CURE RATE OF RESORCINOL AND PHENOL-RESORCINOL ADHESIVES IN JOINTS OF AMMONIUM SALT-TREATED SOUTHERN PINE

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ABSTRACT

A resorcinol resin adhesive of commercial manufacture, formulated for the purpose of gluing ammonium salt-treated wood, gave excellent performance in joints of southern pine. Joints of the treated wood made with this adhesive passed the minimum requirements of a commercial standard for shear strength and wood failure. Six ordinary phenol-resorcinol or resorcinol resin adhesives did not meet the commercial standard minimum requirements for gluing fire-retardant-treated wood. Shear strength and wood failure were higher with all adhesives studied for untreated wood than for treated wood. The determination of the effect of an ammonium salt fire retardant on the increase in viscosity of these adhesives, in the absence of wood, predicted the better performance of the specially formulated adhesive with the treated wood. However, gluing studies were needed to determine the actual level of performance of the specially formulated adhesive.
CURE RATE OF RESORCINOL AND PHENOL-RESORCINOL ADHESIVES IN JOINTS OF AMMONIUM SALT-TREATED SOUTHERN PINE

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INTRODUCTION

The rate at which adhesives cure has always been of importance to the wood industry. In a large measure, this factor determines the gluing requirements for the particular operation for which the adhesive is being considered. For economic reasons, it is important to reduce the curing period to minimum time consistent with maintaining high joint quality (strength and durability).

Work done at the Forest Products Laboratory has shown that the delamination of white oak beams is dependent on adhesive cure temperature and curing time. The curing period was significantly reduced as the cure temperature increased. A more recent approach to reducing the curing period consists of using new fast-curing adhesives which have been introduced to the wood industry by suppliers.

Only a few reports have been issued on the effect of treated wood, particularly fire-retardant-treated wood, on the curing rate of the glueline. It has been shown that typical ammonium salt fire retardants increase the rate of gel of resorcinol resin adhesives while lowering the pH of the adhesive. Both of these factors could change the length of the curing period required to achieve a quality adhesive joint with bonded fire-retardant-treated wood. In work reported on the gluing of ammonium salt-treated southern pine, a period of 2 months was permitted between gluing and testing. A consideration of these factors prompted us to investigate the effect of adhesive age prior to spreading and of cure time on the development of joint strength in bonded southern pine which had been treated with a proprietary ammonium salt fire retardant. Some additional work on the effect of ammonium sulfate (a typical ammonium salt fire retardant) on the viscosity of phenol-resorcinol and resorcinol resin adhesives is also included in this report.

1 Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
PHASES OF STUDY

Research on the rate of development of joint strength for bonded, untreated and ammonium salt-treated southern pine was conducted in two phases. The first phase was concerned with the effect of a typical ammonium salt fire retardant on the viscosity of commercial phenol-resorcinol and resorcinol resin adhesives. In the second phase, the rate of development of joint strength with bonded treated and untreated southern pine was studied. The treated pine was treated commercially with the ammonium salt fire retardant. The wood was bonded with the same adhesives in both phases of the study.

ADHESIVES

Six adhesives were used. Five were commercial types mixed to manufacturers’ recommendations and the sixth (adhesive B) was formulated by mixing the resin of adhesives C and D with formalin (37 pct. aqueous formaldehyde).

Adhesive A -- A slow curing phenol-resorcinol resin with paraformaldehyde hardener.

Adhesive B -- A straight resorcinol resin with liquid formalin hardener (37 pct. formaldehyde) which had been used for work previously reported. The resin was stored for 2 years at 36° F. before use in this study.

Adhesive C -- A conventional straight resorcinol resin with paraformaldehyde hardener which had been used for previously reported work. The resin was stored for 2 years at 36° F. before use in this study.

Adhesive D -- A conventional straight resorcinol resin similar to C with paraformaldehyde hardener. The resin and hardener were used within 2 months after they were received from the manufacturer.

Adhesive E -- A fast curing phenol-resorcinol resin with paraformaldehyde hardener.

Adhesive F -- A resorcinol-type resin with a liquid hardener containing a higher concentration of formaldehyde (about 54 pct.) than conventional formalin solution. The resin and hardener had been used for previously reported work, and the resin was subsequently stored for 2 years at 36° F. This resin was specially formulated for gluing fire-retardant-treated wood.

