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Preliminary Findings on Adhesive Bonding of CCA-Treated Southern Pine

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ABSTRACT

Virtually no southern pine lumber treated with chromated copper-arsenate (CCA) is used in adhesively bonded structural lumber products, either because preservatives interfere with adhesion to the treated wood or because products treated after bonding severely degrade from warp, splits, and checks. Research at the Forest Products Laboratory seeks to identify causes and offer solutions for poor adhesion. Scanning electron microscopy and elemental analysis by energy dispersive spectrometry showed that cell lumen surfaces of CCA-treated wood were thoroughly covered with hemispherical deposits of mixtures of chromium, copper, and arsenic. The metallic deposits were so pervasive that most opportunities for molecular forces of attraction to act between normally polar wood and adhesive were physically blocked. Differential scanning calorimetry was used to determine if Cr^{+6} , Cr^{+3} , Cu^{+2} , and As^{+5} ions, which might be present in excess near the wood's surface, could affect the cure of a phenol-formaldehyde adhesive. Thermograms indicated that all ions accelerated the cure when in solution; however, no such accelerated cure occurred when the CCA preservative was chemically "fixed" in the treated wood. Despite the presence of insoluble metallic deposits blocking molecular-level contact between wood and adhesive, mechanical interlocking by a deeply penetrating phenolic adhesive produced delamination-resistant bonds in CCA-treated wood. Limited tests also showed that a phenol-resorcinol-formaldehyde adhesive could produce delamination-resistant bonds when the wood surfaces were pretreated with a surface modifier.

INTRODUCTION

The wood-preserving industry treated an estimated 7.93 million cubic meters of southern pine lumber with chromated copper arsenate (CCA) preservatives in 1988. This was 37 percent of total southern pine lumber production and 78 percent of all treated lumber production in that year (1,12). Virtually none of the CCA-treated southern pine was utilized in adhesively bonded lumber products such as glulam architectural beams and bridge timbers. Two reasons underlie this lack of product development. First, wood products treated with CCA before bonding delaminate excessively because CCA-treated wood contains chemicals that interfere with adhesion. As a result, the rigorous requirements for structural adhesive bonds cannot be met with consistency. Second, wood products treated with waterborne preservatives after bonding degrade severely from warps, splits, and checks. If the difficulties in bonding CCA-treated wood could be overcome, the potential would be much greater for developing new adhesively bonded products from not only lumber but also veneer, flakes, and fibers.

As early as 1945, scientists at the Forest Products Laboratory (10) recognized that chromium-containing preservatives seriously interfered with the adhesion of many commercial hot- and cold-press adhesives. Since that time, numerous scientists worldwide have searched for compatible adhesives and preservatives, investigated special techniques to improve adhesion, improved adhesive formulations, and sought to identify causes for poor adhesion. The many causes that have been proposed for poor adhesion have been primarily inferred from assumptions that were not substantiated by measurements. All these causes seem quite plausible, and in some cases, they probably are correct. A few of the studies on adhesion were selected as background for the study reported here. This report describes the physical and chemical nature of the surfaces of CCA-treated southern pine and the effect of these characteristics on adhesion. The report is primarily based on studies by Vick and Kuster (23) and Vick and Christiansen (22).

BACKGROUND

The complex chemical and kinetic behavior of copper, chromium, and arsenic in CCA preservatives in fixation reactions to wood, cellulose, and lignin were studied by Dahlgren and Hartford (7-9), Dahlgren (3-6), and, most recently, Pizzi (16-19). According to Pizzi, Cu^{+2} complexes with cellulose and lignin and is physically adsorbed on wood. Chromium arsenate (CrAsO_4) complexes with lignin and precipitates on cellulose, whereas, $\text{Cr}_2(\text{OH})_4\text{CrO}_4$ precipitates on cellulose. After reaction with wood, 95 percent of the CCA system consists of CuCrO_4 and CrAsO_4 . According to Dahlgren, all Cr^{+6} is reduced to Cr^{+3} , and the final products are CrAsO_4 , $\text{Cr}(\text{OH})_3$, and $\text{Cu}(\text{OH})\text{CuAsO}_4$. Both Pizzi and Dahlgren agree that as the acidic CCA solution contacts wood, the pH of the system increases instantaneously as ion-exchange and adsorption reactions occur between the metal ions and wood. The pH eventually reaches a maximum, but while it is increasing, the main

precipitation and fixation reactions occur.

Transmission electron microscopic (TEM) examinations at high magnification (99,000x) by Chow and others (2) showed that the surfaces of each microfibril within the secondary wall of CCA-treated wood were coated by a layer of metallic deposits about 1.5 to 2.0 nm thick. The distribution of these fine deposits was clearly dictated by the orientation of the microfibrils. Using x-ray photoelectron spectroscopy (XPS) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), Ostmeier and others (13) showed that all three components of CCA preservative formed chemical bonds with the aromatic ring of lignin and the carbonyl groups present in wood.

