in a reactor equipped with a reflux condenser. Acetic acid was then added in a stoichiometric amount to obtain melamine monoacetate, over a period of 5 min, and the mixture refluxed for 10 min before cooling to ambient temperature. The precipitate which formed on cooling

was filtered, then oven-dried at 75°C for 72 h at ambient pressure.⁶

Alternate buffer systems

For the alternate buffer systems, the quantity of the buffer on the resin solids content (100 g) was for potassium hydrogen phthalate: To 100 g of MUF resin solids content was added, alternatively, (i) 15% of KH phthalate, (ii) 15% of KH phthalate + 2% HCl, (iii) 15% of KH phthalate + 2% HCl + 2% H₂SO₄ (proportion of SO₄²⁻ ions corresponding to that in ammonium sulfate and hexamine sulfate prepared from the 60% H₂SO₄ solution. In ammonium sulfate, there is 72.73% SO₄²⁻ ions, while in dry hexamine sulfate, there is 55% SO₄²⁻ ions).

For the *p*-toluene sulfonic acid (*p*-TSA)/morpholine complex, the *p*-TSA/morpholine molar ratio was 1:1. The complex was simply prepared by mixing the two materials and lightly warming until the start of the exothermic complex formation reaction. The complex was then cooled and stored.

For the panels where the *p*-TSA/morpholine complex was used, 7.19 g of the complex (equivalent to 4.93 g *p*-TSA and equivalent to the same proportion of SO₄²⁻ ions given by 3% ammonium sulfate). In the case of two of the panels, sodium *p*-toluene sulfonate was added in a proportion to have a pH of the complex + salt of 4.

Titration and buffers action

The titration of the resins was carried out using 20 g resin, of 60% resin solids content, and titrating this with H₂SO₄ at a 10% concentration in water. The results are given in the figures in actual milliliters of this solution which were needed to reach a given pH. The morpholine was first titrated with a 0.1 and a 1 molar *p*-TSA solution, but as these were too weak, a 5M *p*-TSA solution was used for the final titration.

Glue mixes and wood particleboard preparation and testing

The glue mixes of the panels were prepared by adding, to the relevant resin as indicated in the tables, 5% of hexamine sulfate on resin solids, as this corresponded to the same proportion of SO₄²⁻ ions as in the 3% ammonium sulfate used in the controls. In the panels where the *p*-TSA/morpholine complex was used, 7.19 g of the complex (equivalent to 4.93 g *p*-TSA and equivalent to the same proportion of SO₄²⁻ ions given by 3% ammonium sulfate). In the case of two of the panels, sodium *p*-toluene sulfonate was added in such a proportion as to have a pH of the complex + salt of 4.

Duplicate one-layer laboratory particleboards of 350 × 310 × 14-mm dimensions were then produced from industrial wood chips, composed of 70% by weight of beech and 30% by weight of spruce, by adding 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 + maintaining high pressure) followed by a descending pressing cycle of 1 min at 12–14 kg/cm² and 2 min at 5–7 kg/cm², at 190–195°C and for a total pressing time of 5 min. The moisture content of the resinated chips was 12%. All the panels had densities between 0.695 and 0.704 g/cm³. The panels, after light surface sanding, were tested for IB strength after 2 h boiling and 16 h drying at 105°C.

Thermomechanical analysis (TMA)

The resins above were tested by thermomechanical analysis (TMA) on a Mettler 40 apparatus. Triplicate samples of beech wood alone and of two beech wood plys, each 0.6 mm thick bonded with each system, for a total samples dimensions of 21 × 6 × 1.2 mm, were tested in the nonisothermal mode from 40 to 220°C at heating rates of 10°C/min, 20°C/min, and 40°C/min. A Mettler 40 TMA apparatus in three-point bending on a span of 18 mm, exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s), was used. The classical mechanics relationship between force and deflection, $E = [L^3/(4bh^3)][\Delta F/\Delta f]$, allows calculation of the Young's modulus *E* for each case tested and to follow its increase as a function of both temperature and time. The deflections Δf obtained and the values of *E* obtained from them have been proven to be constant and reproducible.^{8,9}

DISCUSSION

Hexamine sulfate improves markedly the resistance to wet conditions and exterior-grade performance of a MUF resin. Consequently, even semiexterior-type MUF resins with such treatment yield boards which are more weather-resistant than those bonded with proper exterior-grade resins (such as phenol-formaldehyde resins and polymeric isocyanates¹). Having ascertained its effect, the most difficult question to answer is why? The low amount of hexamine sulfate used rules out an increase in formaldehyde content as the cause of the improved performance. No MUF resin, even of much higher formaldehyde content, can ever come close to this level of performance. It is clear that such an effect might be due either (i) to a change in the chemistry of formaldehyde and its reactions under the conditions used or (ii) to a transitory kinetic effect, considerably improving the density of crosslinking of the final, hardened resin network.

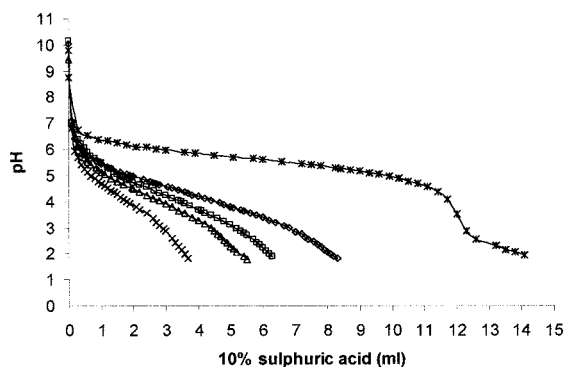


Figure 1 Variation of pH as a function of titration with 10% H_2SO_4 of 20 g of MUF resins of 60% concentration of M:U weight ratio = (\diamond) 47:53, (\square) 40:60, (\triangle) 30:70, and (\times) 20:80 and ($*$) of a 30% hexamine solution in water.

