Paper No.
5617

NACE INTERNATIONAL CORROSION 2015 CONFERENCE & EXPO

Corrosion of Wires on Wooden Wire-Bound Packaging Crates

Samuel L. Zelinka and Stan Lebow
US Forest Service, Forest Products Laboratory
1 Gifford Pinchot Dr.
Madison, WI 53726
USA

ABSTRACT

Wire-bound packaging crates are used by the US Army to transport materials. Because these crates may be exposed to harsh environments, they are dip-treated with a wood preservative (biocide treatment). For many years, zinc-naphthenate was the most commonly used preservative for these packaging crates and few corrosion problems with the wires were observed. Recently, copper based alternatives to zinc naphthenate have been used, and corrosion problems have been observed. Here, we present the results of laboratory corrosion testing of 10 different wood treatments to see which preservatives have the potential to cause corrosion problems. The laboratory test was designed to mimic the production process; wires from packaging crates were attached to wood and dipped in the wood preservative and stored in a polyethylene bag for either 2 or 8 weeks to simulate how the crates are stored in the warehouse. The amount of corrosion was examined both visually and gravimetrically. Zinc naphthenate and Preservative A were the least corrosive preservatives, and there were no statistical differences between these two preservatives. The remaining treatments had at least 5 times more corrosion than these two preservatives. Three of the 10 treatments showed a linear increase in the amount of corrosion with time, suggesting that they were still corroding as rapidly at week 8 as they were at week 2 and present a high risk of corrosion. From these results, Preservative A (a copper ethanolamine complex containing citric acid) appears to be the least corrosive alternative to zinc naphthenate.

Key words: wood, wood-preservatives, organic acids, fasteners

INTRODUCTION

The US Army uses wood for construction of containers (such as ammunition boxes) and shipping materials such as pallets. These products are expected to have a useful life of up to 20 years, and although the majority of their service will be indoors, there may be extended periods of outdoor exposure. The wood may also be exposed in tropical climates that present a severe risk for both insect and fungal attack. To protect the wood from biodegradation, current Department of Defense (DOD) specifications stipulate that the assembled wood products be dip-treated with a wood preservative. A thorough evaluation of the efficacy of preservatives in protecting ammunition boxes was conducted by US Forest Service, Forest Products Laboratory (FPL) and US Army Armaments Research and Development personnel in the 1980's.[1] That study indicated that water-based zinc naphthenate, copper naphthenate, and copper-8-quinolinolate would be effective for treatment of ammunition boxes, and these three preservatives were incorporated into DOD specifications.

Of these, the most commonly used preservative has been zinc naphthenate. However, the manufacturers of zinc naphthenate wood preservative declined to generate the additional data required for US EPA reregistration of the product, and thus this preservative is no longer commercially available. In addition, some concerns about corrosiveness to metal fasteners have been expressed for water-based copper-8-quinolinolate and copper naphthenate. This sequence of developments has raised concerns about future availability of effective wood preservatives for protection of wooden containers and shipping materials.

In the manufacturing process, galvanized wires are attached to several sheets of plywood and the assembly is dipped in the preservative treatment for a minimum of one minute before being removed from the bath. The plywood assemblies are then stored flat in stacks until they are ready to be shipped. Because of how the boxes are stacked, there is little air-flow and the boxes in the middle of the stack may remain wet for long periods of time. It has been observed that boxes dipped in copper-8-quinolinolate and copper naphthenate will occasionally arrive with red-rust when delivered to the Army from the manufacturer, indicating that the galvanized coating has been corroded entirely.

The objective of this paper is to screen currently used and alternative wood preservatives for potential corrosion problems. The testing is focused on the corrosion that occurs immediately after the boxes are dipped in the preservative treatment, and the goal is to compare across treatments. As such, the absolute amounts of corrosion obtained herein are less important than differences across treatments. While the testing gives an accurate estimate of which treatments may exhibit excessive corrosion after treatment, it is not possible to determine an in-field service life of the galvanized coating from these data.

EXPERIMENTAL PROCEDURE

The goal of the laboratory testing was to determine which preservative systems are the least likely to cause corrosion issues in the packaging crates. The test methodology was designed to simulate the production process of the wire-bound crates. To simulate the production process, wires were attached to thin strips of plywood, which were then dipped in the preservative treatment for between 1-3 minutes and then stored in polyethylene bags for either 2 weeks or 8 weeks (nominally 2 months). The sealed polyethylene bags were used to simulate the slow drying with little airflow encountered for the stacked boxes. This represents, in some ways a worst case scenario, since there is no airflow and little potential for the wood to dry. Preliminary testing compared exposures in a room with 90% relative humidity (RH) to the polyethylene bag exposure. In the preliminary testing, less corrosion was observed in the 90% RH room; however, it was harder to differentiate the performance of the wires in different preservative systems. The polyethylene bag method was chosen since little corrosion was observed on the wires exposed to treatments that were known to be non-corrosive, yet still able to

produce measureable corrosion in other preservative systems allowing differentiation of the preservative systems.

Both the wires and the wood-strips used in the testing came from untreated packaging crates that were disassembled. The wires were removed from the crates and cut into segments that were approximately 150 mm long. The actual size of each segment was measured and recorded. Additional segments of wire were examined using scanning electron microscopy to examine the galvanization; a characteristic micrograph is shown in Figure 1. In most places, the thickness of the galvanized coating was between 10 and 20 µm.

