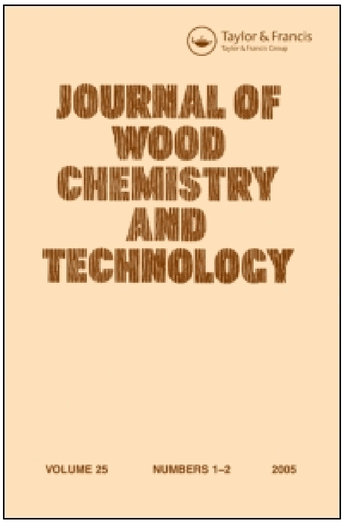

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Wood Enhancement Treatments I. Impregnation of Southern Yellow Pine with Melamine-Formaldehyde and Melamine-Ammeline-Formaldehyde Resins

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WOOD ENHANCEMENT TREATMENTS I. IMPREGNATION OF SOUTHERN YELLOW PINE WITH MELAMINE-FORMALDEHYDE AND MELAMINE-AMMELINE-FORMALDEHYDE RESINS

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ABSTRACT

Southern yellow pine (SYP) was impregnated with melamine-formaldehyde (MF) or melamine-ammeline-formaldehyde (MAF) resins. The dimensional stability, strength properties, weathering, fire resistance and chemical resistance of the impregnated wood were examined. The wood treated with two commercial MF resins or with a synthesized MAF resin exhibited greatly enhanced dimensional stability, fire resistance and resistance to weathering. The chemical resistance increased moderately.

INTRODUCTION

Wood treatments with different kinds of chemicals or resins have been widely studied in order to enhance such wood properties[1] as dimensional stability,[2] biological and chemical resistance,[3] fire resistance,[4] weathering[5] and mechanical properties,[6] etc. A variety of resins can be used for impregnating wood to obtain enhanced properties. The systems used include epoxy resins,[7,8] phenolic resins,[7,9,10] melamine resins,[7,11] urea resins,[7] polyurethane prepolymers[7,12] and unsaturated polyesters, etc.[7] In the course of a research project to develop

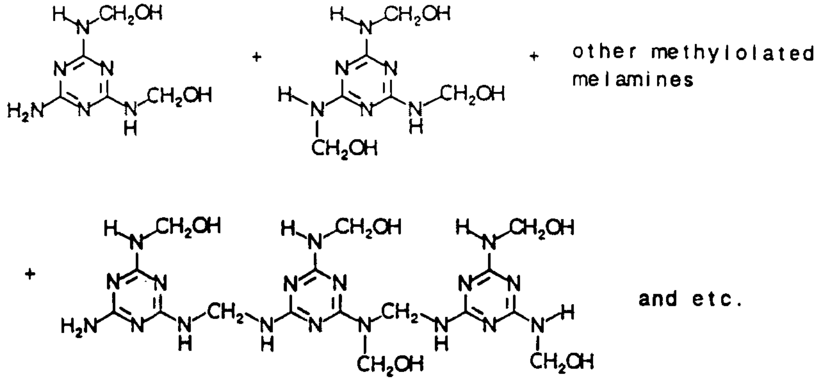

Figure 1. Representative Structures of an A-Stage MF Resin

enhanced wood which can prevent the absorption of chemical warfare agents,[13] different kinds of polymer resins have been selected, impregnated into wood, cured, and the resulting wood properties were examined. MF resins and MAF resins were two important classes of resins used in the initial formulation screening.

MF resins are well known as thermosetting resins used in coatings, adhesives and both paper and textile treatments.[14] MF resins are effective wood adhesives which have been applied in the manufacturing of plywood, particle-board, etc.[15] However, MF resins have not been used for wood impregnation treatments in industry. The MF resins selected for our research are A-stage resins which can be represented as in Figure 1.

MAF resins are new resins just recently reported.[16] They contain ionic groups within their A-stage resin structures at high pH values. Thus they can exhibit unusual features associated with ionomers. After crosslinking, the ionic sites can still exist. Figure 2 is the representative structure of an A-stage MAF resin.

MF resins and MAF resins were selected because they cure rapidly and were expected to chemically bond to the walls of rays and lumens within the wood via N-methylol condensation reactions. Furthermore, these resins are highly

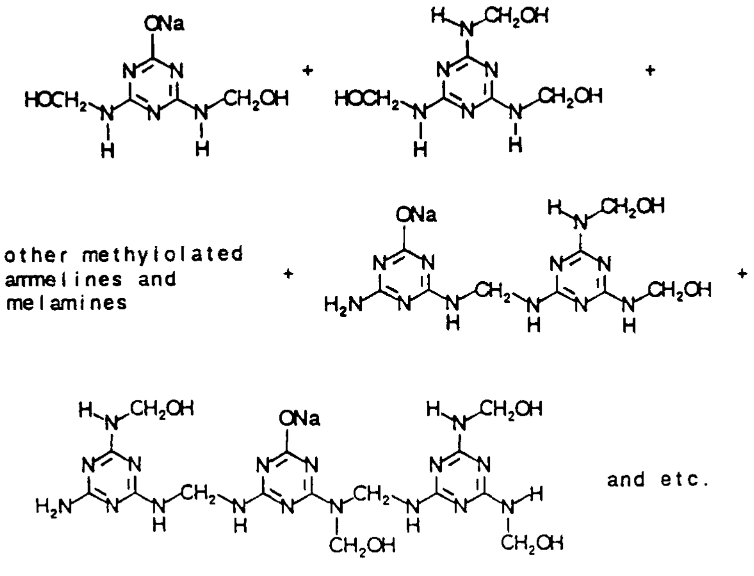

Figure 2. Representative Structures of an A-Stage MAF Resin

crossliked after curing and were not expected to swell in the presence of many chemicals such as oils, solvents, gasoline or chemical warfare (mustard or nerve) agents. Thus, absorption or diffusion of chemicals into the cured resin itself was expected to be minimial. If chemical bonds seal resin to the lumen walls when the resins are cured inside the wood, this also should minimize absorption of chemicals into wood. Furthermore, melamine resins are extremely weather resistant, stable to UV, water resistant and exhibit excellent fire retardant properties.[11] This paper will report and discuss the treatment of southern yellow pine with MF and MAF resins and examine the properties of the treated wood.

