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Peroxide Post-Treatment of Wood Impregnated with Micronized Basic Copper Carbonate

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Abstract: Wood is vulnerable to significant color changes when used in exterior applications. Some copper-based wood preservatives use colorants to minimize this color change. This paper examines the ability of a peroxide post-treatment to turn wood impregnated with micronized basic copper carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) (MBCC) a stable brown color. MBCC-treated wood, with and without peroxide post-treatment, along with associated controls were evaluated for color change, erosion and black-stain fungal resistance after exposure to artificial photo-degradation. The impact of the peroxide treatment on copper leaching was assessed in a laboratory experiment, and the impact on copper reactivity was assessed by electron parametric resonance (EPR) spectroscopy. Peroxide post-treatment of wood pressure impregnated with MBCC was shown to reduce color change by more than 50% compared to controls. Erosion due to photo-degradation and colonization by black-stain fungi were lower in samples treated with MBCC than in untreated controls and were relatively unaffected by peroxide post-treatment. The peroxide post-treatment was associated with increased amounts of mobile copper. This led to increased susceptibility to leaching and to a more than 60% increase in the amount of copper than had reacted with the wood.

Keywords: leaching; micronized basic copper carbonate; peroxide; surface protection; weathering; wood

1. Introduction

The service life of wood products in exterior applications is often limited by loss of appearance rather than loss of structural integrity [1]. As a result, there is a need for wood protection treatments to protect the appearance of the wood as well as against biodegradation by decay and insects. Weathering is a complex series of interactions between moisture, UV and visible light, oxygen, and surface-colonizing fungi [2]. Changes in color arise largely from the photo-degradation of lignin and the colonization by surface-inhabiting black-stain fungi [3].

A wide range of inorganic UV absorbers can be used to improve color stability [4]. This includes copper, which is already present in many residential preservative formulations. Copper-based wood preservatives are known to photo-stabilize lignin and slow the rate of surface degradation and color change from weathering [5–8]. One of the most widely used residential wood protection treatments in North America is micronized copper azole (MCA), which includes micronized basic copper carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) (MBCC) as the primary biocide. Treatment with MBCC gives wood a pale blue/green color. Commercial products often add a colorant to give the MBCC-treated wood a more natural-looking brown color [9]. For exterior preserved wood, iron oxides dominate the market due to their low cost, the wide range of colors that are possible, their photo-protective effects, their compatibility with

preservative formulations and their positive health and environmental profiles [10]. However, the color still fades over time.

It was observed that, in service, wood treated with copper-based preservatives tends to go from green/blue to a brown color as the surface of the wood oxidizes [11]. The use of peroxide to generate stable color complexes in wood impregnated with transitional metal compounds has been reported by Auger [12]. In the present work, we explored this approach using wood impregnated with MBCC followed by a peroxide post-treatment. The aim was to understand the efficacy of this approach in yielding a brown, photo-stable wood surface with the potential to eliminate or reduce the need for the addition of colorants.

MBCC-treated wood with a peroxide post-treatment could potentially also affect preservative efficacy. MBCC has proven to be an effective wood preservative due to the slow solubilization of MBCC and reaction of this solubilized copper with the wood cell wall [13–15]. Oxidation of the wood surface was hypothesized to increase the amount of reacted copper, which could potentially increase biological efficacy.

2. Materials and Methods

These experiments assess the performance of wood pressure-treated with MBCC, with and without a peroxide post-treatment. Specimens were evaluated for their resistance to color change and erosion following accelerated photo-degradation, and their resistance to disfigurement by artificially inoculated and incubated black-stain fungi under optimal conditions. An additional experiment examined the impact of the peroxide post-treatment on copper leaching and on the formation of reacted copper in the wood.

Red pine (*Pinus resinosa*) sapwood was used as a wood substrate throughout these experiments. MBCC was obtained from Timber Specialties Co. (Campbellville, ON, Canada). An iron oxide-based colorant formulation was used as a reference in the accelerated photo-degradation experiment. The MBCC and the iron oxide-based colorant were applied to wood by vacuum-pressure impregnation to target gauge concentrations of 4.0 kg of MBCC per cubic meter of wood and 2.0 kg of iron oxide-based colorant per cubic meter of wood, respectively.

The peroxide post-treatment consisted of a one-minute dip in a 20% solution of aqueous hydrogen peroxide adjusted to pH 6 with a dilute solution of sodium hydroxide at room temperature on air-dried samples. The 20% solution was prepared from a 30% hydrogen peroxide concentrate (Fisher Scientific, Ottawa, ON, Canada, ACS Reagent Grade). The conditions described above were determined based on a series of tests to optimize the peroxide treatment conditions. These tests are described in Appendix A. Factors evaluated included peroxide concentration, pH, storage time, drying and the impact of wood type (heartwood vs. sapwood).