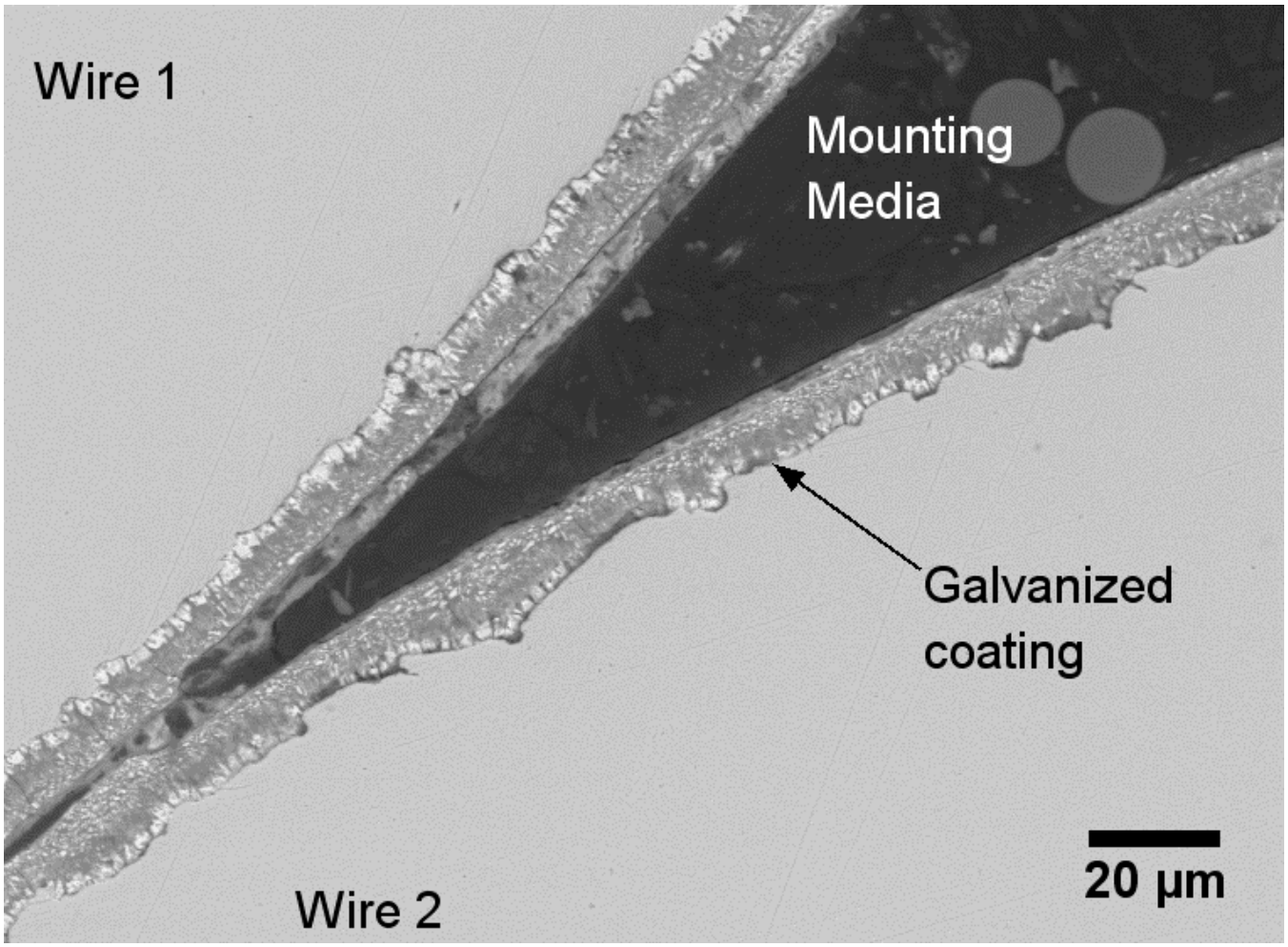

Figure 1: Scanning electron micrograph of the wires tested showing the galvanized coating thickness. Two different wire segments are shown.

Prior to the exposure test, the wires were cleaned in an ultrasonic bath with a soap solution, rinsed with distilled water, and finally rinsed with acetone. Following the cleaning procedure, the wires were weighed and then attached with a plastic fastening ring to a small (25 mm by 178 mm) strip of wood cut from the packaging crate. These assemblies of wood and wire were then dipped into the preservative treatment solutions, removed, and stored in a polyethylene bag for either 2 or 8 weeks.

Following the exposure, the extent of the corrosion was examined both qualitatively with a visual examination and quantitatively, by gravimetric analysis. Photographs of the wires were taken immediately after removal from the polyethylene bags. Afterward, the plastic fastening rings were removed, and the wires were flipped over and photographed again. This second photograph showed both the extent of corrosion when the wire was in direct contact with the wood and also the amount of

corrosion products deposited on the wood surface. Gravimetric analysis was performed by first removing the corrosion products of metal in contact with wood using the method of Zelinka et al.[2] . The wires were placed in an ultrasonic cleaner for 60 minutes in a bath comprised of 50vol% water and 50vol% EvapoRust† (Orison Marketing†), the wires were then wiped dry and weighed.

Table 1 lists the preservatives evaluated, their compositions and concentrations, as well as the time the wood and wires were dipped in the treatment solution. Trade names are avoided, but the active ingredients as well as their concentration in the treating solution are listed. For some preservatives, the general classifications are listed next to the group name. In all but two treating solutions (B and Z), the treatment solutions contained 2% or less of copper and various types and amounts of organic biocides. Previous research has shown that the amount of copper in preservative treatments strongly affects the corrosiveness of the treated wood and that the effect of the organic biocides is small when compared to other differences in preservatives such as pH and copper concentration.[3-5] Two preservatives did not contain copper: zinc naphthenate, which had less than 3% concentration of zinc, and Preservative B, which contained only organic biocides. In addition to these nine preservative treatments, an untreated control group was tested. In this group, the wood-wire assemblies were dipped in a bath of deionized water for 1 minute and sealed in polyethylene bags.