The maximum value of mechanical resistance of a bonded wood joint is higher when the heating rate to cure is slower.¹⁰⁻¹² This is the case both for aminoplastic and phenolic polycondensation resins. The higher mechanical resistance of the hardened resin network at slower heating rates relates to the higher density of crosslinking in the final network that is obtained. This occurs because the polymer has time to adjust by better use of empty volume spaces. It is the same reason for giving a lower value of the glass transition temperature T_g at a slower rate of heating. The slower the resin cures, for whatever reason, the higher is the ultimate mechanical resistance of the joint bonded with it. The extent of this effect is considerable¹⁰⁻¹²: For example, the maximum value of the modulus of a resin, crosslinked at a heating rate of 40°C/min, is 30% lower than that observed at a heating rate of 5°C/min.¹⁰⁻¹² Early immobilization of the resin in a less tightly crosslinked network¹⁰⁻¹² is the cause of this. Conversely, the faster a resin cures, the faster the bonded joint reaches a high value of mechanical resis-

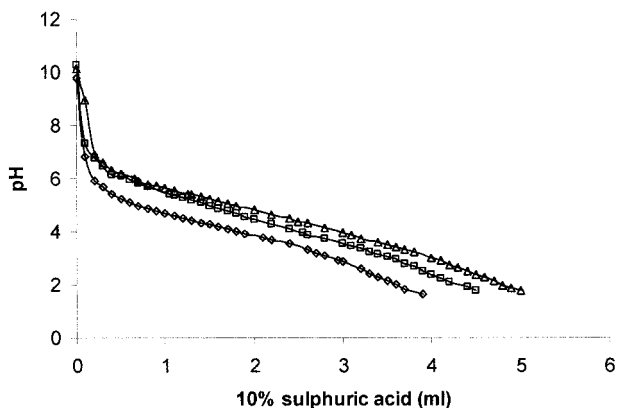


Figure 2 Variation of pH as a function of titration with 10% H_2SO_4 of 20 g of MUF resins of 60% concentration of F/(M + U) molar ratio of 1.9 and M:U weight ratio = (\diamond) 20:80, (\square) 20:80 + 3.43% hexamine, and (\triangle) 20:80 + 5.67% hexamine.

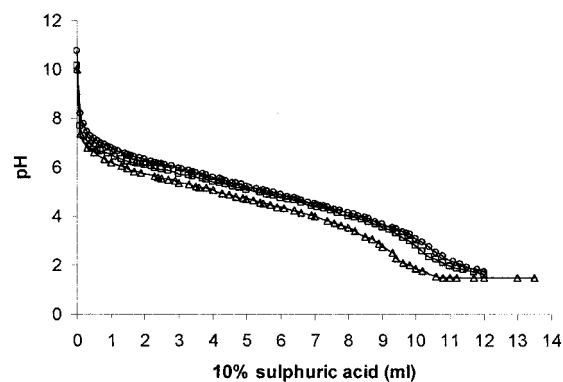


Figure 3 Variation of pH as a function of titration with 10% H_2SO_4 of 20 g of MUF resins of 60% concentration, of F/(M + U) molar ratio of 1.5 and of M:U weight ratio = (\triangle) 47:53, (\circ) 47:53 + 3.3% hexamine, and (\square) 47:53 + 2.0% hexamine.

tance (but the strength does not increase further). It is both an economic and technical necessity to obtain a panel of acceptable strength as rapidly as possible. The two trends work against each other and a compromise between the two should be reached to obtain optimum results. However, this is definitely not always the case for acid-curing aminoplastic resins such as MUF resins. This lack of compromise between the two trends will not be noticed in the MUF resins dry strength, but, rather, in their water and weather resistance, the properties influencing their durability.

These trends indicate that the reason for better or poorer performance of a MUF resin might be closely linked to the buffer action the resin itself exercises during curing. The titration curves of MUF resins, of an F/(M + U) molar ratio of 1.9 but with different M:U weight ratios, varying between 47:53 and 20:80, are shown in Figure 1. The preparation of the different resins was, otherwise, exactly the same. The extent of

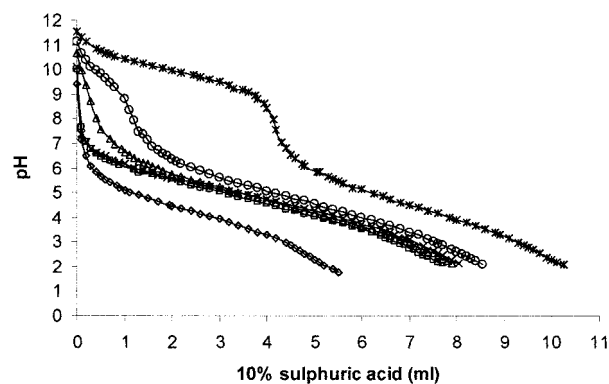


Figure 4 Variation of pH as a function of titration with 10% H_2SO_4 of 20 g of MUF resins of 60% concentration, of F/(M + U) molar ratio of 1.9 and of M:U weight ratio = (\diamond) 30:70, ($*$) 30:70 + 5.7% ammonia at 25°C, (\circ) 30:70 + 5.7% ammonia at 60°C for 2 min, (\triangle) 30:70 + 5.7% ammonia at 65°C for 2 min, (\times) 30:70 + 5.7% ammonia at 80°C for 2 min, and (\square) 30:70 + 5.7% ammonia at 80°C for 5 min.