EFFECT OF AMMONIUM SULFATE ON THE VISCOSITY OF PHENOL-RESORCINOL AND RESORCINOL RESIN ADHESIVES

The procedure used to study the effect of ammonium sulfate on the viscosity of the adhesives was the same as described in a previous report, with the following exceptions: The hardener added to the resin was either a solid (paraform) or liquid (formaldehyde solution). The adhesive was hand stirred periodically between readings of viscosity with a Brookfield Syncret Lectric Viscometer. This insured uniform distribution of the walnut shell flour and hardener in the commercial adhesive throughout the entire run.

RATE OF DEVELOPMENT OF JOINT STRENGTH

Block-Shear Specimens

Joints for block-shear specimens (ASTM Standard Method D 905-49) were prepared from nominal 1-inch untreated southern pine lumber, and southern pine lumber treated with a proprietary ammonium salt fire retardant.

Wood

Flat-grain southern pine lumber, commercially treated with a proprietary ammonium salt fire retardant, was cut into blocks 3/4 by 2-1/2 by 12 inches. Untreated lumber was cut into similar blocks. The average salt retention of the treated lumber, as reported by the supplier, was approximately 5.5 pounds per cubic foot. The treated and untreated blocks were conditioned at 80° F. and 65 percent relative humidity before gluing. The surfaces to be bonded were lightly surfaced on a jointer before the adhesive was spread.

5 Use of trade names is for information only, and does not imply endorsement by the U.S. Department of Agriculture to the exclusion of others that may be equally suitable.
Gluing Conditions

After mixing, the adhesives were permitted to age at 80° F. for periods of 15, 60, or 120 minutes before spreading, except for a shorter 5-minute period with adhesive E. Three grams of adhesive (equivalent to 61 pounds per 1,000 square feet of single glueline) was applied to each mating surface by means of a paint roller. After a closed assembly period of 60 minutes (assembly periods were 10 and 30 minutes for adhesive E), the block assemblies were pressed at 150 pounds per square inch for 20 hours at 80° F.

Shear Tests

Ten joints were made for each combination of variables involving adhesives, adhesive age before spreading, and treated and untreated wood. Five block-shear specimens were cut from each joint for a total of 50 specimens per combination of variables. The 50 specimens were arranged in five groups of 10 specimens each, with one specimen of each joint randomly selected to represent the joint within each group. The five groups of specimens were randomly arranged for testing dry in accordance with ASTM Standard Method D 905-49 after 1, 7, 25, 56, and 180 days’ cure time at 80° F. and 65 percent relative humidity.

RESULTS AND DISCUSSION

The age of the resin and hardener before mixing and the age of the adhesive before spreading have an effect on the quality of joints of bonded wood treated with ammonium salts. An adhesive which was made from 2-month-old resorcinol resin and 2-month-old paraform hardener increased more rapidly in viscosity when ammonium sulfate was added than adhesives made from 2-year-old resin and hardener (fig. 1). A 2-year-old resorcinol resin adhesive, paraform cured, required more time to reach maximum strength than a similar

![Figure 1](image-url)

Figure 1.—Effect of adding ammonium sulfate (25 meq.) on the viscosity of three resorcinol resin adhesives. F, Adhesive F, 2 years old; F', same as F, with ammonium sulfate; B, adhesive B, 2 years old; B', same as B, with ammonium sulfate; D, adhesive D, 2 months old; D', same as D, with ammonium sulfate.

M 137 151
Figure 2.--The rate of development of joint strength of untreated and ammonium salt-treated southern pine bonded with two different batches of resorcinol resin adhesive also differing in age of resin and hardener. D, Adhesive D with 2-month-old resin and hardener aged 60 minutes before spreading on untreated wood; D', same as D, but spread on treated wood; C, adhesive C with 2-year-old resin and hardener aged 60 minutes before spreading on treated wood. M 137 159

2-month-old adhesive (fig. 2). This effect appears to be more dependent on paraform hardener activity than on the resorcinol resin activity after storage. The rate of gelation of a 2-month-old resin and the rate of gelation of a 2-year-old resin was the same with a standardized formalin solution of known formaldehyde concentration. However, the 2-month-old resin with a 2-month-old paraform hardener gelled more rapidly than the 2-year-old resin with a 2-year-old hardener (fig. 3). It is known that paraform which has been tightly sealed in a container will become less active with age due to the formation of large polymeric fragments of formaldehyde. In our basic studies, which have been previously reported, we used standard formalin of known formaldehyde concentration because the paraform hardener decreased in activity with increase in age.  