2.1. Accelerated Photo-Degradation

Assessment of resistance to accelerated photo-degradation included four treatments groups each with six replicates. These included the MBCC treatment, with and without peroxide post-treatment, the iron oxide-based colorant as a reference product, and untreated red pine sapwood as a control. Specimen size was 75 mm long \times 75 mm tangential \times 12 mm radial wood fiber direction.

The sample color was evaluated with a SP60 spectrophotometer (X-Rite, Grand Rapids, MI, USA) using CIE $L^*a^*b^*$ color space. L^* represents lightness on a scale from 0 to 100. Negative a^* values indicate degree of greenness, while positive values indicate degree of redness. Negative b^* values indicate degree of blueness, while positive values indicate degree of yellowness. CIE $L^*a^*b^*$ data were used to calculate ΔL^* (change in lightness), Δa^* (change in green-red color), Δb^* (change in blue-yellow color), and ΔE^* which represents the total color change according to Equation (1).

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (1)$$

A small amount of vinyl polysiloxane (Aquasil Ultra Smart Wetting[®], Dentsply Caulk, Montreal, QC, Canada), approximately 10 mm × 20 mm, was stuck to three samples from each treatment group. This was used to provide an unexposed reference patch from which to measure erosion following Q Sun exposure. After Q-Sun exposure, the silicone was removed from the surface. A 3D profilometer, Contour GT-K1, (Veeco Instruments, Plainview, NY, USA) was used to measure the erosion of the exposed area compared to the unexposed sections. A total of six measurements were taken per sample (three samples/series of treatment) for a total of eighteen replicates per series of treatment.

Samples were placed in a Q-Sun chamber (Q-Lab Corporation, Westlake, OH, USA) for accelerated photo-degradation. The samples were exposed using the ASTM G-155 cycle 1 method [16]. This cycle includes 102 min of exposure to light at 0.35 W/m² irradiance at 340 nm and 63 °C for black panels. The chamber air was maintained at 43 °C and 30% relative humidity. This was followed by 18 min of exposure to water and light at 0.35 W/m² irradiance at 340 nm and 63 °C for black panel. Color measurements were repeated after 1000 h of exposure.

2.2. Black-Stain Fungal Resistance

After inspection at 1000 h of exposure, samples from the accelerated photo-degradation experiment were exposed to an additional 500 h of exposure in the Q-Sun. These samples (exposed for a total of 1500 h in the Q-Sun chamber) were cut into four 35 mm × 35 mm × 12 mm subsamples. In addition, red pine sapwood that had not been exposed in the Q-Sun was included as control, and red pine sapwood pressure impregnated with a solution of 1% propiconazole, and 0.5% 3-iodo-2-propynyl butyl carbamate (IPBC) was included as an additional reference known to control black-stain fungi [17]. Twenty-four replicates (6 replicates of each treatment × 4 subsamples) were produced for each treatment. Group A included two isolates with typical *Aureobasidium pullulans* morphology that were isolated from coated wood in Vancouver, BC, Canada. Group B included two isolates with darker and more yeast-like colony morphology that were slower growing on nutrient plates than group A and were isolated from coated wood in eastern Canada. Group C, isolated from both western and eastern Canada, included a mix of ten isolates of various colony types collected from coated wood affected by black stain after only 2 years of in service exposure. Group D was sprayed with distilled water and used as an uninoculated reference. All subsamples were edge sealed with a marine epoxy (Intergard 740, International Marine Coatings, Singapore) and sterilized by ion beam irradiation with two passes at 17 kGy (Iotron Industries, Port Coquitlam, BC, Canada). Prior to inoculation, the samples were aseptically placed in test chambers with 2 mL of sterile distilled water and left to incubate at 22.5 °C for 48 h to ensure a moist surface for inoculation. Test chambers are described in [17].