EXPERIMENTAL

1. Commercial Melamine-Formaldehyde Resins

Following ten MF resins were obtained from commercial suppliers:

C001 (LA-4M-HS), MF, Astro Industries,

Formaldehyde/melamine mole ratio (F/M) = 1.2-2.5, solids content=60%, pH=9.5±0.2;

C002 (MEL CR-1), methylated MF resin, Astro Industries, F/M=2.5-3.0, solids content=80%, pH=8.5±0.2;

C003 (MEL NW-3A), methylated MF resin, Astro Industries, F/M=4.0, solids content=80%, pH=9.0±0.3;

C004 (PC-6N), methylated MF resin, Astro Industries, F/M=5.0-6.0 solids content=80%, pH=8.8±0.3;

C005 (BTLM 304), MF, powder, BTL Specialty Resin, F/M=2.5;

C006 (BTLM 812), MF, powder, BTL Specialty Resin, F/M=2.1;

C007 (BTLM 830), MF, powder, BTL Specialty Resin, F/M=1.7;

C008 (BTLM 412), Plasticizied MF, BTL Specialty Resin, F/M=1.6;

C009 (BTLM 430), Plasticizied MF, BTL Specialty Resin, F/M=2.2;

C010 (BTLM 829), Plasticizied MF, BTL Specialty Resin, F/M=1.7.

The resins powders were dissolved in water (50% by weight), then used in the impregnation of wood. Other liquid MF resins were directly impregnated.

2. Synthesis of Melamine/Ammeline/Formaldehyde (MAF) Resins

Six MAF resins were prepared with the following F/A/M (Formaldehyde/ammeline/melamine) mole ratios and resin solids contents:

MAF-1, 2.0/0.05/0.95, 64.6%;
MAF-2, 2.5/0.05/0.95, 61.0%;
MAF-3, 3.0/0.05/0.95, 58.5%;
MAF-4, 2.0/0.08/0.92, 64.6%;
MAF-5, 2.5/0.08/0.92, 61.0%;
MAF-6, 3.0/0.08/0.92, 58.5%.

The preparation procedures are as follows. A predetermined amount of ammeline powder and aqueous formaldehyde solution (37% by weight) were charged into the resin kettle and the pH value of the mixture was adjusted to 8.5-9.0 by adding NaOH aqueous solution (4% by weight). The temperature of the mixture was then raised to 90 °C and when the solution became clear, a predetermined amount of melamine was added into the reactor. Afterwards, the temperature was kept at 90 °C and the pH value of the reaction mixture was re-adjusted to 8.5-9.0. The reaction was stopped when the water tolerance of the resin reached 1.5:1 (water : resin) by volume. The reaction time was about 5 hours.

3. Wood Samples Preparations

Defect-free SYP was selected from a local lumber company. The ring orientation of the boards was flat. Boards were planed to a desired thickness and cut into various sizes for specific tests. Sticks cut for treatability tests had dimensions of 0.75 x 0.75 x 4.00 inches (radial [r] x tangential [t] x longitudinal [l]). Cubes (0.75 x 0.75 x 0.75 inches, r x t x l) were cut for water repellent effectiveness (WRE) and antiswelling efficiency (ASE) testing. Wafers were cut with dimensions of 1.25 x 0.078 x 4.00 inches (r x t x l) for impact testing.

Coupons were cut in dimensions of 0.5 x 5.5 x 5.5 inches (r x t x l) for weathering tests. Some of the resin-impregnated and cured coupons were cut into 5-inch diameter disks for chemical warfare agent retention tests. Strips with dimensions of 0.5 x 0.5 x 5.5 inches (r x t x l) were cut from the treated coupons, mentioned above, for toughness testing.

Flame spread test samples were 0.75 x 5.5 x 18 inches (r x t x l). Samples employed in heat and smoke release tests were 6 x 6 x 0.75 inches (t x l x r). Samples used in the smoke chamber tests were 3 x 3 x 0.75 inches (t x l x r). For comparision, blanks and samples treated to 5 pcf with diammonium phosphate (positive controls) were also run.

End-matched blank samples were used for all tests as controls for treated samples (except for the control samples for fire tests).

4. Impregnation Treatments

The full cell treatment schedule was used. Wood samples placed and immobilized in a metal tray were put in a pressure cylinder and subjected to a vacuum of 28 inches Hg for 30 minutes. Then the resin solution was introduced into the tray until the wood samples were totally immersed. After about 5 minutes, the vaccum was released and the pressure inside the cylinder was raised to 150 psig with compressed air and maintained for 60 minutes. The pressure was then released and samples were removed from the tray, weighed and allowed to air dry before curing.

