Field Study on the Effect of Acidic Conditions on the Adhesion of Paint to Western Redcedar

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Previous research results involving sulfur accumulation on cross sections of wood coated with latex paint led us to investigate whether acidic conditions could affect the bonding strength of paint and be a factor in catastrophic paint peeling. Through simulation of acidic dew under outdoor conditions, the study reported herein determined the effect of acid rain and/or dew on painted wood siding. Painted wood was soaked before dawn in various acid solutions for two hours each day, then exposed outdoors for the remainder of the day and night during the summer near Madison, WI. From October to May, the specimens were exposed but not soaked. After four years of exposure to weather and acid, only the painted wood interface for specimens soaked in sulfurous acid at pH 2 indicated deterioration as measured by fracture toughness testing.

INTRODUCTION

Sulfur is produced primarily from coal-fired power plants and nitrogen from the internal combustion engine. When oxidized in the presence of moisture, sulfur and nitrogen form acids. The most common acids are nitric (HNO_3) and sulfuric (H_2SO_4). Sulfur dioxide (SO_2) dissolved in water is called sulfurous acid (H_2SO_3). With the addition of oxygen, sulfuric acid (H_2SO_4) is formed.

Acid rain begins primarily as oxides of nitrogen and sulfur that are generally denoted as NO_x and SO_x. Through a series of complicated chemical reactions, acids are formed. Attempts to duplicate acid rain chemistry have been successful to some extent using a smog chamber. Edney et al. showed that ultraviolet (UV) radiation and heat, in the presence of moisture, promoted the sequential reactions to various compounds, many of which were acidic.[1] The chamber chemistry can be controlled to achieve a wide range of conditions, and Spence et al. found that sulfur dioxide concentration and relative humidity strongly influence paint degradation.[2]

The effects of acid dew were achieved by cooling from the back of the specimens.[2-3] This cooling caused rapid paint erosion of the painted steel specimens, particularly paint formulated with calcium carbonate. However, dew formation on painted wood could not be achieved because of the insulating properties of wood. This research by Edney et al. and Spence et al. focused on acid catalyzed erosion of the paint surface.[1-3] They did not attempt to investigate interracial failure in their initial work.

The follow-up research at the USDA Forest Service, Forest Products Laboratory (FPL), analysis of cross sections of wood coated with latex paint using energy dispersive X-ray analysis showed an accumulation of sulfur compounds at the paint-wood interface when soaked in sulfurous acid.[4] This sulfur accumulation led to investigations on whether acidic conditions could affect the bonding strength of paint and be a factor in catastrophic paint peeling.

Other work at the FPL showed that outdoor exposure of unpainted wood for four to eight weeks dramatically decreased the bond strength of the paint when the weathered wood was subsequently painted.[5-8] It was also shown that acidic conditions could accelerate the weathering of wood.[9] Others have also showm this effect.[10,11] Because it was shown that acidic conditions could accelerate wood weathering and sulfur compounds could accumulate at the paint-wood interface, several studies were initiated to determine the effects of acid on the paint-wood interface. This research included exposing specimens in the smog chamber at the Environmental Protection Agency (EPA), Raleigh, NC, in the wind chamber constructed at FPL, and in the field and laboratory. Acid exposure during a rain event is of relatively short duration because most of the acid is stripped out of the air during the initial rain; therefore, the research reported herein attempted to duplicate acidic dew formation. The formation of dew removes and concentrates acidic gases from the air. Dew is likely to be a major path for aerosol acid to reach a surface.