To prepare a spore suspension for inoculum groups A and B, a solution of distilled water with Tween[®] 20 (Sigma-Aldrich, Oakville, ON, Canada), a polysorbate-based non-ionic surfactant, was used to gently remove spores from the surface of two actively growing plates by gently shaving the sporulating mycelium using a sterile scalpel of each chosen isolate and making up to a final volume of 200 mL. For inoculum C, the solution of sterile water with Tween[®] 20 was again used to remove spores from the surface of one actively growing plate of each of the ten chosen isolates and the final volume made to 400 mL. The solutions were blended with three short pulses in a Waring commercial blender. The inoculum was then filtered through a prewashed sterile glass wool-lined glass funnel to remove large particles that could plug the air brush. Haemocytometer average counts of spore suspensions for inoculum A, B and C were 1.1×10^6 , 0.54×10^6 and 2.2×10^6 spores per millilitre of the 200 and 400 mL spore suspensions, respectively. The inoculum was applied using an IWATA Eclipse (Anest Iwata-Medea, Inc., Portland, OR, USA) HP-BCS airbrush, 5 mL of inoculum was used to evenly coat twelve test pieces at a time. Inoculum sprayed on control plates (1% malt extract agar) developed a healthy growth of black-stain fungi for each inoculum group after a few days of incubation, while plates sprayed with just water inoculum had no growth. Test samples were incubated at 22.5 °C in the dark for six weeks. A weekly in situ spritzing with sterile distilled water was applied by a gentle spray over the sample surface to maintain a suitable moisture content.

Samples were inspected after two, four and six weeks of incubation based on the visual inspection scale described in [18]. However, it was noticed that some fungi altered the color of the surface but had no visible growing mycelia or sporing structures on the surface. For such samples, the discoloration observed on the surface was compared to uninoculated control samples, and a rating was given based on the amount of discoloration present and not only on visible fungal growth on the surface. Ratings of 0 indicated no stain, while ratings of 5 indicated intense and widespread staining of the sample.

2.3. Copper Leaching

Further studies were conducted to assess the impact of the peroxide treatment on the leachability of copper from the treated wood. Thirty samples of red pine (*Pinus resinosa*) sapwood were cut to the dimensions of 50 mm long \times 15 mm radial \times 25 mm tangential wood fiber direction and were conditioned to constant mass at 20 °C and 65% relative humidity (RH). Twenty samples were pressure treated with an aqueous suspension of MBCC to an average gauge retention of 3.2 kg of MBCC per cubic meter of wood. Specimens were reconditioned to constant weight at 20 °C and 65% RH following treatment. Ten specimens were dip treated in a 20% solution of hydrogen peroxide (pH 6) and ten were dip treated in water for five minutes. The wood specimens were then reconditioned to constant weight and evaluated for copper leaching using the immersion cycle specified in section 7.3 of the OECD Guidance document [19]. The mass of the samples was recorded, and the samples were completely immersed in water for 120 min, removed from the water and allowed to drain for 10 s, allowing run-off to return to the water. The leachate samples were collected and stored in the freezer. The test specimens were weighed again and then left to dry at laboratory temperature until the next immersion day. Immersion occurred on days: 1, 3, 7, 9, 11, 14, 16 and 22. Leachate samples were then sent to Maxxam Analytics (Burnaby, BC, Canada) for copper analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). After all immersion cycles had been completed the samples were left to dry at laboratory temperature. Once dry the leached samples were milled to pass through a 40-mesh screen and pressed into pellets. The pellets were measured for total copper using an ARL™ QUANT'X EDXRF Spectrometer (ThermoFisher Scientific, Waltham, MA, USA) [20].

2.4. Copper Characterization

To assess the impact of the peroxide treatment on the form of copper present in the treated wood, six red pine sapwood specimens (25 mm \times 50 mm \times 15 mm) were pressure impregnated with MBCC. Three of these specimens were then dip treated in a 20% aqueous solution of hydrogen peroxide. All specimens were then milled to pass through a 40-mesh screen. The resulting sawdust was analyzed by x-ray fluorescence spectroscopy for total copper. The remaining sawdust from each specimen was analyzed by Electron Paramagnetic Resonance (EPR) spectroscopy at the University of British Columbia (Vancouver, BC, Canada) using the methods developed by Xue et al. [21]. A Bruker Eleksis E500 series continuous wave EPR (Bruker BioSpin GmbH, Rheinstetten, Germany) was used for the analysis. The operating parameters were 77 K, at a frequency 940 GHz (X-band), 100 KHz field modulation and 1 G modulation amplitude. Frequency calibration was independently verified using 2,2-diphenyl-1-picrylhydrazyl. The spectral simulation was achieved using SIMFONIA (Bruker Biospin GmbH, Rheinstetten, Germany). Integration was OriginPro8 (Origin Lab). Baseline correction was applied before calculating the area under the curve. The sample tube was packed with wood sawdust to a height greater than 100 mm so that it exceeded the cavity height, thereby minimizing variation caused by the sample content.