The increase in viscosity of a 2-year-old resorcinol resin adhesive which had been specially formulated for gluing fire-retardant-treated wood (Adhesive F) was considerably less than that of a 2-month-old paraform-cured adhesive (fig. 1). With the addition of 12.5 milliequivalents ammonium ion, the rate of increase in viscosity of the specially formulated adhesive was slower than the rate of increase in viscosity for the control as it approached the point of gelation (fig. 4). The increase in viscosity, which normally occurs during the spreading of a resorcinol resin adhesive on ammonium salt-treated wood and during the closed assembly period, did not appear to be as pronounced with the 2-year-old specially formulated adhesive (Adhesive F) as with the adhesive made from 2-month-old resin and paraform hardener (Adhesive D).

The effect of ammonium sulfate on the viscosity of adhesive F was less than its effect on the other adhesives, suggesting that adhesive F might perform better than the other adhesives in bonding the ammonium salt-treated wood.

Joints made of treated wood with adhesive F were higher in shear strength and wood failure than joints made with the other adhesives used in this study (fig. 5). After 56 days of cure the wood failure was 80 percent, a performance level that was surpassed only by aging this adhesive 120 minutes before spreading (fig. 6). In this case, the wood failure was 80 percent after 7 days of cure at 80°F.
Figure 3.—Effect of resin age on the increase in viscosity of a resorcinol resin adhesive. D, 2-month-old resin from adhesive D cured with 28 percent aqueous formaldehyde; D', same as D, but with paraform hardener; C, 2-year-old resin from adhesive C cured with 28 percent aqueous formaldehyde; C', same as C, but with paraform hardener. M 137 152

Figure 4.—Effect of adding ammonium sulfate on the viscosity of a resorcinol resin adhesive (F). A liquid with a high formaldehyde content (54 pct.) was used as a hardener. M 137 155
Figure 5.—The rate of development of joint strength of ammonium salt-treated southern pine bonded with three resorcinol resin adhesives which had been aged 60 minutes before spreading D, adhesive D plus paraform hardener; B, adhesive B plus liquid hardener (28 pct. formaldehyde); F, adhesive F plus liquid hardener (54 pct. formaldehyde). M 137 160

Figure 6.—The rate of development of joint strength of untreated and ammonium salt-treated southern pine bonded with a resorcinol resin adhesive (F). A liquid with a high formaldehyde content (54 pct.) was used as a hardener. Upper dotted lines represent untreated controls. X, adhesive aged 15 minutes before spreading; Y, adhesive aged 60 minutes before spreading; Z, adhesive aged 120 minutes before spreading. M 137 158
Figure 7.--Effect of adding ammonium sulfate on the viscosity of a resorcinol resin adhesive (D). A solid, paraform, was used as a hardener. M 137 153

Figure 8.--Rate of increase in viscosity of a slow- and a fast-curing phenol-resorcinol adhesive, and subsequent effect of ammonium sulfate on the viscosity of the slow-curing adhesive. E, Adhesive E, a fast-curing phenol-resorcinol; A, adhesive A, a slow-curing phenol-resorcinol; A', adhesive A with the addition of 25 milliequivalent ammonium sulfate. The rate of increase of viscosity for A' was too rapid to permit additional readings to be taken. M 137 154
Thus, the utility and desirability of continuing this type of research through both chemical and gluing tests was established by the fact that the performance of adhesive F as compared to the other adhesives in bonding the treated wood can be predicted from the viscosity data.

