CURE OF PHENOL-FORMALDEHYDE ADHESIVE IN THE PRESENCE OF CCA-TREATED WOOD BY DIFFERENTIAL SCANNING CALORIMETRY[1]

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ABSTRACT

Chromated copper arsenate (CCA) preservatives interfere with bond formation of phenolic-based adhesives on CCA-treated southern pine. Ions of chromium (Cr^{+3}) and copper (Cu^{+2}) are known to complex with phenol and formaldehyde, affecting the rate of cure of the resin. Differential scanning calorimetry (DSC) was used to thermally analyze the cure of a commercial phenol-formaldehyde adhesive in the presence of CCA-treated wood, solutions of CCA preservative, and solutions of model compounds containing ions of Cr^{+6}, Cr^{+3}, Cu^{+2}, and As^{+5}. The DSC thermograms indicated that free metallic ions in solution can accelerate the cure of a portion of the adhesive at less than normal temperatures. However, when the CCA preservative was chemically "fixed" within the southern pine wood, accelerated cure of the adhesive did not occur.

Keywords: Phenol-formaldehyde adhesive, adhesive cure, differential scanning calorimetry, chromium, copper, arsenic, chromated copper arsenate (CCA) preservative, CCA-treated wood.

INTRODUCTION

In 1988, the wood-preserving industry treated an estimated 7.9×10^6 m³ of southern pine lumber with chromated copper arsenate (CCA) preservatives (Micklewright 1990). For two reasons, none of this large volume of treated wood was utilized in adhesively bonded lumber products, such as glulam architectural beams and bridge timbers. First, wood products treated with waterborne preservatives after bonding severely degrade from warp, splits, and checks. Second, wood treated before bonding contains chemicals that interfere with adhesion to the treated wood. As a result, rigorous requirements for structural adhesive bonds cannot be met with consistency and dependability. However, if bonding difficulties in preservative-treated wood could be overcome, the potential would be much greater for developing new adhesively bonded products not only from lumber, but from veneer, flakes, and fibers.

As early as 1945, scientists at the Forest Products Laboratory recognized that chromium-containing preservatives seriously interfered with the adhesion of many commercial hot- and cold-press adhesives. Since then, many scientists worldwide have searched for com-

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patible adhesives and preservatives, investigated special techniques to improve adhesion, developed new adhesive formulations, and sought to identify causes for poor adhesion. Commercially viable solutions have not been forthcoming, and the causes for adhesion interference have not been explored adequately. This paper describes our efforts to identify causes for poor adhesion, specifically to determine if metallic ions in CCA-treated wood interfere with the cure of the phenolic adhesive. Ions of Cr^{+3}, Cr^{+6}, Cu^{+2}, and As^{+5} may be available for reaction, particularly near the surface of the wood.

BACKGROUND

When Knop and Pilato (1985) reviewed the role of metal hydroxides as catalysts in the alkaline hydroxymethylation of phenol, they referred to the work of Peer concerning enhancement of ortho substitution on the phenol ring by the action of metal hydroxides of Fe, Cu, Cr, Ni, Co, Mn, and Zn. Because of their higher chelating strengths, these metallic ions favor ortho substitution more highly than do K, Na, Li, Ba, Sr, Ca, and Mg. Boric acid has a particularly strong chelating action.

Pizzi (1979a) showed that certain bivalent metallic ions can have an accelerating effect, and certain trivalent metallic ions can have a retarding effect on the reactivity of simple phenolics with formaldehyde. In both cases, complexes are formed between the metal, phenol, and formaldehyde. The rates at which these reactions are accelerated or retarded depend on the stability of the complexes and their rates of metal exchange in solution. Specifically, Cr^{+3} forms a stable complex with resorcinol formaldehyde and phenol formaldehyde, thereby retarding reactivity as indicated by a substantially lengthened gel time. In contrast, Cu^{+2} produces an accelerating effect, as indicated by a more rapid gel time than normal. Pizzi (1979b) showed that the reaction between tannin, which is phenolic in chemical nature, and formaldehyde is also accelerated by bivalent metal ions. However, steric hindrance within the tannin prevents the retarding effect of tri-

valent metallic ions such as Cr^{+3}. In his book, Pizzi (1983) concluded that because of their stronger charge, bivalent metallic ions accelerate the phenol-formaldehyde reaction by having a stronger effect on the attack of formaldehyde on the phenol than does the H^+ ion. In the case of the retarding effect of trivalent metallic ions, the metal simply blocks the hydroxymethyl groups.