Initial experiments at EPA using the smog chamber, the wind chamber at FPL, and field and laboratory exposure using

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Table 1—Average (Avg) Fracture Toughness Values in J/m² with Standard Deviation (Std) and Coefficient of Variation (COV)

Acid Solution	Timber 1			Timber 2			Timber 3			Timber 4			Timber 5		
	Avg	Std	COV	Avg	Std	COV	Avg	Std	COV	Avg	Std	COV	Avg	Std	COV
pH 3 NO_3	176	22	13	191	18	9	248	39	16	222	30	13	173	20	12
pH 2 NO_3	182	19	10	197	36	18	234	37	16	231	22	9	180	28	18
pH 3 SO_3	173	18	11	211	32	15	231	22	9	228	34	15	202	52	26
pH 2 SO_3	128	16	12	145	15	10	112	18	16	172	12	7	102	33	32
pH 3 SO_4	181	26	14	231	65	28	227	34	15	239	16	7	177	34	19
pH 2 SO_4	179	21	12	207	42	20	220	22	10	215	37	17	181	26	14
Deionized.....	174	19	11	243	56	23	237	40	17	230	43	19	178	22	12
3 SO_4/NO_3	178	14	8	243	16	6	210	30	14	244	26	11	176	20	11
2 SO_4/NO_3	187	10	5	226	33	15	201	29	14	241	21	9	160	23	14
Control	204	22	11	223	44	20	254	44	17	241	27	11	255	58	23

acids of various concentrations showed no degradation of the paint-wood interface. The failure of these methods was probably caused by their inability to simulate acidic dew formation. Simulating dew was the method chosen most likely to show an acid effect on the paint-wood interface.

The objective of the research reported here was to show the effect of a two-hour acid dip, just before sunrise, on the wood-paint bond strength. This experiment was an attempt to simulate the effects of acidic dew under outdoor conditions.

EXPERIMENTAL PROCEDURE

Acid Solution

Nine 127-L (1.22m × 300mm × 410mm deep) acrylic dip tanks were constructed: one for deionized water control and the other tanks for pH 2 and 3 solutions of nitric, sulfuric, a mixture of nitric and sulfuric, and SO_2 dissolved in deionized water. Nitric acid completely dissociates at both pH values, so 0.01 M for pH 2 and 0.001 M for pH 3 solutions were made by adding 80 ml and 8 ml, respectively, of concentrated HNO_3 to 127 L of deionized water. Sulfuric acid completely dissociates at pH 3; therefore, 0.001 M was made using 3.5 ml of concentrated H_2SO_4. The second pK for H_2SO_4 is 1.92, which results in the second proton being half dissociated at pH 1.92, corresponding to 47 ml of concentrated H_2SO_4. For pH 2, 42 ml was required. For the mixtures, one-half of the amounts of each acid was used. A pH meter confirmed the pH values and was used to control the addition of SO_2 to the ranks. All tanks were vacuumed weekly to remove sediment, refilled with deionized water, and adjusted to the correct pH.

To decrease dissolved oxygen, the SO_2 tanks were allowed to warm prior to adding the sulfur dioxide. While mixing, sulfur dioxide was bubbled through a glass frit into the tank until the desired pH was reached. Glycerine (0.1%) was added to the SO_2 tank to quench oxidation to sulfuric acid. Samples from the SO_2 tanks were acidified and titrated with potassium iodate (KIO_3) to determine the sulfite (sulfurous acid) concentration. This procedure was modified from the Sulfite (428 A.) Iodometric Method.[14] Initially, the analysis was done several times a week to determine the actual SO_2 concentration. Later, the analysis was only done after SO_2 addition, just before draining at one week, and periodically in between. Each dipper had 45 specimens that were soaked in the solutions from 4 to 6 a.m. and exposed perpendicular to the zenith for the remainder of the day. One set of panels was removed and tested after two years and another set removed and tested after four years.