Table 1
Preservatives and Concentrations Evaluated

Preservative	Nominal % Actives in Concentrate	Concentrations evaluated	Dip times (minutes)
A (copper ethanolamine complex containing citric acid)	5.09% Cu	2% as Cu	1
B	5.43% Tebuconazole 5.00% Propiconazole 0.50% Imidicloprid	1.05% total actives	3
C (micronized copper system)	25.5% Cu, 0.50% Tebuconazole 0.52% Propiconazole	2% as Cu	1
D (soluble copper system)	8.78% Cu 0.18% Tebuconazole 0.18% Propiconazole	2% as Cu	1
E	10.08% Cu-8-quinolinolate	1.8% as Cu-8-quin	3
F	5.27% Cu-8- quinolinolate	1.8% as Cu-8-quin	1
G	5% Cu	2% as Cu	1
M (micronized copper system)	33.3% Cu 1.32% Tebuconazole	2% as Cu	1
U (untreated)	Deionized water	-	1
Z (zinc naphthenate)	2.9% Zn	2.9% as Zn	1

† Trade name.

RESULTS

Figure 2 shows the percent weight loss after 2 weeks for each of the 10 preservatives. The wires treated with zinc naphthenate had the lowest amount of corrosion, and thus percent weight loss. Wires exposed to seven of the preservatives exhibited a lower mean percent weight loss than the untreated group, U. The most corrosion was exhibited in wires that had been treated with Preservative C. To determine differences among the groups, the means were compared using a Tukey HSD (honest significant difference) test. There were no significant differences between the zinc naphthenate and Preservative A. The mean percent weight loss from Preservatives G, M, and D, could not be differentiated, but were higher than the group with the zinc naphthenate and Preservative A. Preservative C had the most corrosion, and was statistically different from the next lowest group.

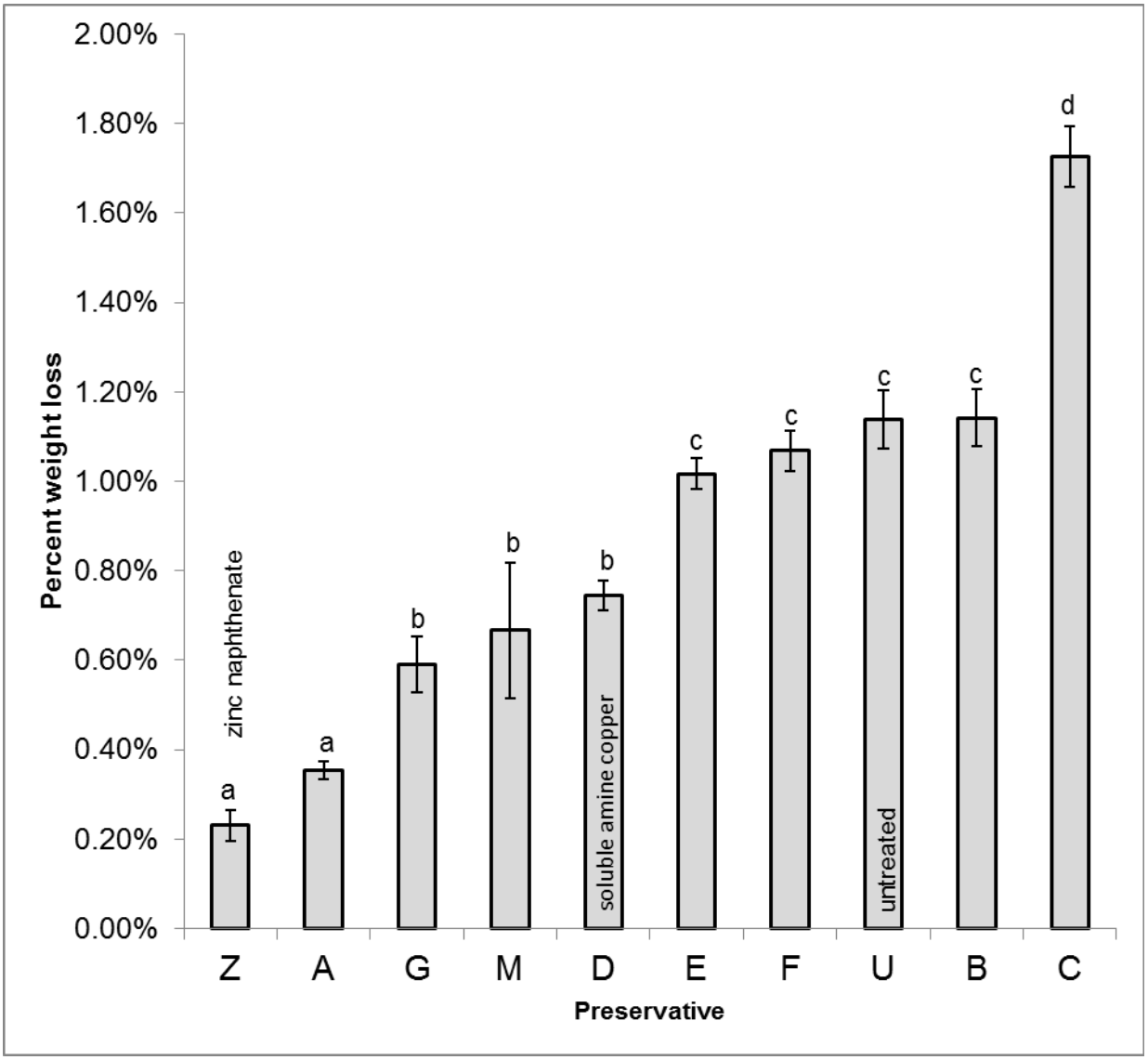

Figure 2: Percent weight loss of the wires after the 2-week exposure. Error bars represent the standard error. The letters above the bars are the results of the Tukey's HSD test; groups with the same letter have means that are not statistically different.