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 (1972a–c), Dahlgren (1972, 1974, 1975a, b), and Pizzi (1981, 1982a–c). 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, $Cr_2(OH)_4CrO_4$ precipitates on cellulose. After reaction with wood, 95% of the CCA system consists of $CuCrO_4$ and $CrAsO_4$. According to Dahlgren, all Cr^{+6} ions are reduced to Cr^{+3}, and the final equilibrium products are $CrAsO_4$, $Cr(OH)_3$, and $Cu(OH)CuAsO_4$. Pizzi and Dahlgren agree that as the acidic CCA solution contacts wood, pH of the system increases instantaneously as ion-exchange, and adsorption reactions occur between the metal ions and wood. Eventually pH reaches a maximum, but while pH is increasing, the main precipitation and fixation reactions occur.

Transmission electron microscopic examinations at high magnification (99,000×) by Chow et al. (1973) showed that the surfaces of each microfibril in the secondary wall of CCA-treated wood were coated by a layer of metallic deposits about 1.5 to 2.0 nm thick. Examinations with scanning electron microscope and energy dispersive spectrometer by Vick and Kuster (1992) indicated that copper, chromium, and arsenic were present in precipitates on the lumen surfaces of the cellular structure of the wood. The surfaces were thoroughly covered with hemispherically shaped deposits, and each deposit consisted of a mixture of chromium, copper, and arsenic. Further visual evidence indicated that the metallic precipi-

tates were bound to the microfibrils in the cell walls.

Ostmeyer and others (1989) used X-ray photoelectron spectroscopy and diffuse reflectance Fourier transform infrared spectroscopy to show that all three components of CCA combine to form chemical bonds with the aromatic ring of lignin and the carbonyl groups present in wood. They found no evidence of one- and two-component reactions of the preservative with aromatic and carbonyl groups—only reactions of all three components. Infrared spectra did not indicate whether metals reacted with carbohydrates.

EXPERIMENTAL MATERIALS AND METHODS

Adhesive

The adhesive was made from a single-stage, phenol-formaldehyde resin called Casophen SP5300D[2] (Borden Packaging and Industrial Products, Columbus, Ohio). The resin contained 43% resin solids. Liquid resin was mixed with the following ingredients (percentages based on weight): 15.4% water, 6.6% Co-Cob filler, 6.1% Glu-X wheat flour, 16.9% resin (first addition), 2.9% of 50% aqueous solution of NaOH, and 52.1% resin (second addition). When one or more of these ingredients were reacted with CCA constituents, the amounts were maintained in these relative proportions.

Preservative materials

The CCA-preservative solution was a commercial formulation in a 47.58% concentrate. Analysis of the concentrate yielded the following average weight percentages: 8.59% Cu, 22.30% Cr, and 16.69% As. The preservative was used as the concentrate and as a 15% aqueous solution, based on the total weight of the three metals in the concentrate. Analysis of CCA-treated southern pine, pressure-treated to a targeted retention of 9.6 kg/m^3, yielded

the following average weight percentages: 0.30% CuO, 0.75% CrO$_3$, and 0.53% As$_2$O$_5$.

Southern pine sapwood (*Pinus* sp.) treated with CCA preservative to retentions of 6.4 and 9.6 kg/m^3 and untreated southern pine were ground to 60 mesh and thoroughly mixed with phenolic adhesive. The adhesive-to-wood mixture was maintained at a 1:1 ratio on a volume basis, but because the density of the adhesive was about twice that of the wood, the ratio of adhesive-to-wood was 2:1 on a weight basis. For one series of tests, the mixture was changed to 5:1 weight ratio.

The metallic ions as model compounds came from the following sources (reagent grade): hexavalent chromium (Cr^{+6}) from chromium trioxide (CrO$_3$) and sodium dichromate (Na$_2$Cr$_2$O$_7$); trivalent chromium (Cr^{+3}) from a hydrate of chromium acetate (Cr(C$_2$H$_3$O$_2$)$_3$), chromium chloride (CrCl$_3 \cdot$6H$_2$O), and chromium oxide (Cr$_2$O$_3$); bivalent copper (Cu^{+2}) from cupric chloride (CuCl$_2$); and pentavalent arsenic from arsenic pentoxide (As$_2$O$_5$). All model compounds were prepared as 15% aqueous solutions based on the weight of metal in each compound, except for the trivalent chromium compounds. Chromium acetate and chromium chloride were hydrates and could not be prepared in such a high concentration; therefore, they were prepared in 6.4% aqueous solutions of metal. Chromium trioxide was also diluted to a 6.4% solution of metal. Chromium oxide is insoluble in water.