In their review of the role of metal hydroxides as catalysts in the alkaline hydroxymethylation of phenol, Knop and Pilato (11) refer to work by Peer on the enhancement of ortho substitution on the phenol ring by the action of metal hydroxides of iron, copper, chromium, nickel, cobalt, manganese, and zinc. Because of their higher chelating strengths, these metallic ions favored ortho substitution to a greater extent than did potassium, sodium, lithium, barium, strontium, calcium, and magnesium. The chelating action of boric acid was particularly strong.

Pizzi (14) showed that certain bivalent metallic ions can have an accelerating effect and certain trivalent metallic ions a retarding effect on the reactivity of simple phenolics with formaldehyde. In both cases, complexes were formed between the metal, phenol, and formaldehyde. The rates at which these reactions were accelerated or retarded depended on the stability of the complexes and their rates of metal exchange in solution. Specifically, Cr^{+3} formed a stable complex with resorcinol-formaldehyde and phenol-formaldehyde, thereby retarding reactivity, as indicated by a sharply lengthened gel time. On the other hand, Cu^{+2} produced an accelerating effect, as indicated by a more rapid than normal gel time. Pizzi (15) showed that bivalent metal ions also accelerated the reaction of tannin, which is phenolic in chemical nature, with formaldehyde. However, steric hindrance within the tannin prevented the retarding effect of trivalent metallic ions such as Cr^{+3} .

OBJECTIVES

The primary objectives of the experiments reported here were to identify causes of poor adhesion to CCA-treated southern pine by determining (a) how the physical and chemical nature of the cellular structure of the wood surface might interfere with adhesion and (b) if chromium, copper, and arsenic ions might be available to interfere with the curing reaction of phenolic adhesive. Secondary objectives were to demonstrate that structural bonds capable of withstanding severe cyclic delamination tests can be made with durable adhesives by (a) mechanical interlocking of the adhesive deep into the wood's structure and (b) use of a surface modifier to improve wetting and penetration of adhesive.

MATERIALS AND METHODS

Adhesives

Three adhesive systems were used for different aspects of the study:

<u>Adhesive</u>	<u>Experiment</u>
Phenol-formaldehyde plywood adhesive	Thermal analysis of curing characteristics in presence of metallic ions
Acid-catalyzed phenol-formaldehyde molding resin	Bonding of treated lumber with radiofrequency (RF) heating
Commercial phenol-resorcinol-formaldehyde adhesive with surface modifier	Delamination of treated lumber

The phenolic plywood adhesive used in the thermal analysis was made from an alkaline, single-stage phenol-formaldehyde resin. The resin was made commercially and contained 43 percent resin solids. The liquid resin was mixed with the following ingredients (percentages based on weight): water, 15.4 percent; Co-Cob, 6.6 percent; Glu-X wheat flour, 6.1 percent; first resin addition, 16.9 percent; 50 percent aqueous solution of NaOH, 2.9 percent; and second resin addition, 52.1 percent.

The adhesive used for RF bonding was made from an alkaline-catalyzed, single-stage, phenol-formaldehyde molding resin. This resin was an experimental preparation that is not available commercially. The resin was cured with an aqueous ammonium nitrate catalyst (with additives) and heat generated by RF. Twenty-five parts of catalyst and 20 parts of a 50:50 blend of 74- μm (200-mesh) birch wood flour and walnut shell flour were added to 100 parts of the resin. Six-ply lumber laminates were prepared by double-spreading adhesive at a rate near 0.49 kg/m^2 ; allowing open and closed assembly times of 10 and 30 min, respectively; and curing under pressure of 345 kPa. The adhesive was cured with a parallel-flow, 12kVA RF generator operating at 27.12 MHz. The plate current was 1.0 A with 4.5-kW RF output for 1 min.

The phenol-resorcinol-formaldehyde adhesive was made commercially for room-temperature laminating of southern pine lumber. The adhesive was mixed with a water slurry of hardener and filler and then applied to the lumber about 1 h after a surface modifier had been sprayed on the lumber to improve the adhesion. Six-ply lumber laminates were prepared by double-spreading at a rate near 0.49 kg/m^2 , allowing 15 mm for both open and closed assembly time, and curing under pressure of 690 kPa for 15 h.

Preservative Treatments

Southern pine sapwood was pressure-treated with CCA preservative by a commercial process to a retention approximating 6.4 kg/m^3 . After air drying, the wood was conditioned to constant weight near 12 percent moisture content. The wood was knife-planed just before bonding. This treated lumber was used for tests of the acid-catalyzed phenolic molding resin.

Southern pine sapwood was pressure-treated in the laboratory with a 47.58-percent commercial concentrate of Type-C CCA preservative to retentions approximating 6.4 and 9.6 kg/m^3 . An analysis of the concentrate yielded the following weight percentages: Cu, 8.59 percent; Cr, 22.30 percent; and As, 16.69 percent. The treated wood was kiln-dried, then conditioned to constant weight near 10 percent moisture content. It was planed just before bonding. This lumber was used in delamination tests of the phenol-resorcinol adhesive with surface modifier.

For the thermal analyses, southern pine sapwood was treated with the same commercial concentrate of Type-C CCA preservative to retentions of 6.4 and 9.6 kg/m^3 . Both treated and untreated southern pine were ground to 250 μm (60 mesh) and thoroughly mixed with phenolic adhesive. The adhesive-to-wood mixture was maintained at a 1:1 ratio on a volume basis and a 2:1 ratio on a weight basis. For one series of tests, the mixture was changed to a 5:1 weight ratio.