5. Curing Scheme

Wood samples (sticks, wafers, cubes and coupons) impregnated with MF or MAF resins were air dried at room temperature for one day. Then the air dried samples were cured in an oven with a temperature program of 40 to 70 °C over the first 20 minutes, 70 to 100 °C over the second 20 minutes, and 100 to 150 °C over the final 20 minutes. In order to obtain a smooth and continuous resin surface which might retard absorption of chemicals, some treated coupons were cured in a hot press. The curing conditions employed were 30 - 100 psi, 300 - 400 °F and 9 - 16 minutes of press time depending on the formulations employed. Some cured samples were coated with selected coating materials. These coatings included coatings of 2-Ton Epoxy from Devcon Corp., Massachusetts, Scotch Weld Adhesives from 3M Co., Minnesota, and an aliphatic polyurethane coating from Red Eagle Paint Co., Alabama. A specific term "CARC" (chemical agent resistant coating) is used to describe this kind of coatings. Metal disks and selected resin treated samples were CARC coated to serve as positive controls and to improve the chemical agent resistance. The coatings were applied using a soft-bristled brush.

6. Testing Methods

(1) Treatability Tests

The ability of the resin formulations to penetrate wood under the treating conditions used was determined by treating SYP sticks. The resin solution retention before air drying, the solid resin retention after curing, and the weight percent gain (WPG) after curing were used as the criteria of treatability. These values were calculated as follows:

$$\text{Resin Solution Retention (RSR)} = \frac{W(1) - W(0)}{\text{Volume of Stick}} \quad \text{(pcf)}$$

$$\text{Solid Resin Retention (SRR)} = \frac{W(2) - W(0)}{\text{Volume of Stick}} \quad \text{(pcf)}$$

$$\text{Weight Percent Gain (WPG)} = \frac{W(2) - W(0)}{W(0)} \times 100$$

where, W(1) = Weight of treated sample before air drying,
W(2) = Weight of treated sample after curing,
W(0) = Weight of untreated sample.

(2) Anti-Swelling Efficiency (ASE) Tests

Cured 0.75-inch cubes and their end matched controls were immersed in distilled water at 25 °C for 24 hours under ambient pressure and, then, under a 150 psig air pressure for 30 minutes in a pressure cylinder. After the pressure cycle, the samples were immersed in water for one week at 25 °C. Then the sample dimensions were measured using an ultradigit micrometer and the water saturated (green) volume, V(2), was calculated. Then the samples were air dried for 24 hours and oven dried at 105 °C until they reached a constant weight. The sample dimensions after oven drying, V(1), were measured and the volumes were calculated. The volumetric swelling coefficient (S) for both the treated and control samples were calculated as follows:

$$S = 100 \times \frac{V(2) - V(1)}{V(1)} \quad (\%)$$

where, V(1) = wood volume of oven dried sample before wetting,
V(2) = wood volume after saturation with water.

The ASE value was then calculated as follows:

$$ASE = 100 \times \frac{S(1) - S(2)}{S(1)} \quad (\%)$$

where, S(1) = volumetric swelling coefficient for the untreated control cube,
S(2) = volumetric swelling coefficient for the treated cube.

(3) Water Repellency Effectiveness (WRE) Tests

The WRE values are defined by the % swelling vs. time data obtained by soaking wood samples in water for 100 minutes.[17] First, the cube samples were equilibrated in a constant humidity chamber at 30 °C and 55% relative humidity and placed under water in a homemade swellometer which was equipped with two linear displacement transducers and a monitoring computer. The expansion of the cube dimension in the radial direction due to swelling was measured continuously by the transducers placed on the top of the sample. The WRE value was calculated using the following formula:

$$\text{WRE} = \frac{\text{Dc} - \text{Dt}}{\text{Dc}} \times 100 \ (\%)$$

where, Dc = radial swelling of control,
Dt = radial swelling of treated sample,

$$\text{Dc or Dt} = \frac{R(2) - R(1)}{R(1)} \times 100 \ (\%)$$

where R(1)= initial radial dimension,
R(2)= radial dimension after 100 minutes.

(4) Impact Strength

The impact strength of wafer samples (0.78 x 1.25 x 4.00 inches) was determined using a BYK-Gardner heavy impact tester, Model IG-1120. Both 6-inch pound and 8-inch pound loads were used to impact the samples at two different spots, 1 inch apart. If the sample failed using the 6-inch pound load, the 8-inch pound loads were not used. The failures were rated 0-5 levels as follows:

5 = Light indentation;
4 = Medium indentation;
3 = Heavy indentation;
2 = Complete indentation (penetration);
1 = Splits or breaks across or along the grain;
0 = Fragmentation.

The relative impact resistance of treated samples was calculated by dividing the impact strength rating of the treated samples by that of the control. Four samples were tested and the values were averaged. This ratio was expressed as a percentage.

(5) Toughness Tests

Toughness, the capacity to absorb energy or resist shock, was determined by using a Toughness Testing Machine (Testing Machines Inc., New York). The test specimen dimensions were 0.5 x 0. 5 x 5.5 inches. Relative toughness was calculated by dividing the average toughness of the treated strips by that of the control and expressed as a percentage.

(6) DS-2 Resistance Tests

DS-2 is the standard military chemical warfare decontamination solution and comprised of 70% diethylenetriamine, 2% NaOH, 28% ethylene glycol and its monomethyl ether. The resistance of the treated wood surface to this solution was studied. A drop (about 0.06 gm) of the solution was placed on the surface of the treated samples and the time for the drop to get absorbed completely was recorded and rated as follows:

0 to 5 min.	Very fast;
6 to 60 min.	Fast;
61 to 240 min.	Medium;
241 to 480 min.	Slow;
481 and over 481 min.	Very Slow.