3. Results

3.1. Accelerated Photo-Degradation

Average color change after 1000 h of Q-Sun exposure was calculated for each treatment group (Figure 1). The MBCC-treated wood became darker and less green. The peroxide post-treatment

greatly reduced these color changes, as the wood was already darker and less green prior to Q-Sun exposure. The iron oxide-based reference treatment became less red and less yellow after Q-Sun exposure. The untreated control became darker and much less yellow. The total color change (ΔE^*) was similar between the peroxide post-treatment and the iron oxide-based colorant reference, and less than the MBCC without the peroxide post-treatment and the untreated control.

Erosion measurements were quite variable but did show a significant reduction in erosion for all samples treated with copper compounds and the proprietary iron oxide colorant (Figure 2). This is consistent with the ability of copper to photo-stabilize wood [5–7,22]. Erosion was similar in MBCC-treated samples with and without peroxide post-treatment.

Figure 3 shows the samples before and after 1000 h of Q-Sun exposure. The discolored spot on three of the samples from each group is from the blue tack that was used to create a reference spot for erosion measurement. MBCC-treated wood changed from a pale green to a medium brown color. This is consistent with field observations of such material [23]. The peroxide treatment resulted in an initial brown-green color that changed to the same medium brown color as the MBCC treatment.

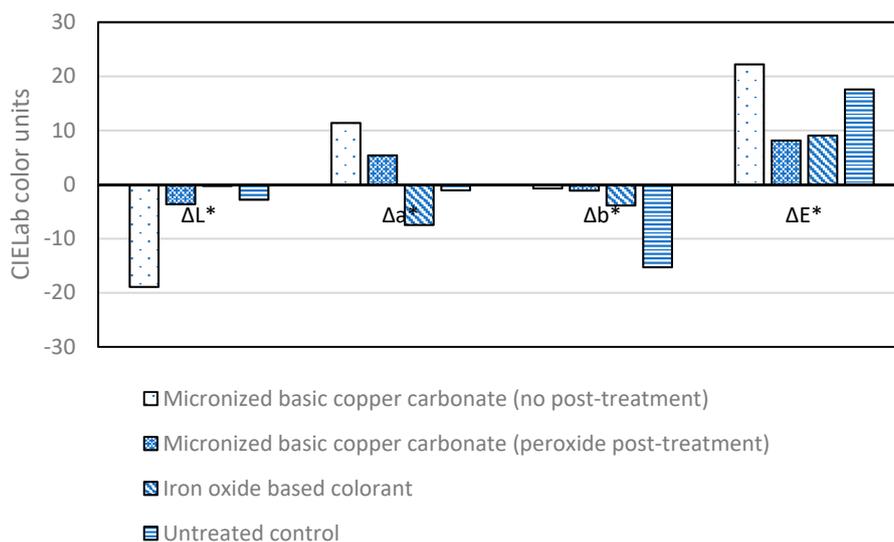


Figure 1. Color change after 1000 h of Q-Sun exposure.

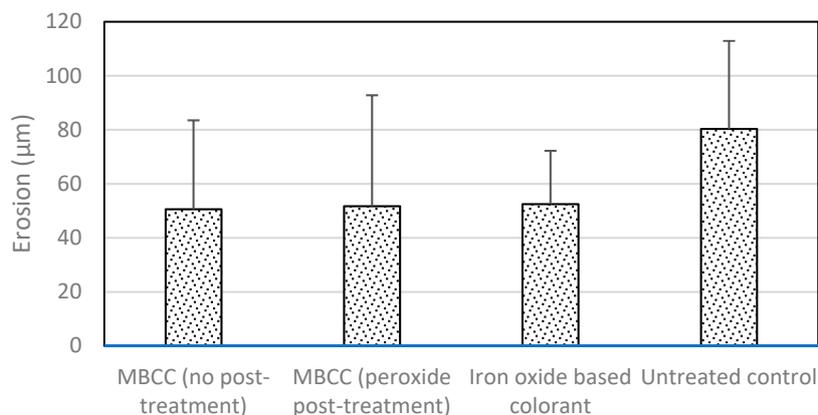


Figure 2. Average and standard deviation of surface erosion after 1000 h of Q-Sun exposure of samples treated with micronized basic copper carbonate (MBCC) with and without peroxide post-treatment, an iron oxide-based colorant, and an untreated control.