For convenience and brevity, terms such as Cr^{+6} ion and As^{+5} ion are used to indicate the particular valence state of the metal in a model compound, even though in aqueous solutions, ions containing Cr^{+6} actually exist as chromate and dichromate ions, and ions containing As^{+5} exist as arsenate ion.

Differential scanning calorimetry

The reactivities of phenolic adhesive in the presence of CCA-treated and untreated southern pine, CCA-preservative solution, and model compounds containing ions of Cr^{+6}, Cr^{+3}, Cu^{+2}, and As^{+5} were measured by differential scanning calorimetry (DSC). The DSC

[2] The use of trade or firm names in this publication is for the reader's information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.
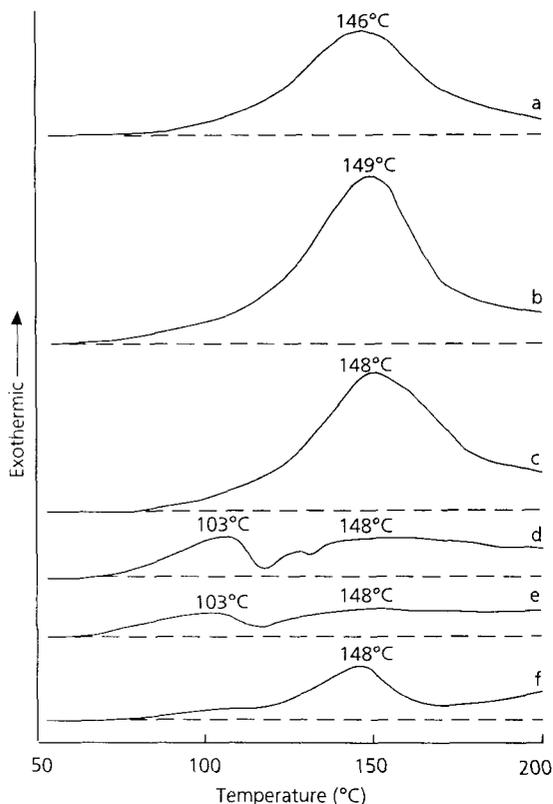
FIG. 1. DSC thermograms of reactions of phenol-formaldehyde resin (a) alone, (b) with NaOH, and (c) with adhesive mixture constituents. Thermograms of adhesive mixture constituents are shown for (d) Co-Cob and wheat flour with NaOH and water, (e) Co-Cob with NaOH and water, and (f) wheat flour with NaOH and water.

thermograms were produced by a Perkin-Elmer DSC-2.

Perkin-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 scan line and the cured adhesive baseline was the measure of the heat of cure. The heats were normalized to the weight of adhesive by subtracting any model compound additives.

The samples for thermal analysis weighed between 18 and 22 mg. Duplicate samples were scanned to establish repeatability.

For temperature accuracy and conversion of chart areas to values for heats of reaction, the melting of an indium sample was used to calibrate the DSC.

RESULTS AND DISCUSSION

Phenolic adhesive constituents

To understand the reactivity of phenolic adhesive in the presence of CCA-treated wood, it was first necessary to understand how individual constituents of the adhesive might contribute to the overall thermal response. Figure 1 shows DSC thermograms of exothermic reactions of phenolic resin alone; phenolic resin with additional NaOH; phenolic resin in an adhesive mixture with fillers, NaOH, and water; and fillers mixed with NaOH and water. Note that the amount of material in all DSC capsules was 18 to 22 mg; therefore, the thermogram heights of fillers without resin were disproportionately greater than if the smaller relative amounts of fillers in the adhesive mixture had been used.