While recording the absorption time, the rate of spreading of the drop was also observed. In general, greater spreading correlated with faster absorption.

(7) 2-Chloroethyl Ethyl Sulfide Resistance and Retention

The second resistance test of the treated wood sample was performed using 2-chloroethyl ethyl sulfide (CEES), a mustard agent simulant. The test was carried out by placing a drop of CEES on the sample (coupon) and allowing it to sit for 5 minutes. The CEES resistance was rated by comparison with an untreated control coupon. The rating scale ranged from poor to very good as shown below:

Very good: Droplets remained after 5 min. without much spreading;

Good:	Droplets remained but significant spreading occurred after 2-3 min.;
Fair:	Droplets absorbed in less than 1-2 min.;
Poor:	Droplets absorbed in less than 0.5 min..

The CEES retention test was also performed for selected samples using a quantitative method of determining the amount of CEES left after washing with DS-2 solution. The method used a Carlo Erba gas chromatograph coupled with a MS80 mass spectrometer. CEES (25 microliters) was placed on a wood sample (1.5 x .85 x .50 inches) and allowed to sit for one hour. The sample was then rinsed copiously with DS-2 solution while scrubbing with a test tube brush. Then the wood sample was suspended in 30 ml of methylene chloride in a polypropylene screwcap bottle. Naphthalene (25 ppm) was added as an internal standard. The bottle was then rotated on a sample rotator for one hour. The extracted solution was transferred to an autosampler vial and analyzed for CEES on the GC-MS. The data were presented as the percent CEES retention.

(8) Chemical Warfare Agent Tests

The warfare agents used in this research include 2,2'-dichlorodiethyl sulfide, $C_4H_8Cl_2S$ (HD), O-ethyl-S-[2-(N,N-diisopropylamino)ethyl]methylphosphonothioate, $C_{11}H_{26}NO_2PS$ (VX) and methylphosphonofluoridic 1,2,2-trimethylpropylester, $C_7H_{16}FO_2P$ (TGD). Visual drop absorption resistance tests and quantitative residuals tests with HD, VX and TGD were carried out at the Midwest Research Institute (MRI), Kansas City, Kansas. For the initial screening of resistance to these three agents a single drop of the appropriate chemical was applied to the surface of the wood/polymer substrate. The physical behavior of the drop was visually observed and noted. These results were used to select or modify formulations that would be used in the subsequent agent resistance tests.

Quantitative evaluations of the removal of the warfare agents were conducted. The agent being tested (100 mg) was applied as drops to the surface of the 5 inch diameter test coupon. After standing for one hour the coupon was decontaminated by applying DS-2 solution, scrubbing with a test tube brush, and rinsing with water. After air drying, the coupon was fitted into a small test chamber for measurement of agent desorption. The air velocity through the chamber was 1 m/s and the desorbed agent was trapped by two liquid impingers arranged in series. The amount of material that was collected in the impingers was determined by gas chromatography-flame photometric detection. This method was conducted according to Test Operation Procedure (TOP) 8-2-111, NBC Contamination Survivability of Small Items of Equipment.

(9) Heat Release Tests

The heat release test (generally known as the OSU Heat Release) was performed at the USDA-Forest Service, Forest Products Laboratory, Madison, Wisconsin according to the ASTM E906-86 method.[18] Data presented in this test include time to ignition and the rates of both heat and smoke release as averages over 5 minutes of burning.

(10) Smoke Release Tests

This method determines the specific optical density of smoke generated by sample exposed to an electrical heat flux according to ASTM E662-92.[19] This test was performed at the USDA-Forest Service, Forest Products Laboratory, Madison, Wisconsin.

(11) Flame Spread Tests

The surface flammability of the treated wood samples was determined using a radiant heat energy source according to ASTM E162-90.[20] The tests were conducted by the Commercial Testing Company, Dalton, Georgia. This test reports data in terms of (a) a flame spread factor, (b) a temperature rise, (c) a heat evolution factor and (d) a flame spread index.

(12) Weathering Tests

Weathering tests were carried out by the South Florida Test Service, Miami, Florida according to ASTM G-26 and MIL STD 810 E, Procedure II.[21] The samples exposed to an irradiance over a period time were evaluated for any deformation and discoloration.

TABLE 1
Treatability of Southern Yellow Pine with Melamine-Formaldehyde Resins[1)]

Resin Types	Resin Formulations	F/M (mol ratio)	Solid Content (%)	Viscosity (cp)	RSR[2)] (pcf)	SRR[3)] (pcf)	WPG[4)] (%)
Methylated MF Resins	C002	2.5-3.0	80	NA[5)]	29	19	49
	C003	4.0	80	NA[5)]	26	13	37
	C004	5.0-6.0	80	NA[5)]	19	10	24
MF Resins	C007	1.7	50	30	46	27	75
	C001	1.5-2.5	60	NA[5)]	42	27	68
	C006	2.1	50	30-35	27	13	35
	C005	2.5	50	45-50	46	18	43
Plasticized MF Resins	C008	1.6	50	25-35	43	23	58
	C010	1.7	50	30	38	19	53
	C009	2.2	50	40	43	20	51

1) Sample size: 0.75 x 0.75 x 4.00 inches sticks.
2) RSR= Resin solution retention.
3) SRR= Solid resin retention.
4) WPG= Weight percent gain.
5) Not available.