The rate of increase in viscosity of resorcinol resin adhesives, due to the interaction of ammonium salts, depends on the rates of several chemical changes. These include the rate of dissociation of the ammonium ion, the rate of interaction of ammonia and formaldehyde, and the rate of interaction of the initial products of the ammonia-formaldehyde interaction and the resorcinol resin. In addition to these, the overall observed phenomenon, the rate of increase in viscosity of the adhesive, is further complicated by the rate of dissociation of paraform when it is used as a hardener. At a concentration of 25 milliequivalents of ammonium sulfate, the effect of paraform dissociation on the increase in viscosity was observed (fig. 7). The dissociation of paraform appears to be rate controlling as its concentration decreases, but the products of ammonia-formaldehyde interaction cause a significant initial rate of increase in viscosity due to the highly reactive methylol amine.

The viscosity of the newly developed slow- and fast-curing phenol-resorcinol adhesives increased very rapidly in the presence of ammonium sulfate. The rate of increase in viscosity of the slow-curing adhesive was impossible to control at 80° F. (fig. 8). These adhesives failed to perform as well as the older type conventional resorcinol resin adhesives in joints made from ammonium salt-treated wood. The wood failure was 0, and the shear strength never was greater than 600 p.s.i. (fig. 9). However, these adhesives performed as well, if not better, than the older type adhesives in joints of untreated wood.

Initial strength of the joint increased as the age of the adhesive increased after mixing resin and hardener (figs. 6 and 10). Adhesives were aged 15, 60, or 120 minutes before spreading, except in the case of the fast-curing phenol-resorcinol adhesive. It was aged 5 or 15 minutes.

The most significant increase in shear strength and wood failure occurred within 7 days of curing for joints of both untreated and treated wood.
All adhesives performed better with untreated wood than with treated wood in shear strength and wood failure. Wood failure from joints made of treated wood bonded with the adhesive specially formulated for treated wood was approximately as high as that for joints of untreated wood; however, the shear strength for the treated wood joints was significantly lower than that for the untreated counterparts (fig. 6).

Results of this study have pointed out again some of the difficulties in bonding wood treated with ammonium salts by means of resorcinol or phenol-resorcinol adhesives.

The limits governing the gluing conditions involving variables such as the age of the resin or hardener, the age of the adhesive after mixing resin and hardener, viscosity of the adhesive at the time of spreading, viscosity of the adhesive at the end of the assembly period, press pressure, cure temperature, and length of cure time are narrower for gluing treated wood than for gluing untreated wood.

**CONCLUSIONS**

Joints made with a resorcinol resin adhesive specially formulated for bonding fire-retardant-treated wood showed satisfactory shear strength and wood failure levels in ammonium salt treated southern pine. These joints met the minimum requirements of Commercial Standard CS 253-63 for shear strength and wood failure.

Other adhesives studied did not produce satisfactory joints in fire-retardant-treated southern pine. With all adhesives used in this study, shear strength and wood failure were higher in joints of untreated wood than in joints of fire-retardant-treated wood.

The age of the resin and hardener prior to mixing, and the age of the adhesive after mixing, have an effect on the quality of bond obtained with treated wood. The effect of age is minimal or obscured within limits of this study for bonds made of untreated wood, regardless of the resorcinol or phenol-resorcinol adhesive used to make the bonds. The effect of age is due primarily to hardener activity rather than resin activity for paraform-cured resorcinol resin.

The slow- and fast-curing phenol-resorcinol adhesives failed to perform as well as the older type resorcinol resin adhesives in bonding am-

(figs. 2, 5, 6, 10).

Figure 10.--The rate of development of joint strength of untreated and ammonium salt-treated southern pine bonded with a resorcinol resin adhesive (C). A solid, paraform, was used as a hardener. Upper dotted lines represent untreated controls. X, adhesive aged 15 minutes before spreading; Y, adhesive aged 60 minutes before spreading; Z, adhesive aged 120 minutes before spreading.
monium salt-treated southern pine.

The most significant increase in shear strength and wood failure occurred within 7 days of curing at 80° F. for joints of both untreated and treated wood.

It appears that the general performance of adhesives specially formulated for gluing fire-retardant-treated wood can be predicted from viscosity data. Viscosity data could be used to select the most effective adhesives from a group to be tested, eliminating costly and time-consuming preliminary studies based on performance in joints. Then actual gluing studies would be required to determine the specific performance level of the selected adhesives.
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