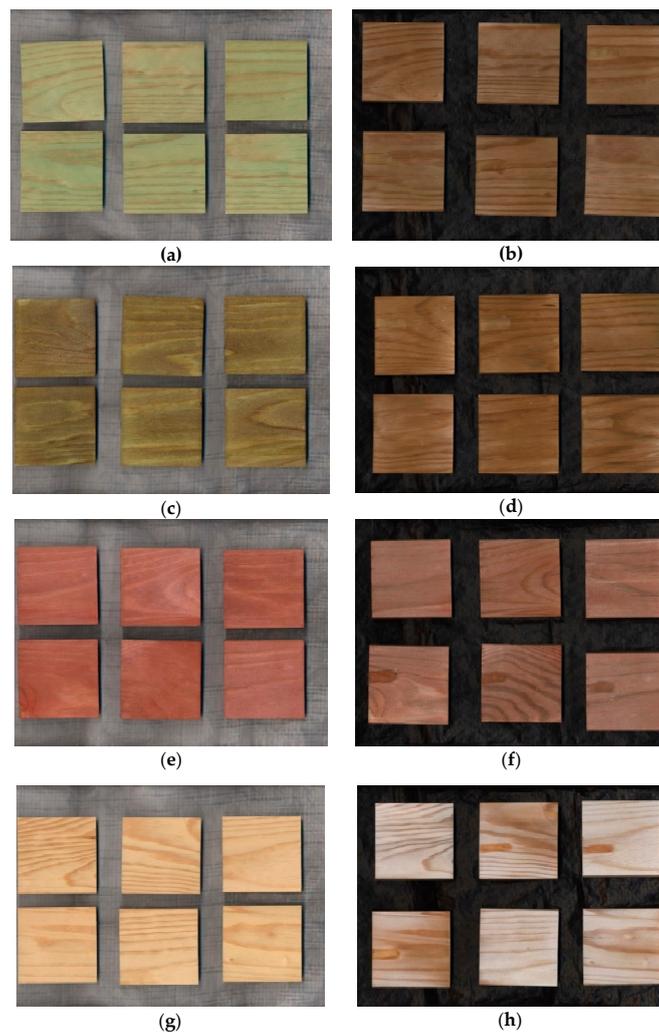


Figure 3. Red pine sapwood before and after 1000 h of accelerated photo-degradation: (a) treated with micronized basic copper carbonate, (b) treated with micronized basic copper carbonate after 1000 h of accelerated photo-degradation, (c) treated with micronized basic copper carbonate with a peroxide post-treatment, (d) treated with micronized basic copper carbonate with a peroxide post-treatment after 1000 h of accelerated photo-degradation, (e) treated with an iron oxide-based colorant, (f) treated with an iron oxide-based colorant after 1000 h of accelerated photo-degradation, (g) untreated, and (h) untreated after 1000 h of accelerated photo-degradation.

3.2. Black-Stain Fungal Resistance

Black-stain fungi aggressively attacked most samples and quickly grew, causing darkening or masking of the original wood color (Figure 4). Note that the white material on some surfaces is epoxy resin from the edge seal. No color changes were observed on the uninoculated controls (Group D). A rating of 5 was assigned to the majority of samples of unweathered and weathered inoculated pine controls after only two weeks of incubation (Figure 5). The unweathered IPBC/propiconazole reference performed well and prevented any fungal growth with an average rating of 0 throughout the test for all inoculum types. The MBCC treatment was associated with lower black-stain ratings than untreated controls. Average stain ratings were near zero for inoculum group A. However, growth of the strains in inoculum groups B and C was evident on the MBCC-treated wood, with or without peroxide post-treatment. The peroxide post-treatment was associated with lower black-stain ratings than MBCC with no post-treatment for inoculum group B, but was similar for group C. MBCC is used to protect wood from fungal decay. This does not include staining fungi, though these data suggest a possible beneficial effect.

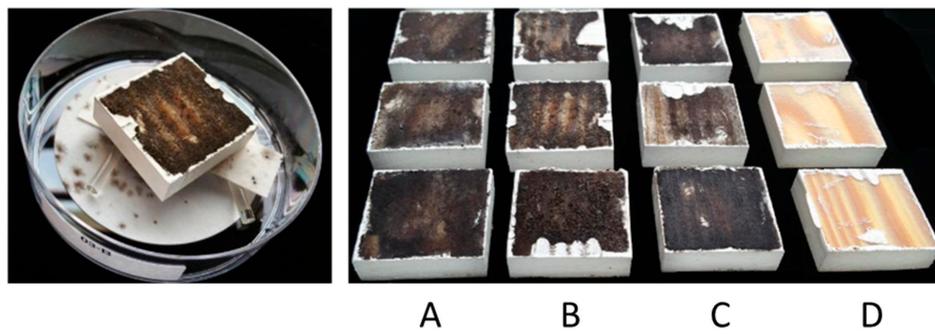


Figure 4. Test assembly showing unweathered red pine sapwood covered with black-stain fungi after two weeks of incubation (left); unweathered red pine sapwood samples after six weeks of incubation with inoculum groups A, B, C and D (uninoculated) (right).