The metallic ions in model compounds came from the following sources (reagent grade): hexavalent chromium (Cr^{+6}) from chromium trioxide (CrO_3) and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$); trivalent chromium (Cr^{+3}) from chromium acetate ($\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3$), chromium chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), and chromium oxide (Cr_2O_3); bivalent copper (Cu^{+2}) from cupric chloride (CuCl_2); and pentavalent arsenic from arsenic pentoxide (As_2O_5). All the model compounds were prepared as 15 percent aqueous solutions based on the weight of metal in each compound, except for the Cr^{+3} compounds. Chromium acetate and chromium chloride form hydrates and would not remain in solution at such a high concentration, so they were prepared as 6.4 percent aqueous solutions of metal. Chromium trioxide was also diluted to a 6.4-percent solution of metal. Chromium oxide is insoluble in water.

Analyses

Microscopic Analyses

High-magnification micrographs were obtained with a JEOL JSM-840 scanning electron microscope (SEM). Semiquantitative elemental analyses were made with a Tracor Northern TN-5500 energy dispersive spectrometer (EDS). Wood surfaces were prepared for microscopic examination by either microtoming or splitting, then coating with gold for SEM study and with carbon for EDS study.

Low-magnification micrographs were made with a Wild M400 Photomakroskop using fiber optic incident light. Specimen surfaces were prepared for microscopic study by sanding with progressively finer grit.

Differential Scanning Calorimetry

The reactivity of phenolic adhesive, as indicated by its thermal behavior in the presence of (a) CCA-treated and untreated southern pine and (b) solutions of CCA preservative and model compounds containing Cr^{+6} , Cr^{+3} , Cu^{+2} , and As^{+5} ions, was measured by differential scanning calorimetry (DSC). Thermograms were produced by a Perkin-Elmer DSC-2.

Perk-Elmer large volume capsules (LVCs) made of stainless steel and fitted with Viton O-rings were used to contain samples during the heating process. By sealing samples in LVCs that withstand vapor pressures to at least 1.5 MPa, the exothermic curing reaction of phenolic adhesive can be detected up to 200 °C without the interfering endotherm of volatile reaction products (e.g., water). The curing reaction involves condensation reactions of hydroxymethyl groups that were previously formed through reaction of formaldehyde with phenol in the presence of an alkaline catalyst.

To obtain reaction exotherms, particularly peak temperatures, LVCs with samples were heated from 20 °C at a rate of 10 °C/min to a maximum of 200 °C. To establish a cured-resin baseline, LVCs were cooled to 20 °C, then reheated to 200 °C. The area between the reaction exotherm scanline and the cured adhesive baseline was the measure of the heat of cure. The heats were normalized to the weight of adhesive only.

The samples for thermal analysis were mixed and weighed, then scanned immediately. They usually weighed between 18 and 22 mg. Duplicate samples were scanned to establish repeatability. The melting of an indium sample was used to calibrate the DSC.

Cyclic Delamination Tests

Each six-ply lumber laminate was cut into three sections and subjected to four cycles of an extremely severe vacuum-pressure water soaking and drying (VPSD) treatment. For a single cycle, the soaking procedure consisted of submerging specimens in water, applying a vacuum of 0.1 MPa of mercury for 30 min, and applying pressure of 0.4 MPa for 2 h. The drying procedure consisted of placing specimens in a forced-air oven at 71 °C for 15 h. The entire procedure was repeated four times. Delamination was measured in each bondline on all end-grain surfaces after the final drying step.

RESULTS AND DISCUSSION

SEM and EDS Analyses of Cell Lumen Surface Deposits

The surface of a cell lumen from untreated southern pine was relatively free of foreign substances (fig. 1); however, naturally occurring warts in varying sizes were sparsely distributed over the lumen surface. The lumen surface of the same species was dramatically different after the wood was treated with CCA preservative.

Figure 2 shows an area of the cell lumen surface completely covered by a heavy concentration of hemispherical deposits, ranging in diameter from about 1.0 μm to essentially invisible at a magnification of 5,000x. In this particular area, very little opportunity exists for the adhesive to make molecular-level contact with lignocellulosic constituents of cell walls because of physical blocking by the chemical deposits. Figure 3 provides a perspective for comparing deposit size with the size of a bordered pit aperture. This and other micrographs show that deposits were not large enough to block primary openings between cells. For mechanical adhesion to occur, these openings must remain open to allow flow of resin into lumens six to eight cells deep from where the adhesive is initially spread.



Figure 1. Surface of cell lumen from untreated southern pine showing relative absence of foreign substances.