RESULTS AND DISCUSSION

1. Wood Treatability

The treatability of wood with MF and MAF resins was demonstrated by the resin solution retention before drying (RSR), the solid resin retention after curing (SRR), and weight percent gain after curing (WPG) for wood sticks treated with these resins using the full cell process for impregnation and the same curing scheme for all samples (oven cured at 40 to 150 °C for one hour). The RSR, SRR and WPG data are listed in Table 1 for MF resins and in Table 2 for MAF resins.

In addition to wood structure, there are many factors which affect wood treatability. The solubility of resin in water, the molecular size or molecular weight, the viscosity of resin solution and the solids content of the resin solution

TABLE 2
Treatability of Southern Yellow Pine with Melamine-Ammeline-Formaldehyde Resins[1]

Resin Type and Molar Content	Resin Formulations	F/(A+M) (mol ratio)	Solid Content (%)	RSR[2] (pcf)	SRR[3] (pcf)	WPG[4] (%)
MAF Resins	MAF-1	2.0	64.6	24	15	29
A/M =	MAF-2	2.5	61.0	30	21	60
.05/.95	MAF-3	3.0	58.5	38	25	63
MAF Resins	MAF-4	2.0	64.6	35	15	37
A/M =	MAF-5	2.5	60.0	32	18	45
.02/.98	MAF-6	3.0	58.5	44	33	101

1) Sample size: 0.75 x 0.75 x 4.00 inches sticks.
2) RSR= Resin solution retention.
3) SRR= Solid resin retention.
4) WPG= Weight percent gain.

play important roles in wood treatment. In this research four classes of melamine resins were used: normal MF, methylated MF, and plasticized MF resins and MAF resins synthesized in our laboratory. The F/M or F/(A+M) mole ratios were varied and all were A-stage resins which dissolved in water to give low viscosity solutions. The treatability data in Tables 1 and 2 show that these melamine resins are readily impregnated into southern yellow pine. WPG values as high as 101% were achieved. The lowest WPG was 24%.

The treatability data for methylated MF resins were related to the F/M ratios (Table 1). With an increase in the F/M ratio, the RSR, SRR and WPG values decreased. With an increase in the F/M ratio, the number of methylol groups and $-CH_2OCH_3$ groups is expected to increase. The treatability using plasticized MF or normal MF resins was related to the resins' viscosities. With increasing resin viscosity the WPG decreased. This is probably related to the difficulty of resin solution penetration into the small voids in wood.

MAF resins with higher solids contents tended to give lower RSR levels. The MAF resins with low solids contents (MAF-3 and MAF-6) penetrated the wood structure more easily than those with high solids contents (MAF-1 and MAF-4). Resins with lower solids content generally have low viscosities to facilitate the diffusion and penetration of resin.

2. Dimensional Stability

The ASE and the WRE measurements evaluate the dimensional stability of the treated wood. MF and MAF resins are expected to be deposited inside the void space within the wood and also bond to hydroxyl groups on the surface of the wood cells. Cured melamine resins are extremely water resistant. Therefore, wood treated with MF or MAF resins should exhibit improved dimensional stability. The ASE and WRE values for wood samples treated with MF or MAF resins are shown in Table 3.

In most of the cases the treatment with MF or MAF resins improved dimensional stability. For example, the ASE and WRE values for resin C004 treated samples were 53% and 96%, respectively. For resin MAF-5 these values were 75% and 98%, respectively. The WRE values of methylated MF resins were higher (above 96%) than those of other MF resins.

The WPG values did not correlate with the dimensional stability.

3. Mechanical Properties

The mechanical properties of treated wood were evaluated by both impact strengths and toughness values relative to untreated controls. Impact strength tests were carried out using oven cured wafers and press cured coupons. The impact strengths of MF resin treated wafers were quite low in most cases (see Table 4). Only resin C006 gave an impact strength equal to that of the untreated wood. Most often values were less than 40% of that of the untreated control. This brittleness appears to be the result of the highly crosslinked, rigid structure of the cured MF resins and of the fact that the resins bond to lumen surfaces while the crosslinking takes place. The volume contraction of the resin during the cure puts stresses on the internal wood surfaces which bind to the resin. This often results in the formation of checks visible on the surface.

TABLE 3
Dimensional Stability of Southern Yellow Pine Treated with MF or MAF Resins[1)]

Resin Types	Resin Formulations	F/M or F/(A+M) (mol)	WPG[2)] (%)	ASE[3)] (%)	WRE[4)] (%)
Methylated MF Resins	C002	2.5-3.0	71	40	98
	C003	4.0	43	30	98
	C004	5.0-6.0	50	53	96
MF Resins	C007	1.7	43	43	86
	C001	1.5-2.5	67	45	91
	C006	2.1	48	41	90
	C005	2.5	46	30	83
Plasticized MF Resins	C008	1.6	48	41	75
	C010	1.7	53	51	90
	C009	2.2	47	23	85
MAF Resins A/M = .05/.95	MAF-1	2.0	76	48	97
	MAF-2	2.5	91	14	97
	MAF-3	3.0	61	8	94
MAF Resins A/M = .08/.92	MAF-4	2.0	61	57	95
	MAF-5	2.5	59	75	98
	MAF-6	3.0	41	36	89

1) Sample size: 0.75 x 0.75 x 0.75 inches cubes.
2) WPG = Weight percent gain.
3) ASE = Anti-swelling efficency.
4) WRE = Water repellency effectiveness.

MAF resins are a new class of resins first made in our laboratories.[16, 22] The crosslink densities of these MAF resins were lower than those of the MF resins and preliminary results have shown that laminates formulated with MAF systems are more flexible.[22] The observed impact strengths of wood treated with MAF resins were generally higher than those for MF resin treated wood, ranging from 53 to 113% relative to untreated wood.