Figure 3 shows the percent weight loss after 8 weeks for each of the 10 preservatives. It appears that this exposure time is more realistic because the relative rankings of preservatives whose corrosiveness has been measured in previous experiments were consistent with the previous testing.[4] For the samples exposed for 8 weeks, treatments A and Z (zinc naphthenate) clearly exhibited the least amount of corrosion, and are at least 5 times less corrosive than the remaining treatments. Of the remaining preservatives, Preservative B is significantly lower than Preservatives F, E, and G, but the difference between Preservative B and the untreated control is not statistically significant. The soluble copper system had the most corrosion, and the difference between the soluble copper system and the next most corrosive system (Preservative M) was statistically significant.

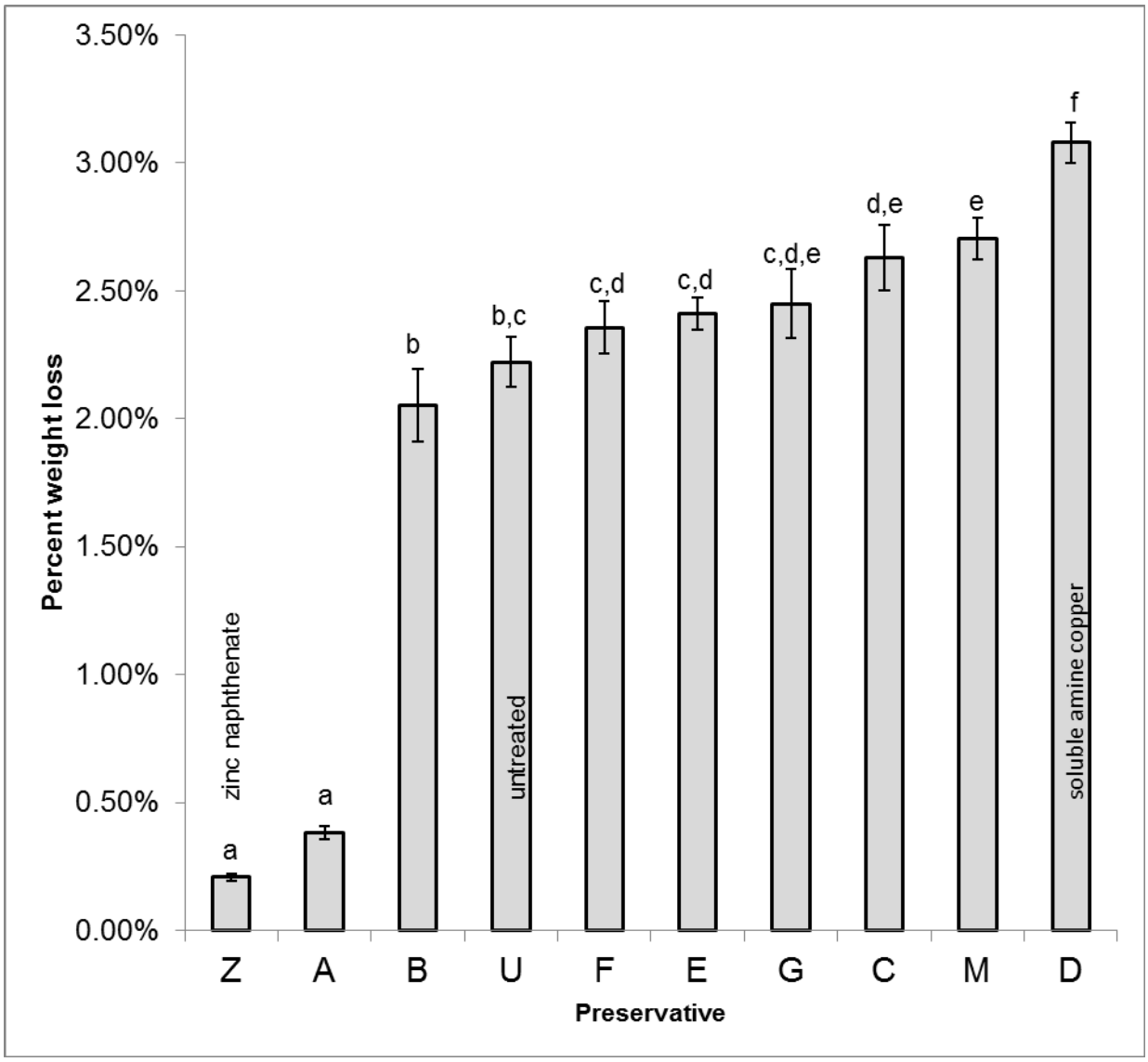

Figure 3: Percent weight loss of the wires after the 8-week exposure. Error bars represent the standard error. The letters above the bars are the results of the Tukey's HSD test; groups with the same letter have means that are not statistically different.