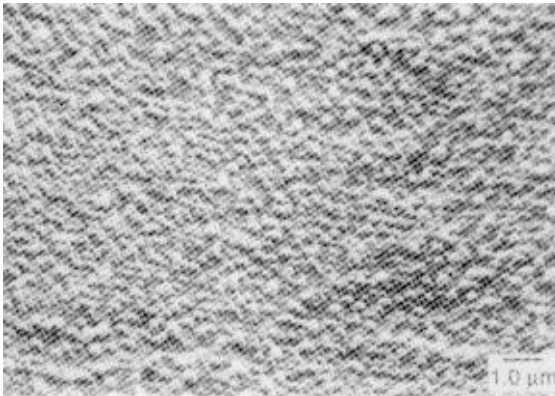


Figure 2. Surface of cell lumen from CCA-treated southern pine. Surface is covered with hemispherical deposits, later identified as mixtures of chromium, copper, and arsenic.

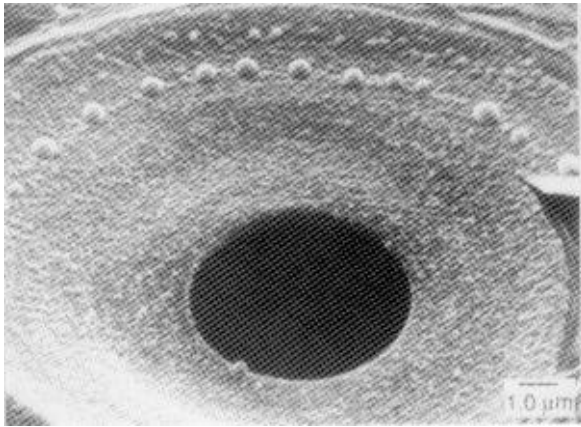


Figure 3. Bordered pit aperture. Figure shows relative size of metal deposits to the opening through which adhesive flowed.

The elemental analyses by EDS indicated that copper, chromium, and arsenic were all present in precipitates on lumen surfaces and that all three metals were combined within a single deposition (fig. 4). Line scans were passed through two hemispherical deposits--first a large one and then, a smaller one (fig. 4). In the micrograph, the cursor points through the two deposits. Tracings on the left (fig. 4) show the proportions of arsenic, chromium, and copper as the electron beam encounters continuously varying concentrations of metals as it passes through the varying sizes of deposits. The highest peaks, which vertically coincide for all three metals, are the tracings for the larger hemisphere. The second highest vertically coinciding peaks are for the smaller hemisphere. The coinciding peaks show that all three metals were combined within a single deposit. The proportions of metals detected in the larger deposit were 43 percent As, 33 percent Cr, and 24 percent Cu. The proportions of metals in the smaller deposit were similar.

Figure 5 shows single-file alignment of deposits parallel to the striations in the lumen membrane. The striations were produced by the underlying bundles of microfibrils. This suggests attachment of metallic deposits to microfibrils. The lumen membrane (with affixed deposits) was peeled away to reveal more clearly the orientation of the microfibrils in the underlying layer (not shown).

That the distribution of fine deposits of metals was dictated by the orientation of cellulosic microfibrils and that the surface of each microfibril was coated by a layer of metallic deposits were shown by Chow and others (2) in their TEM work. Using XPS and DRIFT, Ostmeier and others (13) also showed that all three components of CCA preservative were chemically bonded to the aromatic ring of lignin and the carbonyl groups in wood.

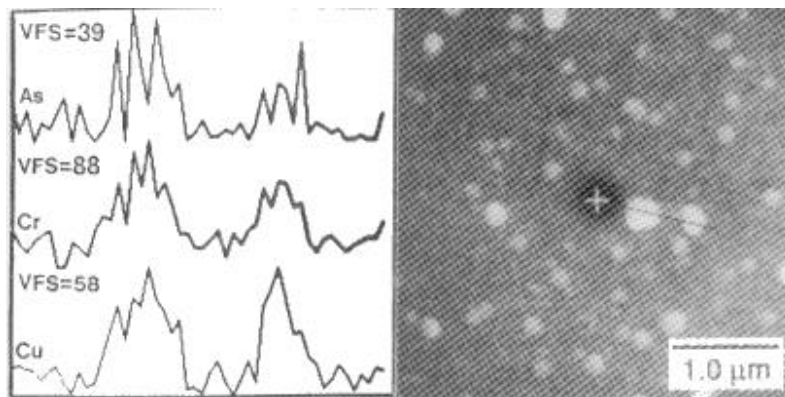


Figure 4. EDS analysis of arsenic (As), chromium (Cr), and copper (Cu) in two relatively large deposits on lumen surface of treated cell. VFS, vertical full scale in x-ray intensity.



Figure 5. Parallel alignment of metallic deposits with run of underlying microfibril bundles in cell wall.

DSC Analyses of Phenolic Adhesive Cure With Metallic Ions

Understanding how constituents of the adhesive itself might contribute to overall thermal responses was prerequisite to reacting phenolic adhesive in the presence of metallic ions of CCA-treated southern pine. The phenolic resin, wheat flour, and Co-Cob reacted exothermally, both singly and in mixtures, with sodium hydroxide (data not shown in this report). Adding sodium hydroxide to either the phenolic resin or a mixture of resin and fillers lowered the peak temperature 2° to 3 °C to near 148 °C from the peak temperature of the phenolic resin alone. Since all

constituents of the plywood adhesive mixture contributed to the overall thermal response, the mixture, rather than the phenolic resin alone, was used in subsequent DSC thermograms. The exotherm for the cure of the adhesive mixture is shown in figure 6a.