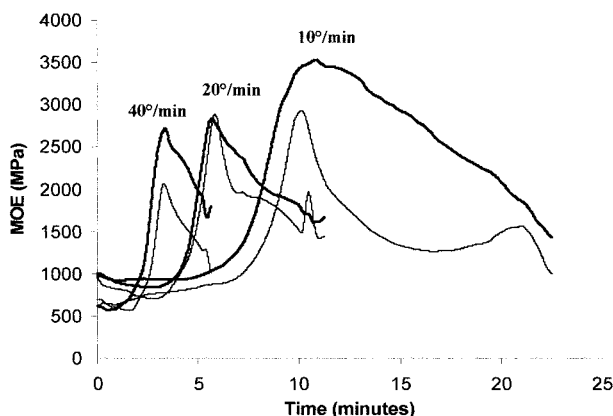


Figure 5 Increase in MOE as a function of time determined by thermomechanical analysis (TMA) of the curing on beech wood joints of a 47:53 MUF resin hardened at equal SO_4^{2-} content with (—, bold trace) hexamine sulfate and (—) of the same resin hardened with ammonium sulfate. Constant heating rates used were 10°C/min, 20°C/min, and 40°C/min.

buffering progressively and markedly decreases, passing from the M:U ratio of 47:53 MUF resin to those at 40:60, 30:70, and, finally, 20:80 (Fig. 1). The progressively steeper slope of the titration curve obtained on decreasing the relative proportion of melamine in the resin shows this. The relative length of the curve in the 3–6 pH range buffering zone also shows this. This decreases from 7, to 5.5, 5.0, and 3.0 mL SO_4^{2-} when passing, respectively, from the M:U 47:53 MUF resin to the 40:60, 30:70, and, finally, 20:80 MUF resins. It means that (i) a MUF of higher melamine content, such as of 47:53, should need more than double the amount of hardener than does a 20:80 MUF to reach the same hardening rate, as exemplified from an equal terminal pH of 3. This is logical for a resin of higher melamine content if one considers that melamine is a strong base.^{13,14} The amount of ammonium sulfate hardener is fixed, in general practice, whatever the type of resin is used. Thus, (ii) the higher the melamine content of the MUF resin, the higher the pH at which the resin hardens and, hence, the slower the hardening rate when $(\text{NH}_4)_2\text{SO}_4$ is used. A too fast hardening rate on wood does not sensibly shorten the press time of the board. It is therefore never convenient to go faster than a certain rate of hardening. An increase in the amount of the ammonium salt hardener, over approximately a 3% hardener on resin solids content, does not yield any great gain in either the curing/hardening rate or in performance.^{15,16} Hence, both the 47:53 and the 20:80 MUF resins will be able to give a good bond at industrially significant short press times. The more buffered—hence, slower—47:53 MUF resin will give a much more durable weather and water-resistant bond. This is a consequence of the buffering action described and not only because the resin contains more melamine.

The titration curve of a 30% solution of hexamine is also shown in Figure 1. This indicates that (i) its buffering action—in reality, the buffering action of the hexamine sulfate formed—is more marked than that presented even by the MUF resin of higher melamine content. The slope in the buffering zone, being flatter, and the buffering zone extending up to 11 mL SO_4^{2-} , show this. (ii) The range of pH's in which the buffering zone occurs is at higher pH's, namely, pH 4.8–6.7. Thus, any addition of hexamine, however small, to a MUF resin will both increase the buffering action of the resin and extend the length of its buffering zone. It will also shift the pH at which the buffering zone operates to a higher pH range. Figures 2 and 3 show exactly this effect: Data for the addition of 3.4 and 5.7% hexamine on resin solids in the case of a MUF resin of M:U 20:80 and an F/(M + U) molar ratio of 1.9 are shown in Figure 2. The data for additions of 2 and 3.3% hexamine, respectively, on resin solids in the case of a MUF resin of M:U 47:53 and an F/(M + U) molar ratio of 1.5 are shown in Figure 3. To reach pH 3, approximately 50% more SO_4^{2-} ion is needed when 5.7% hexamine is present (Fig. 2). In short, at 3 mL SO_4^{2-} , the curve is shifted from a pH of 3 to a pH of 4.25. To reach pH 4, approximately 20% more SO_4^{2-} ion is needed even when just 2% hexamine is present (Fig. 3). Conversely, for the same concentration of SO_4^{2-} ions for the pure resin at pH 3, the pH shifted to 4.2 for the resin to which 3.3% hexamine was added (Fig. 3). In both cases, once hexamine as hexamine sulfate is present, the reaction should be sufficiently fast but still relatively slower than without hexamine, yielding a better strength result as a consequence of the enhanced buffering effect. These results indicate that buffering should be as marked as possible, but also that buffering must be used to maintain the resin within a well-defined and rather narrow pH range. If the pH of stabilization of the titration curve, and, hence, of buffering, is too high, the curing of the resin would be too slow. This would have disastrous results when using industrial short curing times. If the pH of stabilization of the titration curve, and, hence, of buffering, is too low, resin curing would still be too fast to obtain much improved strength, with equally disastrous results.

The above leads to the conclusion that any molecules which are capable of maintaining buffering within certain pH limits, and for long enough, should have the same effect as has hexamine sulfate. The situation is, however, not this simple. Figure 4 shows titration curves of a 30:70 M:U MUF resin alone, of ammonia alone, and of the same MUF resin in presence of a fixed, small proportion of ammonia (5.7% on resin solids). It shows that the addition of ammonia to the MUF at ambient temperature brings the titration curves to a range of pH values that are too high. Notwithstanding the evident buffering action, the pH

TABLE I
Comparison of Hexamine Sulfate with a Different, but Ineffective, Buffer, MUF 20:80, 1:1.9

| Hardener type | Dry IB strength (MPa) | IB strength, 2 h boiling (MPa) | Panel density (kg/m ³) | 2 h boiling, swelling, wet (%) | 2 h boiling, swelling, dry (%) |
|---|-----------------------|--------------------------------|------------------------------------|--------------------------------|--------------------------------|
| 3% (NH ₄) ₂ SO ₄ | 1.15 | 0.05 | 722 | 70 | 49 |
| 3% (NH ₄) ₂ SO ₄ + 5% HCHO | 1.12 | 0.15 | 725 | 52 | 38 |
| K ⁺ phthalate (15%) + HCl (2%) | 1.22 | 0.0 | 765 | 83 | 62 |
| K ⁺ phthalate (15%) + HCl (2%) + H ₂ SO ₄ (2%) | 1.06 | 0.02 | 734 | 70 | 54 |
| K ⁺ phthalate (15%) + H ₂ SO ₄ (2%) | 1.19 | 0.03 | 761 | 74 | 59 |
| H ₂ SO ₄ (2%) | 0.99 | 0.04 | 705 | 66 | 52 |

is far too high to get a hardened network of reasonable performance. Thus, buffering occurs but is out of the compromise pH range within which reasonably good strength results can be obtained. This corresponds to applied reality. Ammonia is sometimes used in the glue mix of aminoplastic resins to lengthen its pot life.¹³ However, in the heat of the press during adhesive hardening, ammonia flash-evaporates. This allows the resin to cure when using reasonably fast hot-press times.