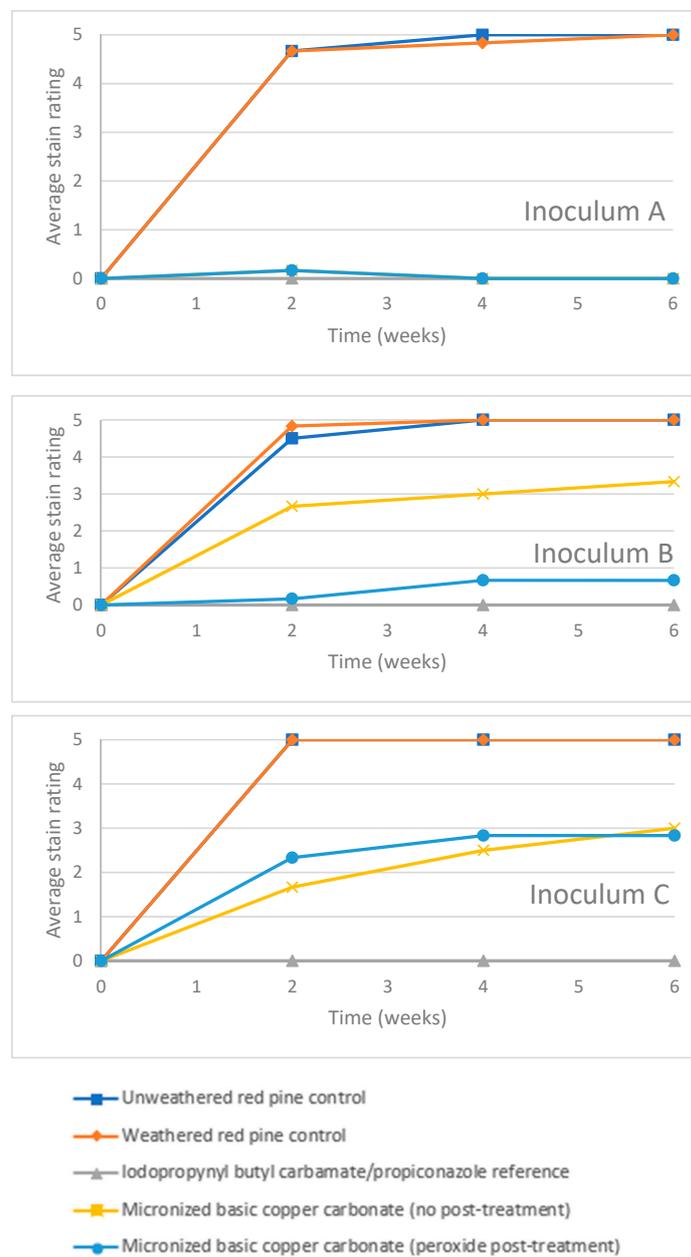


Figure 5. Average stain ratings over a six-week incubation for specimens exposed to strains of *Aureobasidium pullulans* from inoculum groups (A–C).

3.3. Copper Leaching

Copper leaching from the wood treated with MBCC was very low and similar to the untreated control (Figure 6). This is consistent with previous work demonstrating the low leachability of copper from wood impregnated with MBCC [24]. In contrast, copper leaching was much greater in the samples post-treated with peroxide, though this tapered off substantially after 22 days. During the leaching experiment, it was observed that water uptake during immersion was much greater in the peroxide post-treatment group (average 6.4 g) than in the no post-treatment group (average 3.4 g). This increase in water uptake may explain the greater degree of leaching observed.