To determine if ions of CCA preservative might react with the phenolic adhesive, aqueous solutions of model compounds containing Cr^{+6} (CrO_3), Cu^{+2} (CuCl_2), As^{+5} (As_2O_5), and CCA preservative solution were mixed individually with phenolic adhesive as 1.87 percent metal ion, then reacted in DSC capsules. These thermograms are compared with the phenolic adhesive in figure 6.

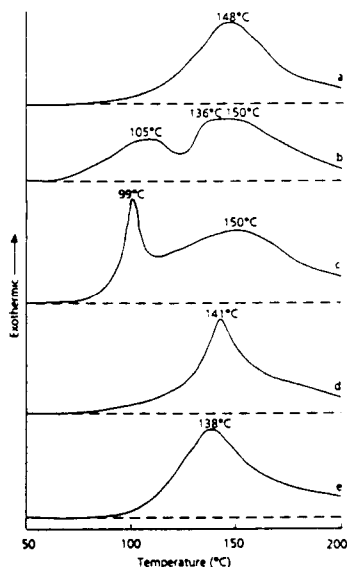


Figure 6. DSC thermogram of reaction of phenolic adhesive mixture: (a) alone, (b) with 1.87 percent weight of total Cr^{+6} , Cu^{+2} , and As^{+5} in solution of CCA preservative, (c) with 1.87 percent weight of Cr^{+6} in solution of chromium trioxide, (d) with 1.87 percent weight of Cu^{+2} in solution of cupric chloride, and (e) with 1.87 percent weight of As^{+5} in solution of arsenic pentoxide.

The solution of CCA preservative (1.87 percent total Cr, Cu, and As ions) reacted strongly with the adhesive, as shown in figure 6b. Two prominent exotherms occurred: the lower one peaked near 105 °C, and the major one peaked in a truncated peak between 136 °C and 150 °C. The contributions of individual metal ions to the composite of all three ions in reaction with the phenolic adhesive can be seen by comparing all five thermograms in figure 6. The Cr^{+6} ion strongly contributed by producing two prominent exotherms--the first peaking sharply at 99 °C, and the second peaking broadly at 150 °C (fig. 6c). The Cu^{+2} produced a sharp but single peak at 141 °C (fig. 6d), As^{+5} produced a single peak at 138 °C (fig. 6e).

Adhesives containing each of the three ions peaked individually between 138 °C and 150 °C (fig. 6c-e) and could have combined to produce a truncated peak between 136 °C and 150 °C, as seen with the CCA preservative solution (fig. 6b). The ions Cu^{+2} and As^{+5} apparently caused a minor acceleration of cure, as indicated by shifts in the exotherm to slightly lower peak temperatures. However, Cr^{+6} produced the sharp exotherm peak at 99 °C (in addition to the peak at 150 °C), which probably contributed to the exotherm peak at 105 °C in the reaction of CCA solution with phenolic adhesive (fig. 6b-c). That the above reactions were not catalyzed by just the acidities of the solutions of model compounds and CCA preservative was demonstrated when adhesive was reacted with either 1 M or 6 M HCl without any apparent effect on the peak temperature of the adhesive. However, note that all solutions of model compounds, acids, and CCA preservative gelled the phenolic adhesive at the point of contact between the liquids. On mixing, the viscosities of most of these mixtures increased noticeably.

Pizzi (16,19) indicated that in CCA-treated wood 60 percent of the chromium is fixed irreversibly as Cr^{+6} , and 40 percent is weakly bound as Cr^{+3} . Dahlgren (3) indicated that all chromium is reduced from Cr^{+6} to Cr^{+3} . Pizzi's studies (14,15) also showed that Cr^{+3} has a retarding effect on the gelation of phenol-formaldehyde resin. With the indicated presence of Cr^{+3} in CCA-treated wood, and the possible availability of this ion for reaction, mixtures of phenolic adhesive containing either 0.80 percent Cr^{+3} from chromium acetate and Cr^{+6} from chromium trioxide, or an insoluble powder of chromium oxide (Cr^{+3}), were reacted in DSC capsules. Both peak temperatures and heats of cure for each mixture are shown in table 1. Compared to the phenolic adhesive alone, the insoluble chromium oxide (Cr^{+3}), dispersed in adhesive at a concentration more than 11 times that of the soluble Cr^{+3} and Cr^{+6} ions, had little to no effect on the peak temperature and a doubtful effect on the heat of cure. Chromium acetate (Cr^{+3}) caused the peak temperature to shift lower by 3 °C to 145 °C, with a small and doubtful decrease in the heat of cure. However, chromium trioxide (Cr^{+6}) decreased the peak temperature to 142 °C from 148 °C and increased the heat of cure by 23 percent. By both measures, the reactivity changes caused by Cr^{+6} were substantial, whereas, Cr^{+3} present as soluble and insoluble ions did not produce significant changes in reactivity.