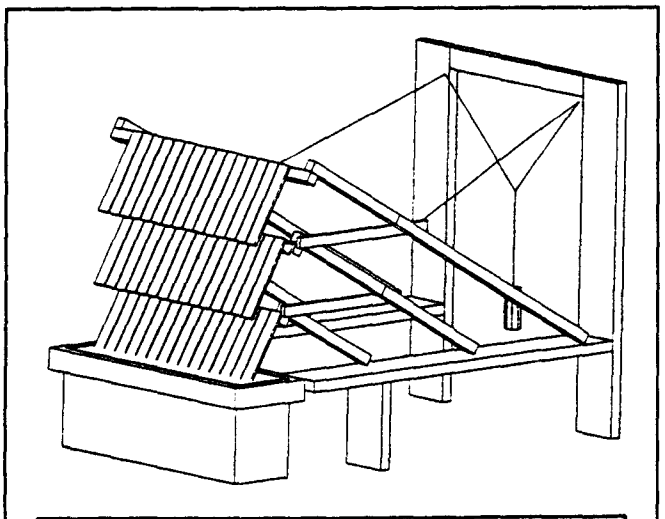

Figure 1—Dipper showing panels entering the tank.

Western Redcedar Panels

Five 150mm × 300mm × 3.66m western redcedar timbers were purchased, cut, and planed to 403mm × 70mm × 13mm panels. Five timbers, all from different trees, were used because of the natural variability of wood. Large timbers also made it possible to cut boards with a 5.7° (10:1 length:width) slope of grain, which was necessary for the sensitive fracture toughness test used.[12] The panels were completely encapsulated in a paint system consisting of an alkyd oil primer and acrylic latex flat topcoat. Nine panels from each timber (total of 45) were attached to each dipper in random order using silicone caulk. One of the nine dippers, indicating how the panels entered the dip tank, is shown in Figure 1. In addition to the deionized water control, a set of panels was kept dry and in the dark in a controlled environment.

Specimens for Mechanical Testing

At two and four years of exposure, 15 panels (three selected from the nine from each timber by a random number generator) were removed from each dipper for fracture tough-

ness testing along with the unexposed controls. The panels were epoxied to mates and each was cut into three specimens and tested. Specimens were tested in accordance with procedures previously reported,[12] and this involved propagating a crack along the paint-wood interface to determine the bonding strength of paint. Five fracture toughness values were obtained from each specimen. Details of the double cantilever beam test are given in Knaebe and Williams.[12] This test procedure was modified from ASTM D 3433-75.[13]

RESULTS

Results from specimens removed after two years of exposure were inconclusive. Results presented here are from the specimens removed after four years of exposure. The average fracture toughness values in J/m^2 with the standard deviation and coefficient of variation (COV) for each exposure were calculated for each timber and are listed in *Table* 1. Results from two timbers are presented in *Figures* 2 and 3. The results from each timber for each exposure are made up of 45 readings (3 panels × 3 specimens × 5 readings), except when problems occurred with the test machine and some data were lost. The fracture toughness values varied among the timbers because of the natural variability of wood, but the trends were the same. Timber 4 *(Figure* 2) provided the least definitive proof that SO_2 damages the wood-paint bond, and Timber 3 *(Figure* 3) most clearly demonstrated the effect of SO_2. Sulfurous acid at pH 2 decreased the adhesive strength of the paint, as the fracture toughness values indicate. The decrease was about 50% for pH 2 H_2SO_3 *(Figure* 3).

DISCUSSION

Because many factors, such as density, growth rate, grain orientation, and age of tree determine the characteristics of wood, five timbers were used. Comparing the results of each timber individually greatly decreased the COV. For all specimens, except those dipped in SO_2, the fracture toughness result essentially represented the cohesive strength of the wood, which was different for each timber. For example, fracture toughness values for specimens cut from timber 4 and dipped in SO_2 were the same as those for specimens cut from timber 1 and not dipped in SO_2, thus grouping data from all timbers served no purpose. The COV for timber 4 *(Figure* 2) ranged from 7 for pH 3 H_2SO_4 to 19 for deionized water.

Previous work that showed an accumulation of sulfur compounds at the paint-wood interface included only latex paint.[4] In our study, the fact that alkyl oil primers are less porous to water may have increased the time to degradation. It is unknown how a latex primer and topcoat paint system would have performed in our study.