Considering peak temperatures in Fig. 1, the phenolic resin alone peaked at 146 C. When 50% NaOH was added to the resin, the reaction was retarded such that the peak temperature increased approximately 3°. With all constituents of the adhesive formulation mixed with resin, the peak temperature was increased 2° to 148 C. By adding NaOH to a mixture of wheat flour and Co-Cob fillers, two broad and low-level exotherms occurred—the first peaking near 103 C and the second near 148 C.

When NaOH was added to Co-Cob alone, two broad exotherms occurred again with the first peaking at 103 C and the second at 148 C—just as occurred with the mixture of Co-Cob and wheat flour. When NaOH was added to wheat flour alone, only a single but relatively sharp exotherm occurred with a peak near 148 C. As indicated by thermograms in Fig. 1, all constituents of the adhesive mixture reacted exothermically with NaOH, either singly or in mixtures. Adding NaOH to either the phenolic resin or mixture of resin and fillers increased the peak temperature 2° and 3° to near 148 C. No other factors appeared in the thermograms that might affect the cure of the adhesive. Because 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.

Adhesive with treated and untreated wood

When the 2:1 weight-ratio (1:1 volume-ratio) mixtures of adhesive and CCA-treated wood were reacted in the DSC, the thermograms differed remarkably in configuration from those produced by the phenolic adhesive alone (Fig. 2). The adhesive mixture alone produced a reaction exotherm with a single, prominent peak that reached a maximum at 148 C. The adhesive with CCA-treated wood produced two prominent exotherm temperature peaks. The first was a broad and low peak that occurred around 88 C; the second was a sharper and higher peak that occurred around 143 C. 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 those for the mixture of adhesive with CCA-treated wood. In both cases, the lower temperature peaks were near 88 C, and the higher were near 143 C. 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 low-temperature exotherms near 88 C.

Note that the configuration of the thermograms changed remarkably when the weight ratio of the adhesive-to-wood mixture was changed from 2:1 to 5:1. Figure 3 shows results from CCA-treated wood, but the reaction exotherm configurations and peak temperatures are the same as those for untreated wood. By increasing adhesive 2½ times, the two-peak thermogram disappeared to form a single-peak thermogram with a slightly truncated rising slope. The main peak temperature was slightly lower at 143 C with the larger proportion of wood in the 2:1 mixture, and the peak temperature was 145 C with much less wood in the 5:1 mixture. The adhesive alone peaked at 148 C. Adding adhesive in increasing proportions to the wood tended to shift the main peak to the higher temperature closer to that of the adhesive alone. Conversely, adding wood in increasing proportions to the adhesive tended to shift the main peak to a lower temperature.

Because CCA-treated and untreated wood were components of the reaction mixture, it was of interest to see how each component might react individually without adhesive, and possibly contribute to the overall reaction of adhesive and wood mixture. Figure 4 shows thermograms of both untreated and CCA-treated wood. The exotherm of untreated wood began at about 78 C, slowly increased to 168 C, then began a somewhat faster increase to 200 C where the DSC scan was stopped. The exotherm of CCA-treated wood was remarkably different in that it began at 78 C, but increased more rapidly from 138 C to peak sharply at 170 C. The chemical reactions that took place are not known, although low-temperature thermal decomposition of wood must have begun in both cases. The total heats of reaction of wood in both capsules were about the same up to 200 C, but the reaction peaked more sharply at 170 C for the CCA-treated wood.

A comparison of calculated heats of cure of phenolic adhesive in the presence of CCA-treated wood and untreated wood is another
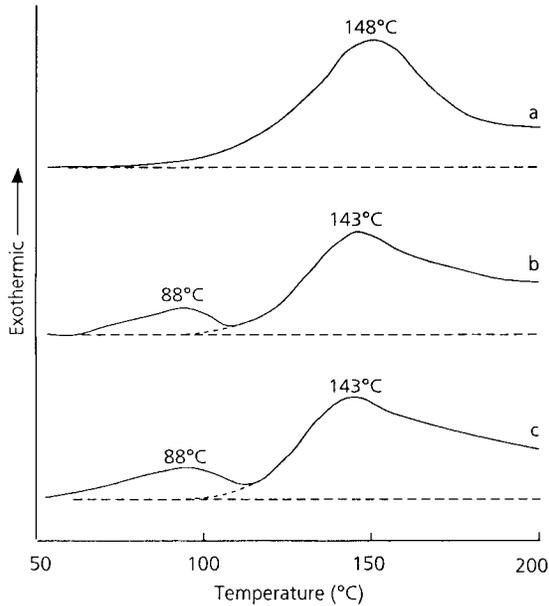
FIG. 2.   DSC thermograms of reactions of phenolic adhesive mixture (a) alone, (b) with CCA-treated (9.6 kg/m³) southern pine in a 2:1 (adhesive-to-wood) weight-ratio, and (c) with untreated southern pine in a 2:1 (adhesive-to-wood) weight-ratio.