Figure 4 shows the ratio of the percent weight loss after 8 weeks to the percent weight loss after 2 weeks. If the corrosion rate was constant during this time period, we'd expect the ratio

to be four. A ratio less than four indicates the corrosion rate was decreasing after 2 weeks. A ratio of 1 suggests that all of the corrosion happened in the first two weeks. Three preservative systems (M, D, and G) exhibited a ratio of 4, suggesting that the corrosion rate was constant throughout the test. These preservatives would be expected to have even more corrosion in longer exposure times since the rate was not decelerating Two preservative systems, groups Z and A had a ratio of 1, suggesting that the corrosion had stopped after 2 weeks and little, if any further corrosion would be expected.

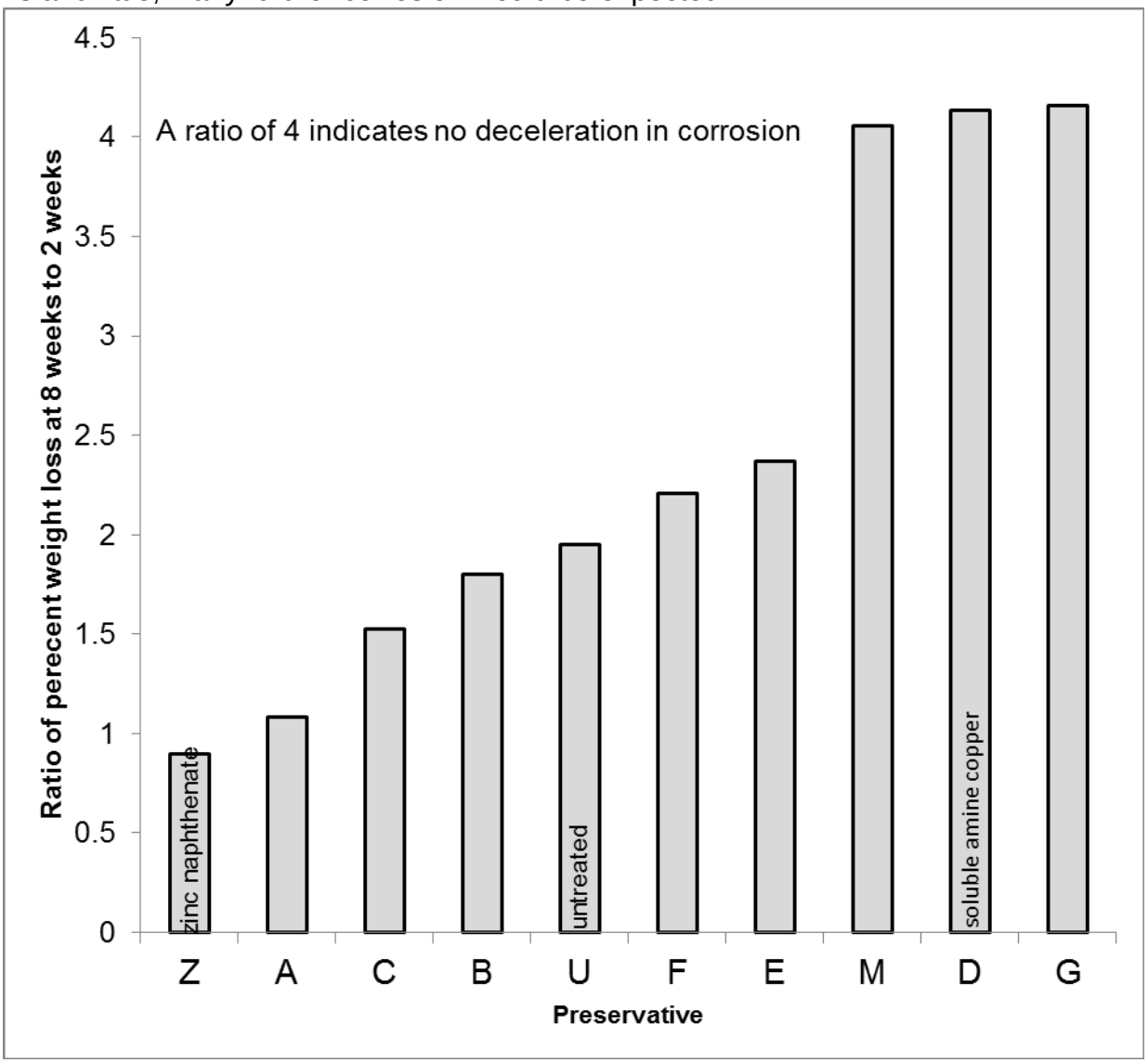

Figure 4: Ratio of percent weight loss after 8 weeks to the percent weight loss after 2 weeks.

Figure 5 shows top view photographs of one wire from each group after the 2 week exposure. The wire that was dipped in the zinc-naphthenate is in the bottom right corner and shows no signs of corrosion. The other wires have white corrosion products consistent with the corrosion of zinc, although the degree of corrosion varies among the wires. The wires from Preservative B, which had no copper in the treatment solution, exhibited some minor splotches of red rust, indicating that the galvanized coating layer had corroded and the underlying steel wire was corroding. In addition to Preservative B, Preservatives C, D, F, and the untreated group (U) had significant amounts of corrosion products visible.

Figure 5. Tops of the wires after a 2-week exposure. Top row (from left to right): A, B, C, D, and E. Bottom row (from left to right): F, G, M, U, and Z.