Such a condition was reconstructed in the case of the titration curves in Figure 4. The buffer action then returns partly within the relevant pH range. However, the appearance of the titration curves in Figure 4, done after warming MUF + ammonia at temperatures between 60 and 80°C, show a few interesting trends: (i) The curves enter in the "useful" pH range only toward 1.5 mL. Thus, the range of the buffer zone is 7 – 1.5 = 5.5 mL of the SO₄²⁻ ion. This is somewhat shorter than the 47:53 MUF curve but comparable to the 40:60 MUF curve in Figure 1. This makes ammonia and ammonium sulfate slightly less effective buffers than is hexamine sulfate. (ii) The higher the temperature used in Figure 4, the lower is the position of the plateau of the titration curve. The maximum temperature used in Figure 4 is 80°C, because, at 100°C, for 2 min or longer, all the ammonia has already been eliminated. The titration curve reverts almost (but not completely) to that of the MUF alone. In wood adhesives application, such as in particleboard, the adhesive is subject to temperatures of 110–120°C in the panel core for at least a couple of minutes. The temperature is as high as 180–210°C on the board surfaces for several more minutes. Any buffering which could be obtained by addition of ammonia and ammonium sulfate is lost under such conditions. Ammonia can therefore not function as a network formation retarder at these higher temperatures, nor can it function as an effective buffer under the conditions predominant in wood boards manufacture. The applied results confirm that the addition of ammonia does not improve the strength of the wood joint.¹³ (iii) Such an effect can exist at lower temperature. More interesting, however, is the fact that the spread of the curves done at 60 and

80°C is narrow. This is an indication that the ammonia copolymerizes with the MUF resin and that residual ammonia remains in the hardened resin network. A small part of it is coreacted with the resin and remains linked within it by methylene bridges. The inclusion of ammonia linked by covalent methylene bridges to and within the hardened resin network has already been observed and is well known in PF resins. It is the first time that this has been shown to occur also in aminoplastic resins.

A similar high-temperature experiment using hexamine maintains the titration curves at a pH lower than using ammonia at lower temperature. This makes for faster curing. The curve, however, remains there, even at the higher temperatures at which the effect of the ammonia is instead lost (curves not shown here).¹⁷

The buffering effect is one of the main reasons why the hexamine sulfate yields better results. This can also be observed by TMA. Figure 5 shows an increase in modulus of elasticity (MOE) curves at three different constant heating rates, namely, 10°C/min, 20°C/

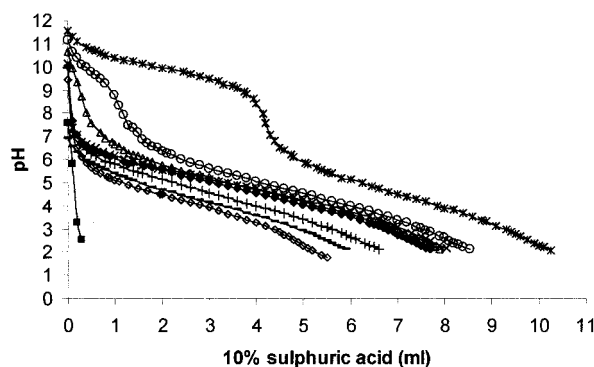


Figure 6 Comparison of variations of pH as a function of titration with 10% H₂SO₄ of 20 g of MUF resins of 60% concentration of F/(M + U) molar ratio of 1.9 and of M:U weight ratio = 30:70, when using hot hexamine and hot ammonia. (■) Pure UF; (◇) pure MUF 30:70; (*) 30:70 + 5.7% ammonia at 25°C; (○) 30:70 + 5.7% ammonia at 60°C for 2 min; (△) 30:70 + 5.7% ammonia at 65°C for 2 min; (×) 30:70 + 5.7% ammonia at 80°C for 2 min; (–) 30:70 + 5.7% hexamine at 75°C for 5 min; (+) 30:70 + 5.7% hexamine at 80°C for 5 min.

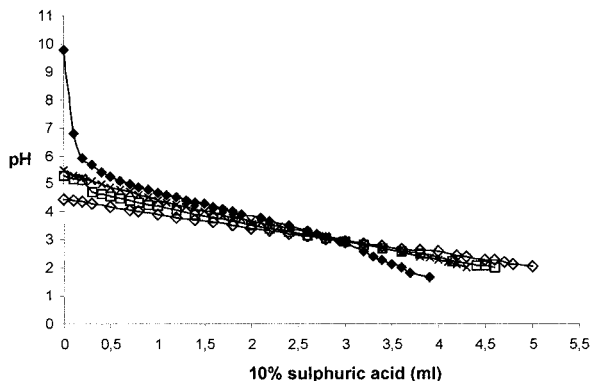


Figure 7 Variation of pH as a function of titration with 10% H_2SO_4 of 20 g of MUF resins of 60% concentration of F/(M + U) molar ratio of 1.9 and of M:U weight ratio = (◆) 20:80 pure, (×) 20:80 + 5% KH phthalate + HCl, (□) 20:80 + 10% KH phthalate + 2 × HCl, and (◇) 20:80 + 20% KH phthalate + 3 × HCl.