Toughness test samples were cured in a hot press. Temperature, pressure and curing time were expected to be the important factors affecting the test results.

TABLE 4
Retention of Impact Strength after Treating Southern Yellow Pine with MF or MAF Resins[1]

Resin Type	Resin Formulations	F/M or F/(A+M)	WPG (%)	Impact Strength Retention (%)[2]
Methylated MF Resins	C002	2.5-3.0	94	30
	C003	4.0	74	57
	C004	5.0-6.0	58	73
MF Resins	C007	1.7	65	12
	C001	1.5-2.5	90	21
	C006	2.1	63	100
	C005	2.5	76	0
Plastcized MF Resins	C008	1.6	81	0
	C010	1.7	31	74
	C009	2.2	67	8
MAF Resins A/M = 0.05/0.95	MAF-1	2.0	61	61
	MAF-2	2.5	83	80
	MAF-3	3.0	96	73
MAF Resins A/M = 0.08/0.092	MAF-4	2.0	61	80
	MAF-5	2.5	59	113
	MAF-6	3.0	49	62

1) Sample sizes: 0.075 x 1.25 x 4.00 inches wafers.
2) Calculated by dividing the treated sample's rating by the rating of the control and multiplying by 100.

Different hot press cycles were used for different resins: MAF-5 resin, a mixture of MAF-5/phenol formaldehyde resin (PM-4, a mixture of 50% MAF-5 and 50% Plenco 761 PF resin), and MF resin C004. Representative test results are shown in Tables 5, 6 and 7 for the MAF-5, PM-4 and C004 systems, respectively. Fairly high toughness values were achieved using resin MAF-5, cured at 350-400 ^{o}F and 50 psi for 12-16 minutes (Table 5). Comparing samples D and E (WPG 17.9-24%) with B and C (WPG 45.9- 46.6%) in Table 5 shows that samples with a low WPG were tougher than those with higher WPG values. PM-4 samples (Table 6) exhibited somewhat higher toughness values than MAF-5 samples. This is consistent with the fact that phenolic resins were observed to improve impact

TABLE 5

Retention of Toughness after Treating Southern Yellow Pine with MAF Formulation, MAF-5. Effect of Different Curing Conditions

Coupons No.	Curing Conditions			Solid Resin Retention (pcf)	WPG (%)	Toughness Retention (%)
	Temp. (°F)	Pressure (psi)	Time (min.)			
MAF-5/A	300	50	12	12.8	37.6	73
MAF-5/B	350	50	12	16.2	46.6	82
MAF-5/C	400	50	12	15.7	45.9	88
MAF-5/D	400	50	12	7.9	24.0	104
MAF-5/E	350	50	16	6.2	17.9	92

TABLE 6

Retention of Toughness after Treating Southern Yellow Pine with a Mixture (PM-4) of 50% MAF-5 and 50% 761 Plenco PF Resins. Effect of Different Curing Conditions.

Coupons No.	Curing Conditions			Solid Resin Retention (pcf)	WPG (%)	Toughness Retention (%)
	Temp. (°F)	Pressure (psi)	Time (min.)			
PM-4/A	350	50	12	8.2	21.5	104
PM-4/B	350	100	16	12.2	32.0	103
PM-4/C	400	100	12	9.9	24.5	111
PM-4/D	350	100	12	10.2	27.0	91

TABLE 7

Retention of Toughness after Treating Southern Yellow Pine with MF Formulation, C004. Effect of Different Curing Conditions.

Coupons No.	Curing Conditions			Solid Resin Retention (pcf)	WPG (%)	Toughness Retention (%)
	Temp. (°F)	Pressure (psi)	Time (min.)			
C004/A	300	100	12	21.8	59	91
C004/B	350	50	10	15.2	42	63
C004/C	400	30-50	9	16.8	48	57
C004/D	400	50	9	20.8	59	72
COO4/E	(Cured at room temp. for 1 week)			23.1	65	72

TABLE 8
Qualitative Chemical Resistance Tests for Treated Southern Yellow Pine

Formulations	DS-2 Resistance	CEES Resistance	Chemical Agents		
			HD1)	VX2)	TGD3)
C003 (MF)	Slow	Good	4)	4)	5)
C004 (MF)	Slow	V. Good	4)	4)	5)
C006 (MF)	Slow	V. Good	4)	4)	5)
C008 (MF)	Slow	V. Good	4)	4)	5)
MAF-3	Fast	Poor	4)	4)	5)
MAF-4	Medium	Fair	4)	4)	5)
MAF-5	Slow	Good	4)	4)	5)
MAF-6	Slow	Good	4)	4)	5)

1) HD = 2,2'-dichlorodiethyl sulfide.
2) VX = O-ethyl-S-[2-(N,N-diisopropylamino)ethyl]methylphosphonothioate.
3) TGD = methylphophonofluoridic 1,2,2-trimethylpropylester.
4) Rapid wetting, coat dissolves and spreads.
5) Bead intact, no visual penetration.

strength and toughness.[13] The optimized hot press curing conditions for PM-4 were 350-400 °F at 100 psi for 12-16 minutes. The toughness values for MF resin C004 were lower than those of either MAF-5 and PM-4 systems. Check and crack formation were observed in the C004 treated samples apparently because of the high crosslinking and volume contraction occurring during hot press curing.