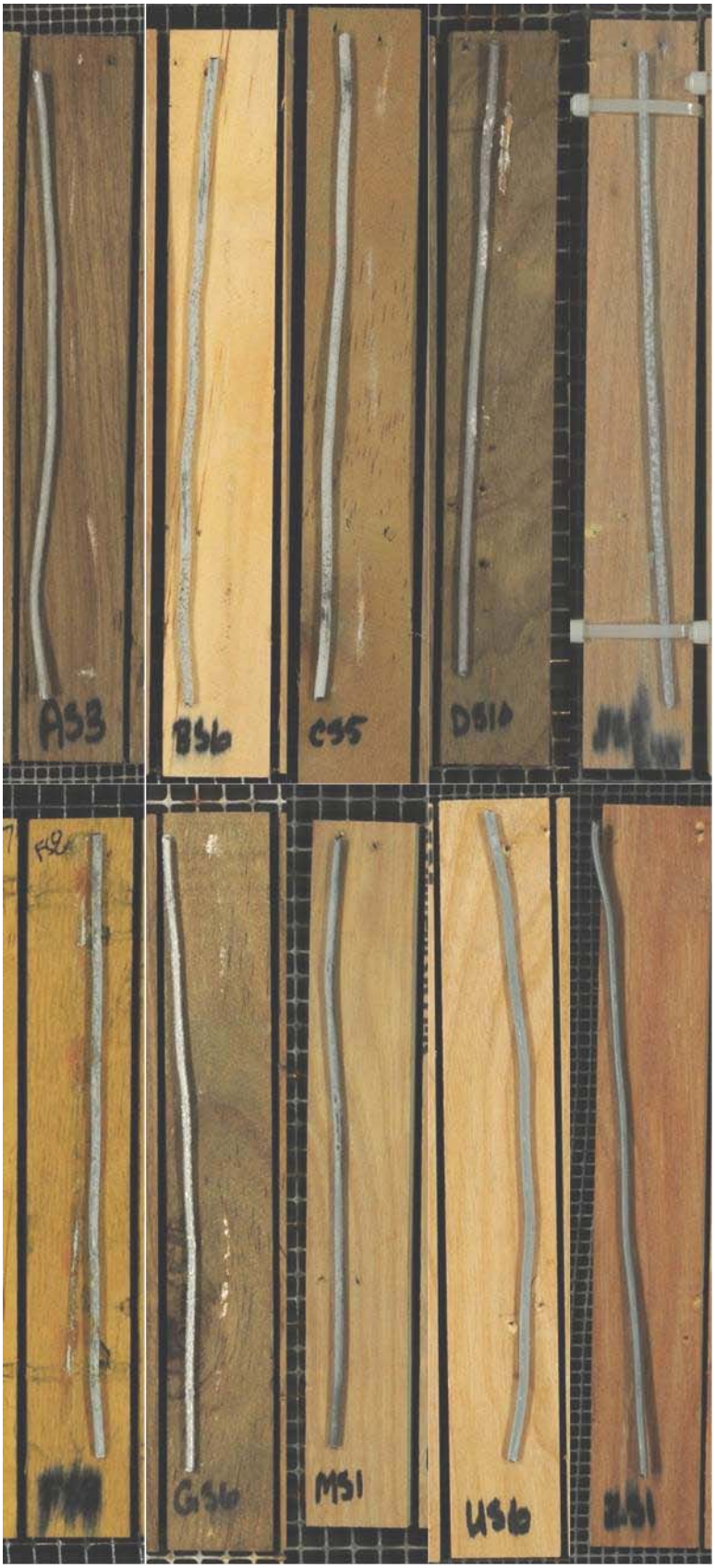

Figure 6: Bottoms of the wires after a 2-week exposure. Top row (from left to right): A, B, C, D, and E. Bottom row (from left to right): F, G, M, U, and Z.

Figure 6 shows the same wires in Figure 5 after they had been turned over to show the side in direct contact with the wood. In some cases, the corrosion products became attached to the wood, and examining the wood that was in contact with the metal gives additional insights into the severity of corrosion. The wire in contact with the wood revealed red rust on wires exposed to Preservative D and F that was not visible from the top view. Half of the treatments (A, C, D, F, and G) resulted in white or red corrosion products deposited on the wood.

Table 2 summarizes the visual inspection of the corrosion products by placing the different treatments into groups according to the amount of corrosion exhibited.

Table 2
Summary of the Visual Inspection after 2 Weeks Exposure

	Preservative
No visible corrosion	Z
White rust, slight	A, E,G,M
White rust, moderate-heavy	B,C,U
White and red rust on surface, heavy deposits on wood	F,D

Figure 7 shows the top view of the wires after 8 weeks of exposure. After 8 weeks of exposure, all but 2 wires (groups A and Z) exhibit red rust. For the remaining groups, the red rust appears as small, red dots on top of a layer of white corrosion products and these red dots are evenly distributed throughout the wire. Because of this distribution of rust, it is difficult to visually rank the different treatments exhibiting red rust based upon the amount of the wire covered with red rust.

Figure 8 shows the same wires in Figure 7 after they have been rotated 180 degrees to show the metal that had been in direct contact with the wood. For six of the eight wires exhibiting red rust, corrosion products were deposited on the wood, and differences between treatments could be observed. The amount of corrosion products deposited on the wood can be used to separate the treatments. These observations are summarized in Table 3, which groups the different treatments according to their corrosiveness.