min, and 40°C/min of the same MUF resin (47/53, 1.9). This is when ammonium sulfate or hexamine sulfate are used as hardeners, at parity of the SO_4^{2-} ion content on the resin solids content. As expected, the maximum value of the MOE decreases with increase in the heating rate. The slower the heating rate applied, the later the MOE maximum presents itself.¹⁰⁻¹² The curves describing the MOE increase and the maximum MOE values are always lower for the ammonium sulfate hardener than for the hexamine sulfate hardener. Thus, if the buffering action causes a higher MOE maximum value due to slower curing, it appears also to contribute to shift the curves of the MOE increase to faster times. For example, in the case of the 10°C/min curve at 9 min, the ammonium sulfate-catalyzed case presents an MOE of 1700 MPa. The hexamine sulfate case presents an MOE of 2500 MPa (Fig. 5). Equally, at 40°C/min, the two cases present MOE values of, respectively, 1500 and 2350 MPa. This acceleration is confirmed by the consistently faster gel times observed¹ for MUF resins catalyzed with hexamine sulfate even at a parity of SO_4^{2-} concentration. The stability of the buffered environment definitely contributes to a greater regularity of the reaction within the correct pH range in which networking does occur. Thus, this yields networks of higher crosslinking density and higher strength. The effect of having a

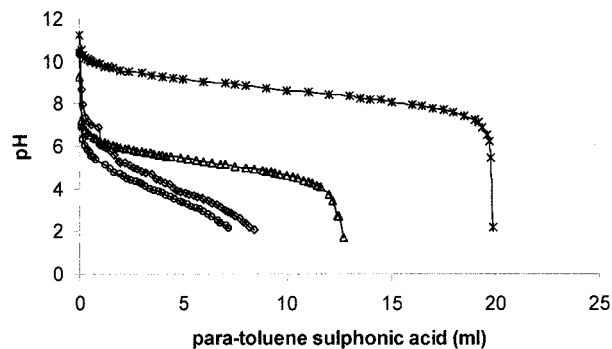


Figure 8 Curves of variation of pH as a function of titration with 5M *p*-TSA of 20 g of a MUF resins of 60% concentration and M:U weight ratio = (C) 47:53, (Δ) of a 30% hexamine solution in water, (*) of liquid morpholine 30% solution, and (◇) of the same MUF + 10% morpholine.

higher maximum value of the MOE the slower the resin is not the predominant effect under conditions of fast hot press/curing time. This is clearly not the reason why the reaction, and the increase in strength of the joint, is faster (Fig. 5).

In conclusion then, hexamine sulfate, as a consequence of its strong buffering action on the MUF resin, yields titration curves at a pH higher than the equivalent proportion of SO_4^{2-} ions introduced as ammonium sulfate. The hardening reaction is faster notwithstanding this. It is normally assumed, in acid-setting aminoplastic polycondensation resins, that pH and acid concentration are the same single parameter determining the rate of polymer buildup, networking, and hardening. Under normal conditions, this is indeed the case. The pH value or acid content can equally well be given to define the rate of hardening and the gel time of these resins. In reality, the assumption that the two parameters are the same is incorrect. It is just the amount and strength of the reservoir of acid which determines the rate at which gelling, setting, and hardening occur. This is equally valid whether the acid is free or is masked in a buffer equilibrium. The pH is only a useful, easy measure of the amount of free acid present.

The proportion of free and buffer-hidden acid introduced in the glue mix is therefore the essential parameter determining MUF resin hardening. The resin then just needs a higher pH than usual to obtain the same

TABLE II
Comparison of Hexamine Sulfate with a Different, Equally Effective, Buffer, MUF 47:53, 1:1.9

| Hardener type | IB strength, 2 h boiling (MPa) | Panel density (kg/m ³) | 2 h boiling, swelling, wet (%) | 2 h boiling, swelling, dry (%) |
|--|--------------------------------|------------------------------------|--------------------------------|--------------------------------|
| 3% (NH ₄) ₂ SO ₄ | 0.30 | 701 | 36 | 22 |
| 3% (NH ₄) ₂ SO ₄ + 5% HCHO | 0.35 | 700 | 37 | 23 |
| 0.5% <i>p</i> TSA + 3% Na ⁺ <i>p</i> -TSA | 0.13 | 702 | 48 | 31 |
| Morpholine/ <i>p</i> -TSA (7.2%) + Na ⁺ <i>p</i> -TSA | 0.35 | 700 | 38 | 22 |

TABLE III
Alternative Buffers MUF 47:53, 1:1.9

| Hardener type | IB strength, 2 h boiling (MPa) | Panel density (kg/m ³) | 2 h boiling, swelling, wet (%) | 2 h boiling, swelling, dry (%) |
|--|--------------------------------------|--|--------------------------------------|--------------------------------------|
| 3% (NH ₄) ₂ SO ₄ | 0.30 | 701 | 36 | 22 |
| Morpholine/ <i>p</i> -TSA (7.2%) | 0.31 | 723 | 38 | 22 |
| Morpholine/ <i>p</i> -TSA (7.2%) + Na ⁺ <i>p</i> -TSA | 0.36 | 718 | 37 | 21 |
| Morpholine/ <i>p</i> -TSA (7.2%) + 0.1 morpholine | 0.34 | 718 | 39 | 23 |
| Morpholine/ <i>p</i> -TSA (7.2%) + 0.2 morpholine | 0.34 | 718 | 38 | 22 |
| Morpholine/ <i>p</i> -TSA (7.2%) + 0.3 morpholine | 0.28 | 713 | 35 | 21 |

rate of hardening. It is, however, the free acid—hence, the pH—which determines the rate of hydrolysis. It is just this then which determines the degradation reaction that occurs simultaneously with hardening in all aminoplastic resins. The two reactions form an equilibrium, generally shifted in favor of polymerization. The presence of the buffer induces an increase in pH between 25 and 50%, yielding faster hardening as a consequence of the higher SO₄²⁻ ion content. The same buffer, however, induces a much lower extent of degradation as a consequence of the higher pH. As the network so formed is then much tighter and less touched by degradation, the result is a much lower thickness swelling of the wood board. The panel has therefore a much greater resistance to water. The effect of a greater MOE, that is, slower resin curing, appears then to play an important role in the improvement of MUF resins caused by hexamine sulfate. However, this role is the lesser one of the two mentioned. The shifting of the polycondensation ⇌ degradation equilibrium to the left, as a consequence of the increased pH, is perhaps the more determinant factor. This is confirmed by the MOE increase curves of hexamine sulfate-catalyzed MUF resins, being faster curing than the equivalent ammonium sulfate-catalyzed ones (Fig. 5). It is confirmed also by the effect being valid within the narrow buffering range of pH's mentioned. At a much higher pH, polycondensation is far too slow, and at much lower pH's, degradation is predominant (see results of panel case bonded with a MUF just

catalyzed with sulfuric acid, with no buffers, even at the same SO₄²⁻ ion concentration, in Table I).