FIG. 3.   DSC thermograms of reactions of phenolic adhesive mixture (a) alone, (b) with CCA-treated (9.6 kg/m³) southern pine in a 5:1 (adhesive-to-wood) weight-ratio, and (c) with CCA-treated (9.6 kg/m³) southern pine in a 2:1 (adhesive-to-wood) weight-ratio.

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. 2) showed two similar exothermic reactions. The lower temperature peaks were caused by some unidentified reaction between the wood and phenolic adhesive. These peaks did not occur with either the phenolic resin alone or the mixed phenolic adhesive (Fig. 1a, c). 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 (Fig. 2b, c). The calibration of exotherm area with heat quantities allowed calculation of the heats of cure for these two adhesive-wood mixtures. 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
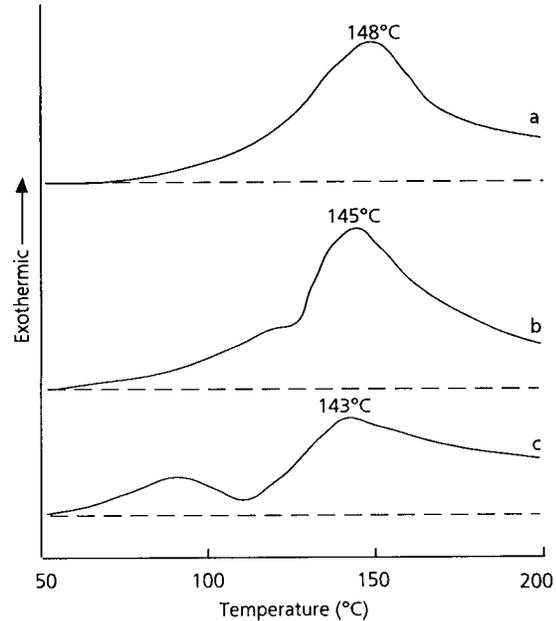
for the adhesive with CCA-treated wood (at 9.6 kg/m³ retention). This was a difference of only 2% which agrees closely, considering the difficulties in taking representative samples of the mixtures for DSC scans.
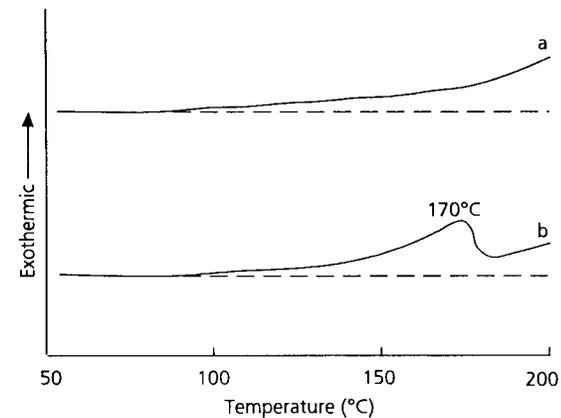

FIG. 4.   DSC thermograms of reactions of (a) untreated southern pine and (b) CCA-treated (9.6 kg/m³) southern pine.
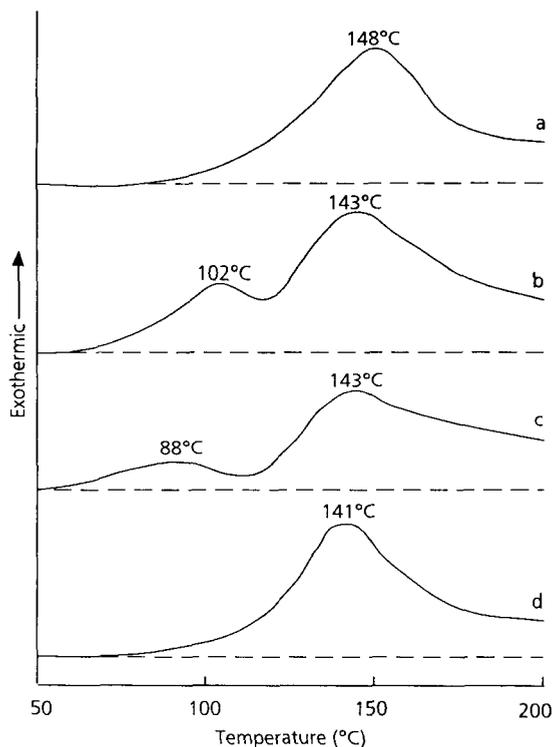
Fig. 5. DSC thermograms of reactions of phenolic adhesive mixture (a) alone, (b) with a 1.75% solution of CCA preservative, (c) with CCA-treated (9.6 kg/m³) southern pine in a 2:1 (adhesive-to-wood) weight-ratio, and (d) with a NaOH-precipitated and dried CCA preservative.