Table 3
Summary of the Visual Inspection after 8 Weeks Exposure

	Preservative
No visible corrosion	Z
Only white rust visible	A
Red rust on surface, but no deposits on wood	U
Red rust on surface, slight deposits on wood	B,F,G,M
Red rust on surface, heavy deposits on wood	C,D,E

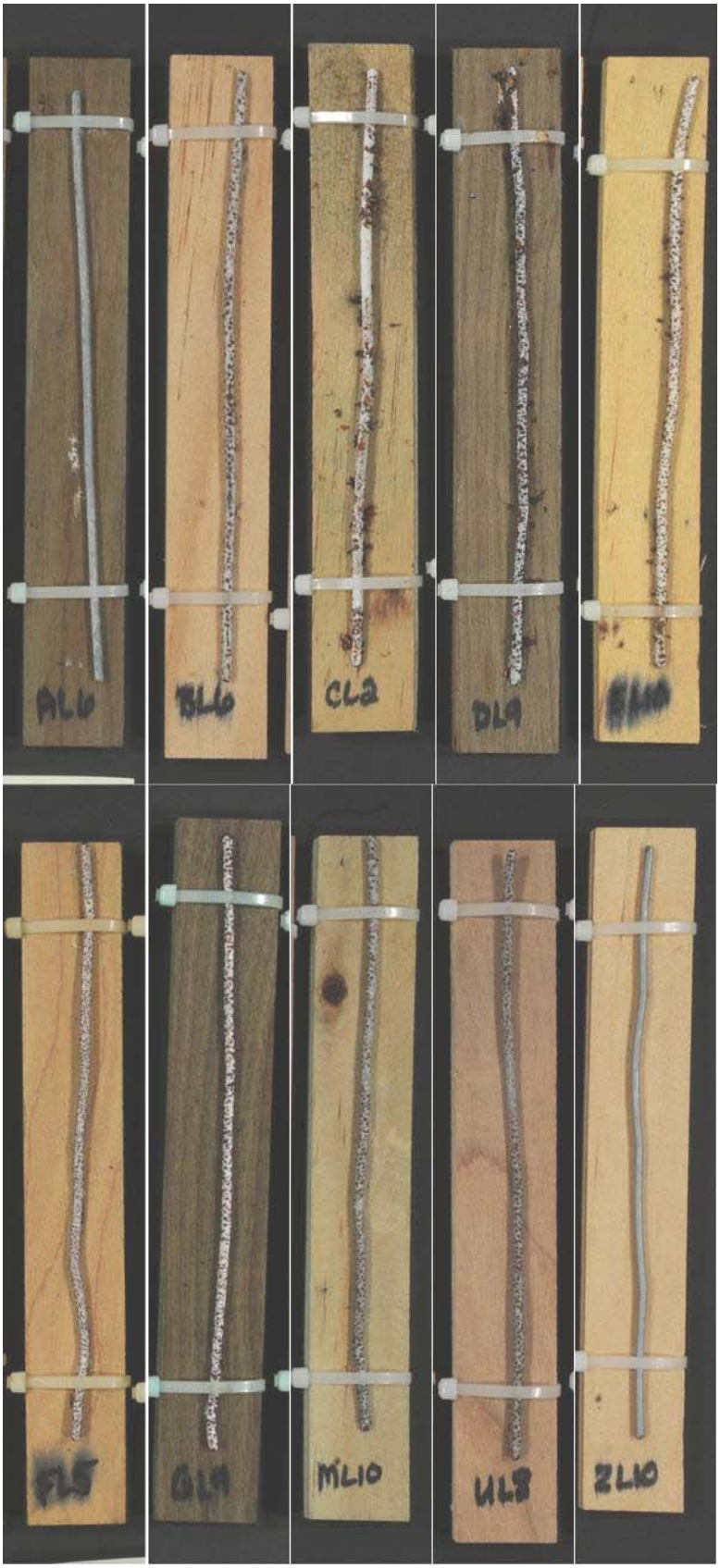

Figure 7: Tops of the wires after an 8-week exposure. Top row (from left to right): A, B, C, D, and E. Bottom row (from left to right): F, G, M, U, and Z.

Figure 8: Bottoms of the wires after a 2-week exposure. Top row (from left to right): A, B, C, D, and E. Bottom row (from left to right): F, G, M, U, and Z.

DISCUSSION

The goal of this work was to examine the corrosiveness of different preservative treatments that could be used to protect wire-bound wooden packaging crates. Wires were attached to strips cut from wire packaging crates, dipped into a preservative solution and stored in a polyethylene bag for either 2 or 8 weeks.

The exposure condition was chosen to be a challenging representation of what may occur in the production of the wire-bound packaging crates. In the production process, the crates are typically stacked on top of each other, dipped and then stored until they are shipped. This process is difficult to replicate in the laboratory, since there are, in actuality, a wide range of potential conditions the boxes could face post-treatment, depending on the ambient environment and how tightly they are stacked. The polyethylene bag method was chosen as it represents a worst case scenario (no airflow) and the goal of the test was to differentiate different wood preservatives. However, this environment may have been over-challenging, since even the untreated controls (dipped in deionized water) exhibited red rust and significant corrosion in the 8 week test. Despite this, the preservative treatments could be grouped into several groups according to their corrosiveness.

In all exposure conditions, the wires exposed to the zinc naphthenate treatment exhibited little, if any, corrosion. Furthermore, they had five times less corrosion than wires that were strapped to wood and dipped in water, suggesting that the zinc naphthenate was acting as a strong corrosion inhibitor. This behavior should not be surprising, since the treatment is made up of soluble zinc ions and the wires are coated with solid zinc. Unlike the preservatives with cupric ions, where it is thermodynamically favorable for the cupric ions to be reduced and the zinc to oxidize, the zinc ions in solution should not cause a displacement reaction. If anything, excess zinc ions in solution may solidify on the wire surface, increasing the thickness of zinc coating. This compatibility between the zinc ions in solution and the galvanized wires is the reason for the low amount of corrosion exhibited by the wires dipped in the zinc naphthenate solution.