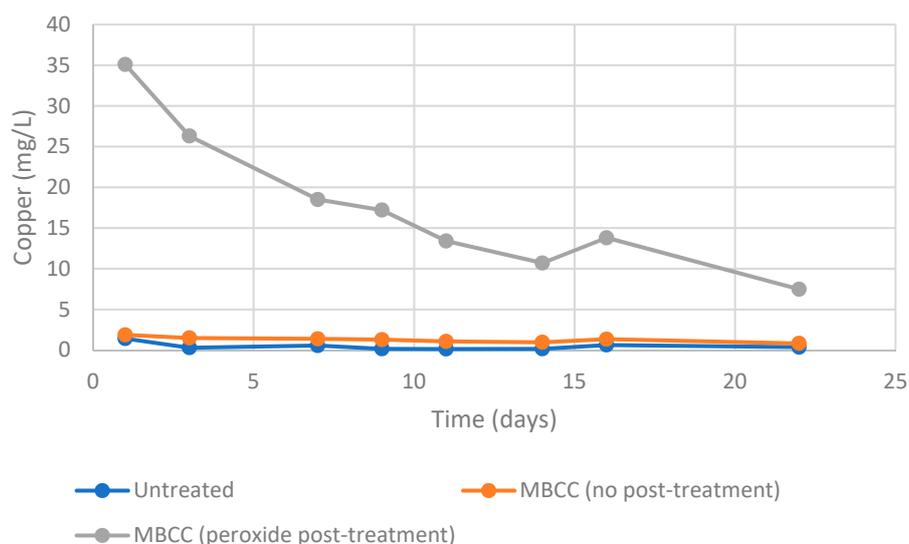


Figure 6. Concentration of copper in leachates from wood impregnated with micronized basic copper carbonate, with and without peroxide post-treatment.

3.4. Copper Characterization

The total copper content in the MBCC-treated wood measured by X-ray fluorescence is shown in Table 1. Total copper concentration averaged 5.6 mg/g in material with no post-treatment and 5.0 mg/g in material with the peroxide post-treatment. Reacted copper concentration averaged 2.62 mg/g in material with no post-treatment and 4.24 mg/g in material with the peroxide post-treatment. These data demonstrate an association between the peroxide post-treatment and increased levels of reacted copper. The reacted copper content in the wood treated with micronized copper carbonate is typical of values previously reported [21,25]. The peroxide treatment may generate more reactive sites in the wood, leading to enhanced reaction between the wood and the micronized basic copper carbonate. The peroxide reaction with lignin is known to oxidize ketonic carbonyl groups [26].

The EPR spectral parameters provide information on the electronic structure of paramagnetic copper complexes in wood. There was very little variation between material with and without peroxide post-treatment, indicating that the compounds being created during the post-treatment have very similar configuration and bonding as the reacted copper (Table 2). The A_z parameter is consistent with a copper–oxygen bonding typical of the copper carboxylate bonding formed in wood [21].

Table 1. Average total copper measured by X-ray fluorescence and reacted copper measured by EPR in MBCC-treated wood, with and without a peroxide post-treatment.

Treatment	Total Copper (mg/g)	Reacted Copper (mg/g)
No post-treatment	5.57	2.62
Peroxide post-treatment	5.04	4.24

Table 2. Average EPR spectral data from MBCC-treated wood, with and without a peroxide post-treatment.

Treatment	g_x	g_y	g_z	A_x	A_y	A_z
No post-treatment	2.078	2.084	2.373	5	45	131
Peroxide post-treatment	2.076	2.084	2.375	5	46	133

4. Discussion

The color change and erosion data confirm the value of copper in wood protection for its ability to partially photo-stabilize wood as has been previously been reported [5–8]. The improved resistance to black-stain fungal colonization of the MBCC-treated samples is consistent with previous work showing that copper can inhibit these organisms. Plasma-deposited copper has been found to inhibit the growth of *A. pullulans* [27]. However, some copper tolerance has also been observed with these fungi [28]. This may indicate why only some growth was observed. The copper tolerance of the fungal strains used has not been otherwise assessed. The natural looking mid-brown color produced by the peroxide post-treatment of MBCC impregnated wood suggests that an attractive and fade resistant brown color at point of sale could be achieved. This could potentially reduce or eliminate the need for the addition of colorants, which are widely used in wood treated with MBCC-containing preservatives [9,10].

The performance against different black-stain inocula varied considerably, though the performance trends were similar. This highlights the importance of carefully choosing test isolates and in evaluating field-collected, fresh isolates, not mutilated through long storage and inclusion of more than one strain to better understand performance. The optimized growth conditions of this accelerated set up led to very rapid attack that would not be observed in field studies. Field studies on the growth of black-stain fungi on MBCC-treated wood would be useful to better understand the effect of the MBCC treatment. Co-biocides, such as the propiconazole used in micronized copper azole type C, would likely also contribute to efficacy in the field.