When a 2:1 weight-ratio mixture of adhesive and CCA-treated wood was reacted in the DSC, the thermograms differed remarkably from those produced by the phenolic adhesive alone. The adhesive mixture alone produced a reaction exotherm with a single prominent peak that reached a maximum at 148 °C (fig. 7a). The adhesive with CCA-treated wood produced two prominent exotherm peaks. The first was broad and low and peaked around 88 °C; the second was sharper and higher and peaked around 143 °C (fig. 7b). Whether the retention level of CCA-treated wood was 6.4 or 9.6 kg/m³, the exotherms were the same. When phenolic adhesive and untreated southern pine were reacted, the thermograms were essentially the same as the mixture of adhesive with CCA-treated wood (fig. 7c). Apparently, the fixed CCA preservative in wood had no more effect on the cure of phenolic adhesive than did the untreated wood. However, it is not understood why the presence of wood, either treated or untreated, should cause the exotherms near 88 °C.

Table 1. Effects of chromium (Cr^{+3} and Cr^{+6}) model compounds on heat of cure and peak temperature of phenolic adhesive.

Chromium ions	Heat of cure (per weight of adhesive)	Change	Cure Peak temperature	Change
	(J/mg)	(percent)	(°C)	(°C)
None	0.116	--	148	--
Insoluble Cr^{+3}	0.127	+9.5	147	-1
Soluble Cr^{+3}	0.109	-6.1	145	-3
Soluble Cr^{+6}	0.143	+23.3	142	-6

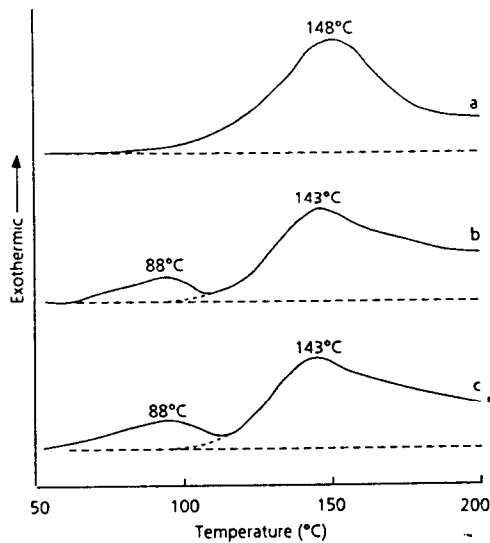


Figure 7. DSC thermogram of reactions of phenolic adhesive mixture: (a) alone, (b) with CCA-treated (9.6 kg/m^3) southern pine in a 2:1 weight-ratio, and (c) with untreated southern pine in a 2:1 weight-ratio.

A comparison of calculated heats of cure of phenolic adhesive in the presence of CCA-treated wood and untreated wood is another means of determining whether the CCA treatment affected the cure of phenolic adhesive. The DSC thermograms of mixtures of adhesive with either untreated or CCA-treated wood (fig. 7) showed two similar exothermic reactions. The lower temperature peaks were caused by

some unidentified reaction between the ground wood and phenolic adhesive. These peaks did not occur with either the phenolic resin alone or the mixed phenolic adhesive. Consequently, only the higher temperature, larger peaks of the wood-adhesive mixtures could be attributed to adhesive curing. To estimate adhesive exotherm area from thermograms, the low-temperature side of the larger peak was extrapolated back to the beginning of the exotherm along the baseline, as noted on figure 7b and 7c. The heat of cure per weight of adhesive (wood weight factored out) was 0.152 J/mg for the adhesive with untreated wood and 0.149 J/mg for the adhesive with CCA-treated wood (at 9.6 kg/m³ retention). This was a difference of only 2 percent, which agrees very closely considering the possible difficulties in taking representative samples of the mixtures for DSC scans.

Mechanical Interlocking of Phenolic Adhesive in Wood

Phenolic wood adhesives form the most durable bonds to wood because they readily penetrate the wood's structure and cure into a thermoset material that is highly resistant to water and heat. Phenolic resins are highly polar and can form hydrogen bonds with polar functional groups on lignocellulosic constituents in cell walls. However, in view of the fixation of insoluble metallic compounds to cell walls, functional groups that might have been available for hydrogen or covalent bonding on untreated wood simply are not available on treated wood because these sites are physically blocked. Thus, the only remaining opportunity for effective bonding is through mechanical interlocking of adhesive deep within the wood's structure.

Figure 8 shows how a low-molecular-weight phenolic adhesive interfaced with the deposit-covered surface of a cell lumen. The dark area on the right half of the micrograph is the cured phenolic adhesive. While liquid, the adhesive made intimate contact with the cell wall; when the adhesive solidified, the cell wall left impressions of the protruding hemispherical deposits and microfibrillar bundles in the adhesive. An edge view of the lumen membrane with its deposit-covered surface is visible at the center of the micrograph. The cell wall was torn away to reveal impressions of deposits in the solidified adhesive. In the process of removing the cell wall, adhesion between adhesive and cell wall was not great enough to cause failure of the cell wall. Actually, there was no evidence of cell wall failure from penetrating adhesive or physicochemical bonding--merely evidence of intimate contact of the resin with the cell walls. Yet, this phenolic adhesive made excellent bonds to the CCA-treated wood such that no delaminations occurred in the bondlines, even after four cycles of severe VPSD.