Fig. 6. DSC thermograms of reactions of phenolic adhesive mixture (a) alone; or with 1.87% weight of (b) total Cr⁺⁶, Cu⁺², and As⁺⁵ in solution of CCA preservative; (c) Cr⁺⁶ in solution of chromium trioxide (CrO₃); (d) Cu⁺² in solution of cupric chloride (CuCl₂); and (e) As⁺⁵ in solution of arsenic pentoxide (As₂O₅).

Adhesive with CCA preservative

Previously discussed DSC exotherms indicated no differences in cure of phenolic adhesive in the presence of either CCA-treated wood or untreated wood. However, when phenolic adhesive was reacted with a 1.75% aqueous solution (percent metal, weight basis) of CCA preservative, which approximated that used to treat southern pine to a retention of 9.6 kg/m³, two prominent exothermic peaks resulted. The lower temperature peak occurred at 102 C, and the higher peak occurred at 143 C. In Fig. 5, this thermogram is compared with that of the phenolic adhesive alone and the adhesive with CCA-treated wood. Note that the peak temperature of the adhesive in the presence of both the solution of CCA preservative and CCA-treated wood was 143 C, so that both were 5 C lower than the peak tem-
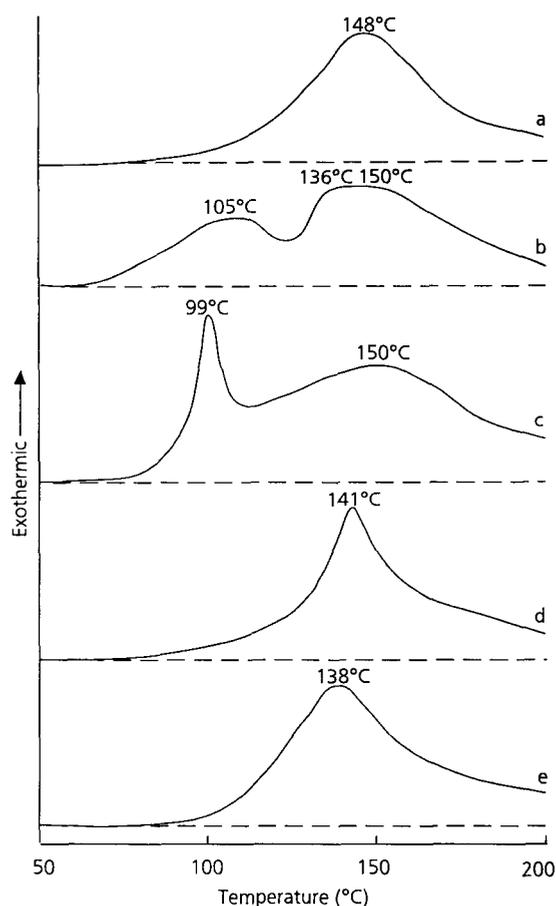
perature of the phenolic adhesive alone. In the solution of CCA preservative, all ions of Cr⁺⁶, Cu⁺², and As⁺⁵ were available to complex with the phenolic adhesive. This availability of ions produced a reaction with the phenolic adhesive that peaked at 102 C, which was far lower than the major peak temperature of 143 C. When CCA-preservative solution of the same concentration was precipitated with 1 M NaOH, dried, and then reacted with the phenolic adhesive, no similar exotherm was apparent in the lower temperature range. The peak temperature was 141 C—very near the