The heat stability of the hexamine sulfate buffer is the third contributing factor that has been established. This means that it gives longer permanence of the buffer effect in relation to other potential buffers, under standard resin curing conditions. From the comparison of the titration graph, there is clear proof of the covalent reaction and inclusion of some ammonia in the hardened MUF resin network (Fig. 4). This is valid for ammonia (Fig. 4), and, hence, also for ammonium sulfate, both at ambient and at progressively higher temperatures. The same occurs even for methyleneimines and methyleneamines derived by the co-reaction of hexamine sulfate with the MUF resin (Fig. 6).

To confirm the effects observed and to determine if some alternatives to hexamine sulfate could be found, different buffers were tested. Figure 7 shows the titration curves of a 20:80 MUF resin alone and to which 5% potassium hydrogen phthalate and HCl were added according to buffer tables in the literature.¹⁸ The slope of the curve in these gives practically no advantage when compared with the resin alone. This indicates that the buffer effect is not enough within the wanted pH range. Further continuation of the curve is at pH ranges which are too low to be of any interest for application to wood adhesives. Thus, one can foresee that little or no improvement, when using this buffer system, will be obtained when used in conjunc-

TABLE IV
pH Values of Different Components and Mixes

| Components/mixes | pH |
|--|----------|
| MUF 47:53 alone | 10.86 |
| MUF 47/53 + morpholine | 11.06 |
| MUF 47/53 + morpholine (+) <i>p</i> -TSA* | 5.80 |
| MUF 47/53 + morpholine + 0.1% morpholine | 11.10 |
| MUF 47/53 + morpholine + 0.1% morpholine + <i>p</i> TSA | 5.94 |
| MUF 47/53 + <i>p</i> TSA | 4.68–5.2 |
| Morpholine/ <i>p</i> TSA in water (7.19 in 3 g water) | 1.5–1.8 |
| Morpholine/ <i>p</i> TSA (7.19 in 3 g water) + 0.1 g morpholine | 7.75 |
| MUF 47/53 + 0.72 g [morpholine/ <i>p</i> TSA in water (7.19 in 3 g water)] | 6.30 |
| MUF 47/53 + 0.36 g [morpholine/ <i>p</i> TSA (7.19 in 3 g water) + 0.1 g morpholine] | 6.45 |

* Preformed complex.

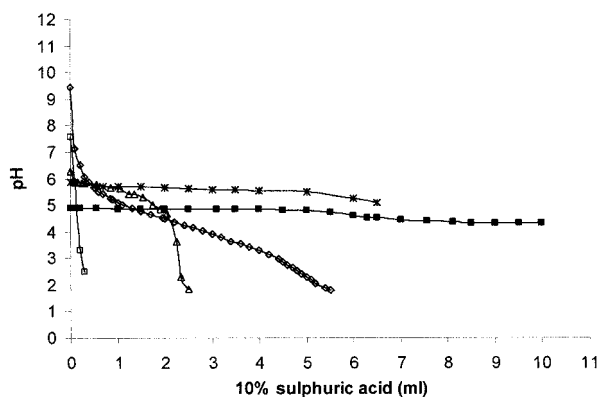


Figure 9 Comparison of curves of variation of pH as a function of titration with 10% H_2SO_4 of 20 g of UF resins of 60% concentration of (\square) F/U of 1.5 and ($*$) of the same UF + 20% of melamine in the form of melamine monoacetate, (\triangle) of the same UF + 10% of melamine in the form of melamine monoacetate, (\blacksquare) of a 30% melamine monoacetate solution in water, and (\diamond) of a 30:70 MUF resin of 1.9 molar ratio as the control, showing at which percentage of melamine acetate the curves go out of the correct pH buffer range to justify the impossibility to use with UF higher amounts of melamine acetate.

tion with MUF resins in board making. The wood particleboard results shown in Table I confirm this forecast. Different variations on the phthalate + HCl buffer theme all give poor wet IB strength results on the boards (Table I). The hexamine sulfate case composed by the reverse route, by premixing ammonium sulfate with formaldehyde and preheating this mix briefly at 80°C ,¹⁹ is the only one giving an acceptable result in Table I. A similar result was obtained with the buffer composed of *p*-TSA + sodium *p*-toluene sulfonate.¹⁸ These titration curves are not shown here. Only the poor board result in Table II is shown.

Toluene sulfonic acid/morpholine complexes of known composition are high-performance hardeners for MF paper impregnation resins.¹ Thus, titrations with a *p*-TSA solution of a morpholine solution, of a MUF resin to which morpholine has been added, and of hexamine were done (Fig. 8). These indicate that the buffering that would be derived from a morpholine/*p*-TSA mix is considerable. In Figure 8, for example, one can observe how much stronger morpholine is in creating a buffer than is hexamine. However, the pH's at which it buffers (pH 8–10) are much higher and outside of the pH range that is of interest. The pH range of interest is much lower: See hexamine curve in Figure 8. The system is, however, simple and flexible enough to be able to bring such curves within the pH range wanted by small variations in the relative proportions of morpholine and of *p*-TSA. This is the case, within limits, as shown by the experimental board results in Table III and the pH values reported in Table IV. The values of pH at which buffering occurs are around pH 5.7–6.5, slightly on the higher side of the

pH range of interest (see Table IV). They still give boards in which the wet IB strength is improved to 20%. This indicates, however, that a lower pH in the accepted range 3–6.5, as in hexamine sulfate, would yield a higher hardening rate and, hence, a better result.