Figures 9 to 12 show bonds to CCA-treated southern pine in a six-ply lumber laminate after VPSD delamination tests. Figure 9 shows a cross-section of a typical bondline where thick-walled, high-density summerwood in one adherend was bonded to thin-walled, low-density springwood in the other adherend. Adhesive penetration was four to eight cells deep in the springwood and one to three cells deep in the summerwood. The deep penetration undoubtedly accounted for the uncommonly high resistance of the bonds to delamination.

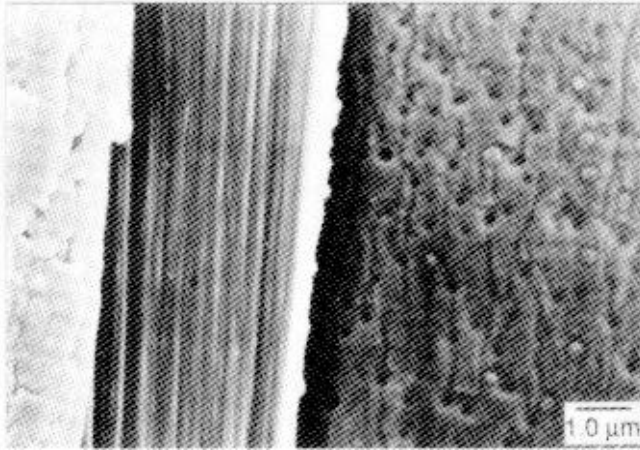


Figure 8. Impression of metallic deposits and striations in lumen membrane from underlying microfibrils as they are cast in the solidified adhesive (right). Note tendency of deposits to align with microfibrils in castings.

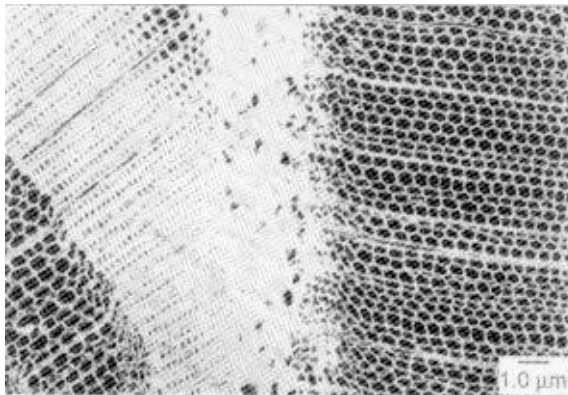


Figure 9. Deep penetration of adhesive into springwood and summerwood, which accounted for uncommonly high resistance of wood to delamination in cyclic delamination tests.

Figure 10 shows a bondline of such high integrity that it resisted shearing forces that actually ruptured high-density summerwood bands both above and below the bondline. After four severe VSPD cycles, none of the bonds in several six-ply lumber laminates ruptured within the bondline. The ruptures always occurred outside the bondline, either at the juncture of the penetrated adhesive and wood, or well beyond the bondline. Figure 11 shows typical ruptures where the edges of summerwood bands in one laminate met the wide summerwood bands in an adjacent

laminate. Ruptures occurred near or sometimes at the bondline but never within the bondline. Figure 12 is a typical example of where two summerwood bands, which normally are very difficult to penetrate with adhesive, were bonded with such high integrity that the rupture occurred far above the bondline at the juncture of springwood and summerwood. When delaminations occur in either untreated or treated southern pine lumber joints, the ruptures almost invariably develop at the junction of two summerwood bands. The reason for failure in most cases is simply inadequate penetration of the summerwood.

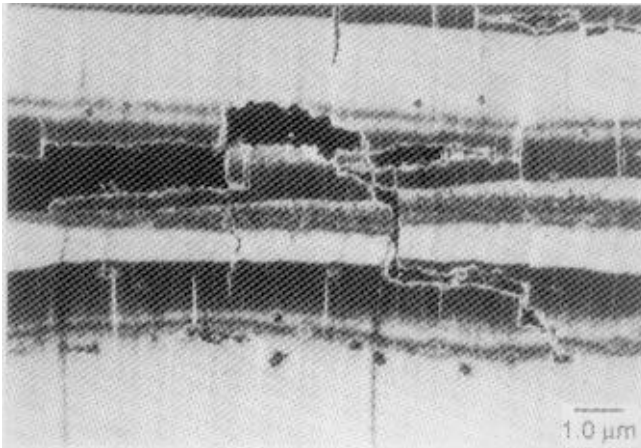


Figure 10. Bondline showing such high resistance to delamination that rupture occurred through high-density summerwood bands. Note deep penetration of adhesive.

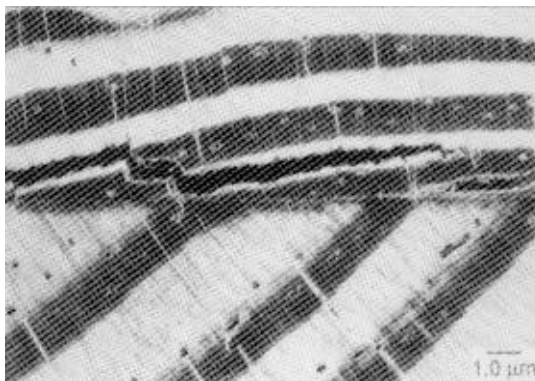


Figure 11. High-integrity bondline showing rupture within wood adjacent to bondline, but never within bondline.