The pH of the H_2SO_3 tanks slowly increased during the week because of loss of SO_2 into the atmosphere. The pK values for H_2SO_3 are 1.81 and 6.91, so the concentration of SO_2 required for pH 2 is greater than it would be for H_2SO4_3 because only one proton is dissociated. In other words, H_2SO_3, if permitted to oxidize to H_2SO_4, would nearly double the hydrogen ion concentration and lower the pH. The two processes are in competition and without glycerine, oxidation to sulfuric acid would predominate. The glycerine did not completely quench the oxidation. Sulfite analysis indicated that

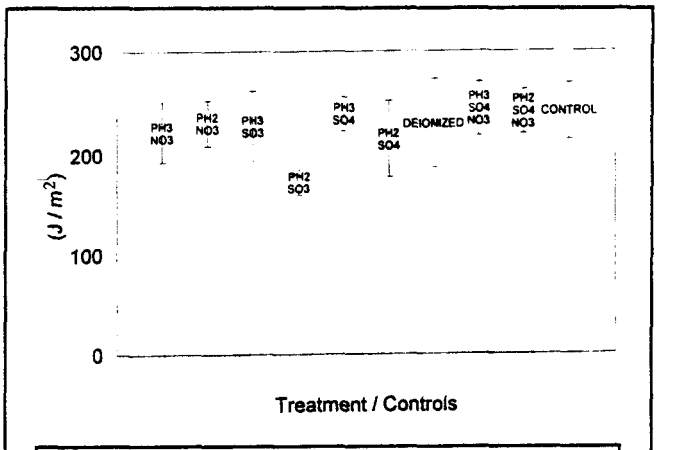

Figure 2—Fracture toughness values for timber number 4.

SO_2 left the system by either escaping or oxidizing at a half-life between one and two days. After one week, only 1 to 5% of the SO_2 remained. With the pH increasing about one-third of a pH unit, which is half the hydrogen ion concentration, one-fourth of the SO_2 oxidized to H_2SO_4 each week. For this reason, the SO_2 tanks were completely refilled each week. For the other acid solutions, the pH remained constant. Even one inch of rain did not appreciably change the concentrations of the 14-in. deep solutions. The solutions containing nitric acid grew some algae, which were removed each week when the tanks were vacuumed, refilled, and acidified.

CONCLUSIONS

Under fairly severe acidic dew conditions, degradation of the paint-wood interface was negligible in this study. Degradation can only occur if SO_2 is present. It is extremely unlikely that acidic dew can cause catastrophic paint peeling except in locations near an SO_2 source. In these locations, dew containing H_2SO_3 may be a factor in early catastrophic paint peeling. The increased weathering rate of the paint surface can still occur but is independent of the degradation shown in our research.

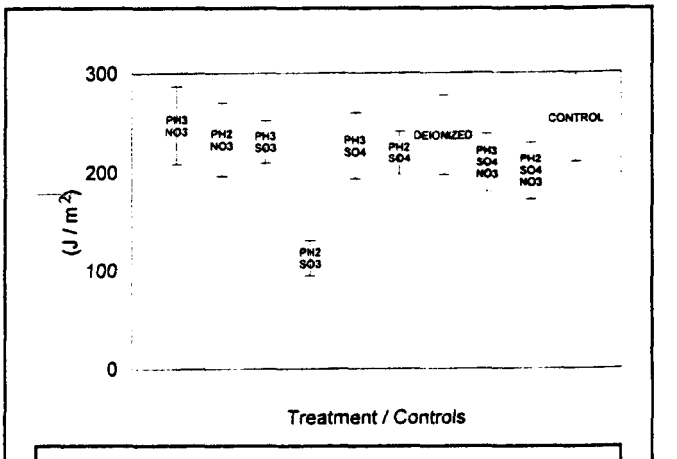

Figure 3—Fracture toughness values for timber number 3.

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