4. Chemical Resistance

Melamine resins were expected to form some chemical bonds to the ray and lumen walls within wood via N-methylol condensation reactions. Furthermore, cured melamine resins are highly crosslinked and not expected to swell in the presence of most chemicals. Hence, it was hoped that chemical warfare agents would be prevented from penetrating into the treated wood. The results of qualitative visual resistance tests for DS-2, CEES, HD, VX and TGD are given in Table 8. Several systems gave good or very good CEES and TGD resistance values and all systems gave no adverse results on DS-2 testing. Unfortunately, HD and VX appeared to wet the treated wood surfaces since these liquids spread

TABLE 9
Quantitative Chemical Resistance Tests for Treated Wood Samples Compared with Metal Samples

Formulations	Sample No.	CEES Retention (%)	Chemical Agent Residuals (ug/100 cm^2) HD	Chemical Agent Residuals (ug/100 cm^2) VX
C004 (MF)	S3	7.67	843	-
	M4	-	-	10000
	M11	-	-	250
C004 (MF)	1-5	-	0	58
[CARC Coated]	1-7	-	0	14
MAF-5	P-1	6.23	611	-
PM-4$^{1)}$	J-1	3.94	744	-
C004/	W9-1	-	-	300
WU208$^{2)}$	W9-2	-	-	700
Metal Disks	Metal$^{3)}$	-	0	0
[CARC Coated]	RE-1$^{4)}$	-	3100	>1800

1) PM-4 is a mixture of 50% MAF-5 and 50% Plenco 761 PF resins.
2) WU 208 is a phenol-formaldehyde (F/P = 1.55) resin.
3) Coated with 2-Ton Epoxy resins.
4) CARC coating provided by Red Eagle Paint.

out. However, all these visual HD, VX and TGD tests were carried out on oven-cured samples and not on the better quality press-cured samples which have smooth continuous surface resin layers.

Quantitative CEES, HD and VX absorption tests were performed on press cured samples. The results are shown in Table 9. The results indicated significant HD and VX uptakes by the resin treated samples. Consequently, MF, MAF or MAF/PF resin treatments alone were not satisfactory for these chemical warfare agents. When an additional surface coating was applied using CARC coatings, the MF resin treated wood surfaces totally blocked HD uptake. Furthermore, the VX absorption was cut down substantially using a CARC coating on MF (C004) treated wood. Microcracks and checks formed at the surface of MF and MAF treatments must have contributed to the initial failure of the MF and MAF resin treatments. Once these microcracks were covered by the CARC coatings, the MF systems behaved better. However, even the CARC coated samples did not pass the very low, required VX residual limit of 4.3 ug/100 cm^2.

MF and MAF resin systems were originally considered attractive because they could chemically bond to the internal wood lignocellulosic surfaces. Curiously, this desirable property probably contributed to their failure in chemical warfare agent and simulant absorption testing. The good adhesion to cell walls subjected the wood structure to increasing stresses as the volume contraction took place during curing. Since MF and MAF resins are rigid, brittle and highly crosslinked and have high Tg values, high internal stresses have developed and are not relieved by an elastic strain on the part of the resin. Thus, the wood deforms by forming checks and microcracks to relieve these stresses. These microcracks take up chemical agents applied to the wood surfaces.

5. Fire Retardance

Several MF or MAF resins imparted excellent fire retardant properties to southern yellow pine after impregnation and curing. The results were expected since melamine, itself, has been used as a fire retardant.[11] The fire retardant properties of the treated SYP were measured using three methods: the OSU (Heat and Smoke Release) Chamber (Table 10), the Smoke Density Chamber in both the flaming and non-flaming modes (Table 11), and the 2-foot Flame Spread Tunnel test (Table 12). For comparison, control (untreated SYP) and positive control (SYP treated to 5 pcf with diammonium phosphate [DAP]) samples were also run. DAP was chosen since both mono- and diammonium phosphate are among the most effective fire retardants known[23] due to the synergistic combination of nitrogen and phosphorus. However, they have the disadvantage of being easily leached. Since melamine has been used as fire retardant, MF and MAF resins were expected to have good retardant properties in addition to being leach resistant.

TABLE 10
Fire Retardant Results on Treated Southern Yellow Pine from OSU Chamber Tests (ASTM E906-86)

Treatment Resin/Additives[1]	Resin/Additive Retention after Curing (pcf)	Results[2]		
		Ignition Time (Second)	Heat Release Rate (kw/m^2)	Smoke Release Rate ($1/min.-m^2$)
Control	0	33	108	6.7
Control	0	68	119	6.2
Positive Control (DAP)	4.9	N.I[3]	23	1.2
MF C004	17.8	61	132	3.6
MF C006	11.1	N.I[3]	28	2.5
MF C006	12.0	N.I[3]	48	1.7
MF C006	20.0	N.I[3]	4	10.0
MF C006/MAP/PA	9.0/0.7/0.1	137	65	1.6
MF C006/MAP/PA	11.5/1.2/0.3	~300	31	1.0
MF C006/MAP	13.6/3.5	N.I[3]	36	3.7
MAF-5	5.9	49	104	1.2
MAF-5	10.1	115	68	0.8
MAF-5	13.8	95	75	0.7
MAF-5/MAP	8.0/0.9	188	44	1.0
MAF-5/MAP	19.9/2.1	N.I[3]	9	2.1

1) DAP is diammonium phosphate, MAP is monoammonium phosphate and PA is phosphoric acid.
2) Average of two duplicate samples.
3) "N.I" indicates the sample which did not ignite.

The OSU Chamber (Table 10) appeared to give fairly reproducible results. This can be seen by two sets of controls where only the ignition time varied significantly, and the two samples treated with the MF C006 resin to approximately the same level (11.1 and 12.0 pcf) where only the heat release rate varied.