Recently, a different system to improve waterproofing of UF and MUF wood panel adhesives was reported.^{3,4,6,7,20–22} This was by addition of small amounts of melamine acid salts, as hardeners in the glue mix. These salts are of low solubility at ambient temperature but more soluble at higher temperature. The addition of melamine acetate salts in adhesive glue mixes allows the use of MUF resins of lower melamine content. It also allows the use of UF resins to which are added a lower total amount of melamine. These resins, of lower melamine content, have performance characteristics of the top of the range, generally higher melamine content MUF adhesive resins. Improvements in the panels' IB strength, greater than 30–100%, were obtained by this method for such resins. The improvement was partially ascribed to the decrease in melamine wastage due to the elimination of an excessive concentration of melamine at the resin's network crosslinking nodes.^{3,20} It was also ascribed to the more effective homogeneous reaction due to increased melamine solubility at higher temperature when using a melamine salt.^{2,3,6,7,20,23,24}

As this system for upgrading MUF resin performance is very effective, it was decided to check if buffering occurred and, if so, if it was of any importance. The titration of pure melamine acetate indicates a material of considerable buffering capacity (see Fig. 9) when compared to that of a 30/70 MUF resin. Addition of a relatively small proportion (5–15%) of this material improves considerably the buffering capacity of both UF resins (Fig. 9) and of MUF resins (Fig. 10). Furthermore, it does this by maintaining the pH in the correct range for maximum effectiveness of

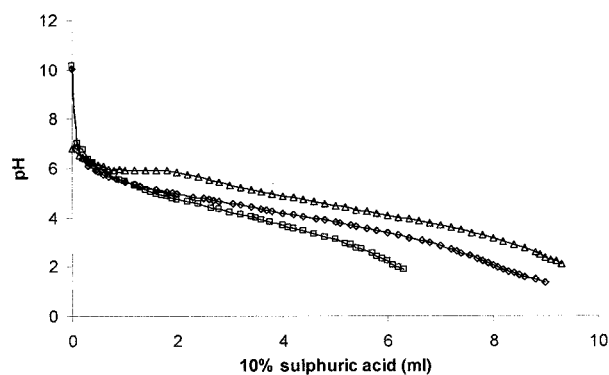


Figure 10 Curves of variation of pH as a function of titration with 10% H_2SO_4 of 20 g of MUF resins of 60% concentration of F/(M + U) of 1.9 and of M:U weight ratio = (\square) 40:60 and (\diamond) 47:53 and (\triangle) of the MUF 40/60 + 10% of melamine acetate.

TABLE V
Comparison of Sequential and Nonsequential MUF Formulations of (M + U):F 1:1.2 With and Without 1.4% Monoethanolamine (on Resin Solids)

| Formulation | Hardener type (%) | | Ethanol-amine (%) | Panel density (kg/m ³) | IB Strength, 2 h boiling (MPa) | Thickness, swelling, dry after 2 h boiling (%) |
|-------------|--------------------|------|-------------------|------------------------------------|--------------------------------|--|
| NS, control | NH ₄ Cl | 3 | 0.0 | 701 | 0.0 | 89.7 |
| NS | SH4 | 7.4 | 0.0 | 718 | 0.0 | 79.9 |
| NS, control | NH ₄ Cl | 3 | 1.4 | 706 | 0.15 | 29.9 |
| NS | SH4 | 3.7 | 1.4 | 710 | 0.19 | 26.7 |
| NS | SH4 | 7.4 | 1.4 | 713 | 0.22 | 26.9 |
| NS | AS + F | 7.4 | 1.4 | 694 | 0.26 | 22.4 |
| S, control | NH ₄ Cl | 3 | 0.0 | 711 | 0.15 | 30.1 |
| S | NH ₄ Cl | 3 | 1.4 | 697 | 0.11 | 32.5 |
| S | SH4 | 7.4 | 1.4 | 722 | 0.12 | 27.1 |
| S | SH4 | 11.1 | 1.4 | 722 | 0.17 | 31.5 |

NS, nonsequential; S, sequential; SH, hexamine sulfate; AS + F, (NH₄)₂SO₄ + HCHO.

the buffering effect, for a well-defined proportion of melamine acetate addition. Thus, in Figure 10, one can see that a 40/60 MUF resin + melamine acetate, to reach a 47:53 M:U ratio, has a better buffering action than that of a straight 47:53 MUF resin. The boards' results obtained with this system are beyond doubt, corresponding to what is observed and can be forecast from the titration curves in Figure 10 and have already been reported.^{2-7,13,18}

An interesting limitation in the case of the application of these salts to UF resins is their upper limit of 15% of melamine, added by weight on resin solids, which can be used.^{3,4} This is exclusively because, when one uses too high an amount of these salts, the pH range of buffering starts to become too high and to drift out of the limits of optimum performance. This is evident, for example, in Figure 9, where 20% melamine addition in the form of melamine acetate is a good buffer for a UF system. However, this occurs at a very reasonable pH of 5.8, which already starts to be out of the range for optimal performance. This means

that the applied improvement observed in this case cannot be, and is not, all due to the improvement given by buffering the system. While buffering is an important contributor, other effects already identified also contribute.^{2-4,6,7,20-24} Figure 9 also shows that the addition of 10% melamine, in the form of melamine acetate, to a UF resin gives better buffering than that of a 30/70 MUF resin and within the correct limits for better performance already reported for these systems.^{3,4}

As regards the use of hexamine sulfate, the effect of a small proportion of monoethanolamine used as shelf-life stabilizer is also of interest. Table V shows the results of wood boards bonded with both sequential and nonsequential low molar ratio MUF formulations with and without monoethanolamine. These show that nonsequential MUF formulations not containing a small proportion of monoethanolamine give a very bad performance (Table V). In these cases, the use of hexamine sulfate alone does not improve the situation. When a small amount of monoethanolamine