Preservative A, a copper ethanolamine complex containing citric acid, exhibited an extremely low amount of corrosion relative to the other groups. Surprisingly, preservative A contained cupric ions yet performed better than the untreated control group where the wires were dipped in water. Since one of the likely corrosion mechanisms involves the reduction of cupric ions, one may expect this preservative to be more corrosive than the untreated group using deionized water. Preservatives A, G, and D all had the same copper concentration in the treatment solution (2%). Beyond cupric ions, Zelinka et al. have shown that preservative treatments can modify the pH of the wood and as the pH is lowered, the more corrosive it is to embedded fasteners.[4] preservative A is alkaline (pH =10.2) and this may be one reason why it is less corrosive. However, Preservative G and Preservative D also have a pH above 9 and still exhibited more than 5 times the corrosion as Preservative A. The active biocides in Preservative A were similar to the other preservatives tested, and it is unclear why this preservative exhibited such a low amount of corrosion. In short, from the chemical aspects that were analyzed, it is unclear why Preservative A has such a low corrosion rate. It is possible that this preservative contains a proprietary corrosion inhibitor or some other additive that has resulted in the low observed corrosion rates.

The differences in corrosion among the remaining 8 treatments were small, and each of these 8 treatments had a much higher corrosion rate than either zinc naphthenate or Preservative A. Preservative B had a small, but statistically significant lower amount of corrosion from the remaining preservatives. However, it was still much more corrosive than zinc naphthenate or Preservative A. The soluble copper azole solution (Group D) had the greatest amount of corrosion, which was expected, as soluble copper systems have been shown to be corrosive in previous testing of embedded fasteners.[2-5]

In addition to ranking the amount of corrosion after the 8 week test, the ratio of the corrosion rate between the 2 and 8 week test can be used to identify preservatives whose corrosion rate is not decreasing with time. The ratio of the percent weight loss between the 8 week and 2 week test was equal to the ratio of exposure time (4) for Preservatives M, D, and G. This ratio indicates that the corrosion rate did not change during the exposure time, and suggests that the amount of corrosion would continue to increase at the same rate for longer exposures. Because the corrosion rate is not slowing down with time, these preservatives may have a higher likelihood of causing corrosion problems if the crates are exposed to prolonged moisture.

The results of these tests can be used to compare the relative amounts of corrosion that would be expected to occur in the production of the boxes. There have been no efforts to understand the corrosion performance of the wires after they have been deployed in the field. The test represents a rather extreme condition (no airflow after treatment). The amount of corrosion that the packaging materials exhibit depends not only on the preservative treatment, but is a strong function of the wood moisture content, and manufacturing processes that allow the packaging materials to dry more quickly after treatment that may help prevent corrosion problems.[6]

CONCLUSIONS

Nine different preservative treatments and an untreated control were evaluated for their corrosiveness towards wire-bound packaging crates. Wires were attached to strips of wood, dipped in the preservative treatment, and then stored in a polyethylene bag for either 2 or 8 weeks to simulate the time between treatment and shipment. After 8 weeks, 7 of the 9 preservatives and the untreated control caused red-rust to form on the galvanized wires.

The only two wires that did not exhibit red rust were the zinc-naphthenate treatment, which was previously the most commonly used preservative, and Preservative A, a copper ethanolamine complex containing citric acid. The active biocides in Preservative A were similar to other preservatives tested, and it is unclear why this preservative exhibited such a low amount of corrosion.

The percent weight loss of three of the preservatives (M, D, and G) increased linearly with time, indicating the corrosion rate was constant through the 8-week test. These preservatives have a high likelihood of having corrosion problems since the corrosion rate is not decelerating with time, and would experience even greater amounts of corrosion in longer exposures.

The goal of this research was to find alternatives to zinc naphthenate that do not pose a corrosion concern to metal fasteners. The testing clearly indicates that Preservative A is the best alternative. The remaining preservatives all exhibited red-rust in the 8 week test and more than 5 times the corrosion that was observed in the zinc naphthenate solution.

ACKNOWLEDGEMENTS

This work was performed by US Government researchers on official time and is therefore in the public domain and not subject to copyright. The authors acknowledge funding from the US Army Armament Research Development and Engineering Center.

REFERENCES

1. R.C. De Groot, M. Stroukoff, “Efficacy of Alternative Preservativs used in Dip Treatments for Wood Boxes.” FPL-RP-481, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory., Madison, WI, 1986.

2. S.L. Zelinka, D.R. Rammer, “Corrosion Rates of Fasteners in Treated Wood Exposed to 100% Relative Humidity,” ASCE Journal of Materials in Civil Engineering, 21 (2009) 758-763.

3. S.L. Zelinka, Chapter 23. Corrosion of Metals in Wood Products, in: M. Aliofkhazraei (Ed.) Developments in Corrosion Protection, InTech, Rijeka, 2014, pp. 568-592.

4. S.L. Zelinka, D.S. Stone, “Corrosion of metals in wood: Comparing the Results of a Rapid Test Method with Long-term Exposure Tests Across Six Wood Treatments,” Corrosion Science, 53 (2011) 1708-1714.

5. G. Kear, H.-Z. Wu, M.S. Jones, “Weight Loss Studies of Fastener Materials Corrosion in Contact with Timbers Treated with Copper Azole and Alkaline Copper Quaternary Compounds,” Corrosion Science, 51 (2009) 252-262.

6. S.L. Zelinka, D. Derome, S.V. Glass, “The Effect of Moisture Content on the Corrosion of Fasteners Embedded in Wood Subjected to Alkaline Copper Quaternary Treatment,” Corrosion Science, 83 (2014) 67-74.