Treatments with melamine resin C006 gave very good fire retardant properties (Table 10), as expected for a melamine resin. For example, at the highest treatment level of 20 pcf, the samples did not ignite and had a significantly lower

TABLE 11
Results from Smoke Density Chamber Tests (ASTM E662-92)

Treatment Resin/Additive[1]	Resin/Additive Retention after Curing (pcf)	Smoke Obscuration Index (SOI)[2]	
		Non-flaming Mode	Flaming Mode
Control	0	169.7	54.4
Positive Control (DAP)	4.9	21.1	34.0
MF C006	12.3	33.9	4.1
MF C006	42.9	17.0	181.6
MAF-5	6.0	44.1	12.5
MAF-5/DAP	12.0/2.1	22.4	18.5

1) DAP is diammonium phosphate.
2) Average of three samples.

heat release rate than the positive controls. This high melamine level also caused a high smoke release rate. Lower level of MF C006, approximately 12 pcf, gave results which were close to that obtained by the positive control. The addition of small amounts of monoammonium phosphate (MAP) and phosphoric acid to MF C006 appeared to help lower the smoke emission.

The melamine-ammeline resin MAF-5 gave poorer ignition times and heat release rates but their smoke release rates were better than the melamine resin C006 (Table 10). The addition of small amount of MAP appeared to help this property by lowering the heat release and increasing the time to ignition. Since cured melamine resins are water resistant, it would be expected that MAP or DAP added in conjunction with melamine resin would become fairly leach-resistant.

The methylated melamine resin C004 provided little fire retardant properties (Table 10). This was probably due to methyl and methylol content which resulted in a higher "hydrocarbon content".

The results from the smoke density chamber tests (Table 11) showed that the MF resin C006 and MAF-5 resin gave lower smoke obscuration index (SOI)

TABLE 12
Results from Flame Spread Test on Treated Southern Yellow Pine (ASTM E162-90)

Treatment Resin/Additive[1]	Resin/Additive Retention after Curing (pcf)	Flame Spread Index (I_s)[2]
Control	0	100.9 (4)
Positive Control (DAP)	5.0	3.7 (4)
MF C004	32.3	82.3 (4)
MF C006	11.1	18.9 (2)
MF C006	33.7	0.0 (2)
MAF-5	10.5	28.8 (2)
MAF-5	14.0	8.4 (2)
PM-4	3.8/4.3	31.3 (2)
PM-4	6.4/7.2	7.5 (2)

1) DAP is diammonium phosphate and PM-4 is a mixture of 50% MAF-5 and 50% Plenco 761 resins.
2) The number of replications is shown in parenthesis.

values than the untreated samples in the non-flaming mode. In addition, the samples treated to very high levels (42.9 pcf) with MF C006 gave a slightly lower non-flaming SOI value than the positive controls. However, this same treatment gave a higher flaming SOI value than the untreated samples. All other MF resin-treated samples gave lower flaming SOI values than the positive controls.

The flame spread index (IS) values (Table 12) were lower for the melamine resin-treated samples than for the untreated controls. The methylated melamine resin C004, however, gave only a slightly reduced IS value, as would be anticipated from the OSU results in Table 10. All other melamine resins gave significantly lower IS values than the control. In addition, the level of MF resin added appeared to be a significant factor, with higher melamine resin levels giving lower IS values. One set of samples, treated to the high level of 33.7 pcf with MF C006, had an IS of 0. The combination of melamine-ammeline resin and phenolic resin (PM-4) also appeared to give fairly low IS values, with the samples treated at 13.6 pcf giving an IS of 7.5, as compared to the positive control value of 3.7.

In summary, it appears that wood treated to moderate levels (6 to 13 pcf) with melamine resins will give ignition time, heat release, SOI and IS values which are comparable with that obtained by a 5 pcf DAP treatment. At higher melamine resin treatment levels of up to 35 pcf, or with the addition of moderate amounts of DAP or MAP, all fire retardant properties except perhaps for smoke generation can exceed those obtained by treatment with 5 pcf of DAP. The use of a highly methylated resin (high F:M ratio of 5-6), however, provides less pronounced fire retardant properties.

6. Weathering

The coupon samples treated with C004, C006, MAF-5 and PM-4 formulations were sent to South Florida, Miami, Florida for weathering test (ASTM G-26 and MIL STD 810 E Procedure II). All samples passed this test. These treated coupons exhibited excellent weathering properties. No deformation and no discoloration were observed with any of these samples.

CONCLUSIONS

1. Southern yellow pine is treatable with water soluble A-stage MF or MAF resins using the full cell process. The resin retention or weight percent gain of the treated wood can be controlled by changing of resin type, resin solids content, or resin viscosity.
2. Changes in wood properties are apparent after treatments with MF or MAF resins. Improvements in dimensional stability, fire resistance and weathering resistance are achieved.
3. Wood treatments with methylated MF resin C004 or MAF-5 resin resulted in the best dimensional stability. Most water repellency effectiveness values for the treated woods are higher than 90%.

4. Samples treated with MF resin C006 gave the best fire resistance: their properties were better than samples treated with diammonium phosphate. The fire resistant properties of other MF or MAF formulations are better than those of control samples.

5. Mechanical properties were often degraded by resin treatments apparently because the cured resins formed inside the wood were rigid and brittle. However, MAF resins with a PF resin added (PM-4) maintained strength properties equal to the untreated wood.

6. The treated wood provided chemical resistance to DS-2, CEES and TGD. However, the treatment can not impart an adequate decontaminability of the warfare agent VX even without a surface coating.

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