TABLE VI
Comparison of the Effect of Monoethanolamine on the Performance of Sequential and Nonsequential MUF Formulations [(M + U):F = 1:1.2; M:U = 47:53]

| Formulation | Hardener type (%) | | Ethanol-amine (%) | Panel density (kg/m ³) | IB strength, 2 h boiling (MPa) | Thickness, swelling, dry, 2 h boiling (%) |
|-------------|--------------------|---|-------------------|------------------------------------|--------------------------------|---|
| NS | NH ₄ Cl | 3 | 0.0 | 701 | 0.0 | 89.7 |
| NS | NH ₄ Cl | 3 | 1.4 | 706 | 0.15 | 29.9 |
| NS | NH ₄ Cl | 3 | 3.0 | 711 | 0.08 | 35.2 |
| NS | NH ₄ Cl | 3 | 6.0 | 718 | 0.06 | 42.6 |
| S | NH ₄ Cl | 3 | 0.0 | 703 | 0.15 | 31.2 |
| S | NH ₄ Cl | 3 | 1.4 | 697 | 0.11 | 32.5 |
| S | NH ₄ Cl | 3 | 3.0 | 706 | 0.0 | 35.2 |
| S | NH ₄ Cl | 3 | 5.0 | 718 | 0.0 | 42.6 |

NS, nonsequential; S, sequential.

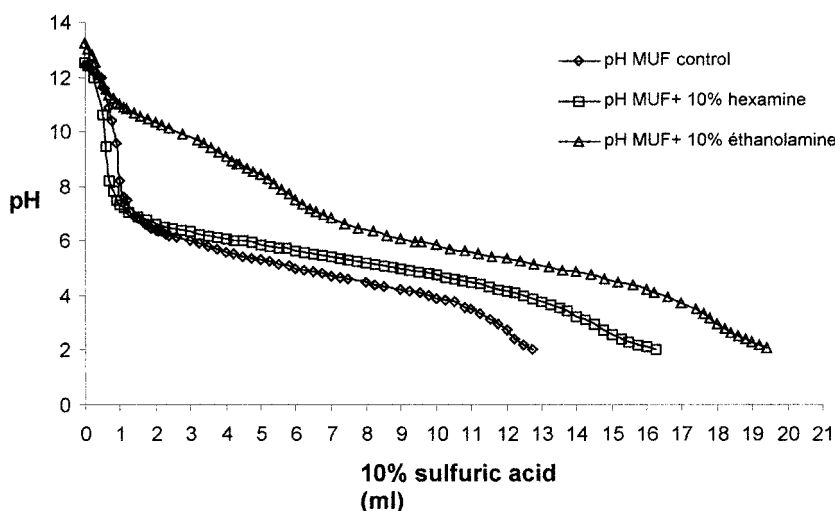


Figure 11 Curves of variation of pH as a function of titration with 10% H_2SO_4 of 20 g of sequential MUF resins of 60% concentration of F/(M + U) of 1.05 and of M:U weight ratio = 47:53. (◇) MUF alone, control; (□) MUF + 10% hexamine; (△) MUF + 10% éthanolamine.

is added, the performance of the nonsequential MUF adhesive markedly improves. Addition of hexamine sulfate further improves the performance of the resin once monoethanolamine is present (Table V). The strong sequential MUF adhesive formulations behave differently. Here, addition of monoethanolamine decreases the performance of the adhesive (Table V). Higher amounts of hexamine sulfate need to be added, when monoethanolamine is present, to reverse this trend (Table V). The proportion of monoethanolamine was increased beyond 1.4% to determine if to this corresponded a further improvement in some resins' performance (Table VI). The results in Table VI show that this is not the case. It is evident that the effect of monoethanolamine is important in relatively weaker MUF formulations. In this case, its effect is synergistic rather than competitive, with that of hexamine sulfate. The reasons for this behavior are evident from the titration curves in Figure 11. At a higher proportion of monoethanolamine, as in Figure 11, the buffer curve is mostly higher than the pH range where optimal hardening occurs. Furthermore, the buffering action is not even in the first part of the curve. Thus, small amounts of monoethanolamine will work well as a buffer and improve inherently weaker MUF resins performance, but increasing its amount will not.

CONCLUSIONS

Iminoamino methylene bases intermediates are obtained by the decomposition of hexamethylenetetramine stabilized by the presence of strong anions such as SO_4^{2-} and HSO_4^- , or hexamine sulfate. They markedly improve the water and weather resistance and the wet IB strength performance of hardened MUF resins used as wood adhesives. The effect is induced

by very small amounts, between 1 and 5% by weight, of this material on the resin solids content. This strong effect allows the use of MUF resin of much lower melamine content while still allowing good performance of the bonded joints. The effect is closely linked to the strong buffering that hexamine sulfate has on MUF resins in the correct pH range for their hardening. The effect was not due to any increase in the molar ratio of the resin as a consequence of hexamine sulfate addition. The reasons for the hexamine sulfate behavior linked to its buffering appeared to be due to a variety of effects.

The reasons initially presumed to cause such effects are, namely:

- (i) The improved strength performance the slower that the resin is cured did not appear to be the main cause. This appears to play a role mainly in the context of the induced regularity of the reaction and stability of conditions being maintained during resin networking, due to the buffer.
- (ii) The shifting of the polycondensation \rightleftharpoons degradation equilibrium to the left as a consequence of the increased pH appeared to be the more determinant factor. This was confirmed by the MOE rate of increase for hexamine sulfate-catalyzed MUF resins being higher than for the equivalent ones catalyzed by ammonium sulfate (Fig. 7). It was also confirmed by such an effect occurring within the narrow buffering range of the pH's mentioned. At a much higher pH, polycondensation is far too slow to occur, and at much lower pH's, degradation is predominant.

- (iii) The heat stability of the hexamine sulfate buffer was established as the third contributing factor. Thus, the hexamine sulfate effect, in relation to other potential buffers, is of longer duration, under standard resin heat-curing conditions.

Alternate systems based on morpholine/*p*-TSA hardeners or melamine salts of carboxylic acids, presenting the same buffering within the wanted parameters ranges, were also shown to have a comparable effect.

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