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

DSC sample (mg)	Adhesive-to-additive weight ratio	Chromium additive	State	Cr as portion of additive (weight %)	Heat of cure (J)	Calculated adhesive weight in DSC sample (mg)	Heat of cure per weight of adhesive (J/mg)	Cure peak temperature (0°C)
19.1	—	—	—	—	2.21	19.1	0.116	148
20.7	7:1	Cr_2O_3	Solid	68	2.31	18.1	0.127	147
19.4	7:1	$Cr(C_2H_3O_2)_3$	Solution	6	1.85	17.0	0.109	145
20.1	7:1	CrO_3	Solution	6	2.51	17.6	0.143	142

normal 143 C peak temperature of adhesive with CCA-treated wood. Apparently, one or more ions of Cr^{+6}, Cu^{+2}, and As^{+5} that were available for reaction in solution were not available when precipitated with NaOH. Perhaps the lack of reaction of phenolic adhesive with one or more ions in the NaOH-precipitated solution of CCA is analogous to the lack of reaction of the adhesive with the fixed and precipitated CCA preservative in the treated wood.

To determine which ions of CCA preservative were reacting with the phenolic adhesive, 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% metal ion, then reacted in DSC capsules. These thermograms are compared with the phenolic adhesive in Fig. 6.

In Fig. 5, a comparison of a and b shows that the solution of CCA preservative reacted strongly with adhesive. However, a similar strong reaction occurred with a slightly less-concentrated solution (1.87% total Cr, Cu, As), shown by comparing Fig. 6a and b. Two prominent exotherms occurred again, with the lower one peaking at 105 C, and a major peak that was truncated 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 (Fig. 6). The Cr^{+6} ion strongly contributed by producing two prominent exotherms—with the first peaking sharply at 99 C, and the second broadly rounding at 150 C. The Cu^{+2} produced a sharp but single

peak at 141 C, and As^{+5} produced a single peak at 138 C. Adhesives containing each of the three ions peaked individually between 138 C and 150 C; in the adhesive with the CCA preservative solution, the ions could have combined to produce a truncated peak temperature between 136 C and 150 C. It appears that Cu^{+2} and As^{+5} caused a minor acceleration of cure, indicated by shifts to slightly lower peak temperatures; however, Cr^{+6} caused a strong shift of part of the exotherm to a much lower peak temperature near 100 C. The previous reactions were not catalyzed just by the acidities of the solutions of model compounds and CCA preservative. This 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 preservatives gelled the phenolic adhesive at the point of contact between the liquids.

Pizzi (1981, 1982c) indicated that in CCA-treated wood, 60% of the chromium is fixed irreversibly as Cr^{+6}, and 40% is weakly bound as Cr^{+3}. Dahlgren (1972) indicated that all chromium is reduced from Cr^{+6} to Cr^{+3}. Pizzi's studies (1979a, b) 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 1.87% Cr^{+3} from chromium acetate hydrate or Cr^{+6} from chromium trioxide or an insoluble powder of chromium (Cr^{+3}) oxide was reacted in DSC capsules. Peak temperatures and heats of cure for each mixture are given in Table 1.

Compared to the phenolic adhesive alone, the insoluble chromium (Cr^{+3}) oxide, 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 (Cr^{+3}) acetate caused the peak temperature to decrease by 3° (from 148 C to 145 C), with a small doubtful decrease in the heat of cure. However, chromium (Cr^{+6}) trioxide decreased the peak temperature by 6° (from 148 C to 142 C) and increased the heat of cure by 23%. By both measures, the reactivity changes caused by Cr^{+6} were substantial.

CONCLUSIONS

Thermograms by differential scanning calorimetry (DSC) indicated that a solution of chromated copper arsenate (CCA) preservative caused a strong exothermic reaction with phenol-formaldehyde adhesive in which a portion of the adhesive cured at less than normal temperatures. Individual metallic ions of Cr^{+6}, Cr^{+3}, Cu^{+2} and As^{+5} in model compounds also reacted with the adhesive, but only Cr^{+6} accelerated the cure in the same low-temperature range as did the solution of CCA preservative. However, when the CCA preservative was chemically "fixed" within the wood, no such accelerated reaction of the adhesive was evident. Based on this analysis by DSC, the presence of CCA-treated southern pine did not interfere with the normal curing reaction of phenol-formaldehyde adhesive.

ACKNOWLEDGMENT

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