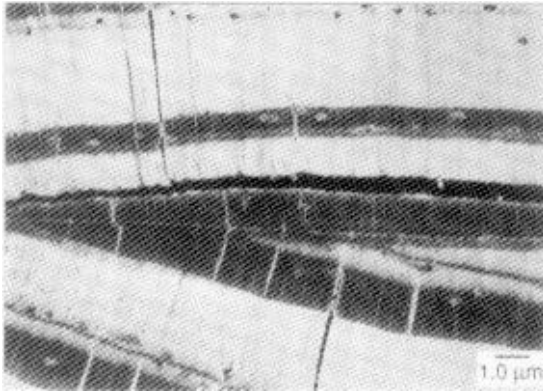


Figure 12. Juncture of two difficult-to-penetrate summerwood bands where delamination normally would be expected to occur. In this case, high integrity of bond forced rupture at juncture of springwood and summerwood bonds above bondline.

Surface Modifier With Phenol-Resorcinol Adhesive

Early in the 1980s, Vick (20) demonstrated that a surface treatment of 12 percent aqueous solution of sodium hydroxide on lumber before bonding greatly improved the adhesion of a gap-filling phenol-resorcinol adhesive to the unplanned surfaces of CCA-treated plywood and lumber. Sodium carbonate was also an effective treatment but not as effective as sodium hydroxide. Because of this surface treatment, adhesively bonded shear walls (without nails) for wood foundations were more than twice as strong in racking as walls with nailing alone or with nailing plus adhesive and no surface treatment (21).

A commercial phenol-resorcinol adhesive, developed for laminating southern pine lumber, was used in conjunction with a commercial surface modifier to laminate CCA-treated lumber. The modifier was used to improve adhesion to CCA-treated southern pine. The wood was treated with CCA preservative to a retention of 9.6 kg/m³.

After four severe cycles of VPSD, nine specimens from six-ply lumber laminates developed an average 3.2 percent delamination. Figure 13 shows cross-sections from three laminates that represent considerable variation in density and grain angles to the bondlines. Virtually no delamination can be seen in these sections, even though stresses were great enough to cause fractures to extend almost continuously across the blocks at several places. It is particularly noteworthy that long fractures developed through the plane of several summerwood bands, as can be seen in the section on the right. These limited tests indicated that the combined phenol-resorcinol adhesive and surface modifier were quite effective--the bonds were much more resistant to stress rupture than the wood itself.

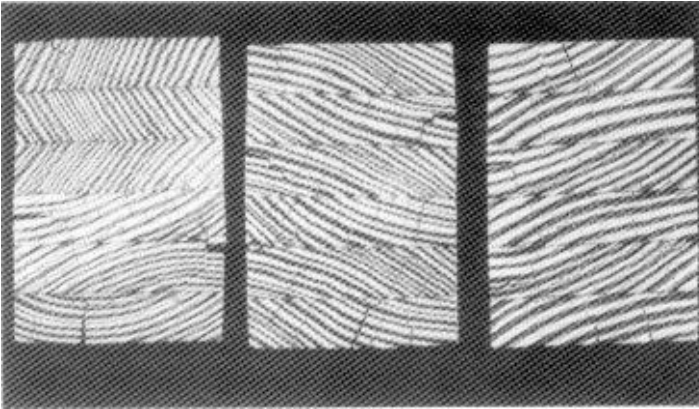


Figure 13. Cross-sections of three lumber laminates after severe cyclic delamination tests, showing virtually no delamination despite stresses so great that fractures extended across the sections and within several summerwood bands. See fractures in summerwood bands in section on the right.

CONCLUSIONS

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) showed that cell lumen surfaces of southern pine treated with chromated copper arsenate (CCA) were thoroughly covered with deposits consisting of mixtures of chromium, copper, and arsenic. According to the literature, these metals are chemically bound to lignocellulosic constituents of cell walls. The SEM and EDS analyses support these findings by showing alignment of metal deposits with the microfibrils in cell walls. By virtue of their physical presence, these deposits block most opportunities for bonding by molecular-level forces of attraction between polar wood constituents and adhesive.

Differential scanning calorimetry (DSC) thermograms indicated that a solution of CCA preservative caused a strong exothermic reaction with phenol-formaldehyde adhesive in which a portion of the adhesive reacted at lower than normal temperatures. Individual metallic ions of Cr^{+6} , Cr^{+3} , Cu^{+2} , and As^{+5} in solutions of model compounds also reacted with the adhesive, but only Cr^{+6} reacted in the same low-temperature range as the solution of CCA preservative. However, when the CCA preservative was chemically “fixed” within the wood, no such accelerated reactions of the adhesive were evident.

Despite the presence of insoluble deposits blocking contact between adhesive and wood, tests demonstrated that mechanical interlocking by a deeply penetrating phenolic adhesive can produce bonds to CCA-treated southern pine that will resist severe cyclic delamination tests. Limited tests also demonstrated that a

phenol-resorcinol adhesive could produce delamination-resistant bonds when the lumber surfaces were pretreated with a surface modifier.

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