This study did not examine the use of peroxide dip treatment before pressure treatment with MBCC. Given the increased water uptakes observed in the leaching experiment, peroxide pre-treatment could potentially improve preservative solution uptake. This could make it easier for treaters to meet preservative penetration and retention requirements and lead to better treated products and/or more rapid treatment schedules. A more detailed assessment of the interaction between peroxide and copper carbonate should be conducted to optimize the treatment so that it maximizes reacted copper and minimizes leaching while still producing the desired brown color.

Peroxide is a common ingredient in deck cleaning products. These data suggest that treatments may result in increased copper mobility and increased levels of reacted copper. Bleach-based deck cleaners have been associated with increased copper leaching from CCA-treated decking [29]. The authors of that study note that amount of copper leached would not be a concern in a residential context. It is unclear to what extent a peroxide-based deck cleaner would mobilize copper from wood treated with a MBCC-containing preservative.

The potential impact of increased copper leaching and reactivity on long-term durability should be investigated. The increased water uptake and copper leaching observed in this study suggest a potential loss of durability. However, the increased amount of reacted copper suggests a potential improvement in durability. Previous work has found that copper from MBCC-treated wood is resistant to leaching and that the leached wood retained its resistance to decay fungi [30].

EPR has been used previously to study the reaction chemistry of copper-based wood preservatives in wood [15,31]. While several analytical tools are useful for quantifying copper in organic matrices, most techniques cannot provide information on the copper species present or the bonding of the copper to the wood components. One technique that can identify copper–ligand bonding is EPR. However, it too is limited to copper species that are paramagnetic. While this is usually not a problem it could be limiting, in that it cannot detect species for example that are antiferromagnetic or Cu(I) species. Studies by Piesach and Blumberg [32] have shown that the unpaired electron chemical shift in mononuclear

$S = 1/2$ Cu(II) species and hyperfine coupling to the $I = 3/2$ copper nucleus along axial direction (the g_z and A_z respectively) are most sensitive to electronic and geometric perturbations in the bonding to the copper ion. All the spectra obtained in this study were very similar. They all exhibited strong g_z values of ≈ 2.373 , and A_z tensors of ≈ 131 G which are typical of copper-wood complexes formed with only copper-oxygen bonding. This supported the hypothesis that all of the copper complexes being formed both with, and without peroxide treatment, were identical in the coordination chemistry of the copper. This would suggest that the peroxide treatment is forming carboxylic acid functional groups which are then able to mobilize copper from the remaining basic copper carbonate. The high solubility of the copper compounds formed suggests that, unlike the natural carboxylic acid functional groups present in wood, those formed by the peroxide post-treatment may be wood-degradation products. In the basic copper carbonate present in the MBCC, the copper is antiferromagnetically coupled in the solid state, and so is EPR silent.

5. Conclusions

Peroxide post-treatment of wood pressure impregnated with MBCC may help to minimize color change due to photo-degradation. Erosion due to photo-degradation and colonization by black-stain fungi were similar in samples impregnated with MBCC, regardless of the peroxide post-treatment. The peroxide post-treatment was associated with increased copper leaching, but also with increased reacted copper.

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Appendix A. Peroxide Treatment Optimization

White spruce (*Picea glauca*) was cut into $1 \times 10 \times 50$ mm³ strips from sapwood and dip treated with a 1% solution of MBCC intended to simulate the surface of lumber pressure impregnated with a micronized copper containing preservative. These treated strips were used to examine the color change associated with oxidizing the copper when exposed to hydrogen peroxide. Initially a solution of 30% hydrogen peroxide was applied to dried copper treated spruce test strips, and a very dark brown color was produced, confirming that oxidation was possible. To produce the desired brown hue, testing was conducted to optimize hydrogen peroxide concentration and pH. Higher pH was obtained by addition of dilute sodium hydroxide. Lower pH was obtained by addition of dilute hydrochloric acid. Reaction time, drying method as well as influences from species and substrates were also explored.

The initial screening test looked at the effect of hydrogen peroxide concentration on color (Figure A1). A 10% solution (pH 6) resulted in an uneven light brown color. Treatments with 20% (pH 5) and 30% (pH 4) solutions resulted in a more uniform medium brown color.



Figure A1. The effect of hydrogen peroxide concentration on the color of spruce treated with MBCC (left to right: untreated, MBCC treated (no peroxide), MBCC-treated 10% peroxide at pH 6, MBCC treated 20% peroxide at pH 5, 30% peroxide at pH 4).

When treated with a 20% solution of hydrogen peroxide, pH 6 was found to best yield a medium brown color (Figure A2). Treatment with a 10% solution at varying pH levels resulted in only light brown coloration at all pH levels and an uneven tone across the samples.

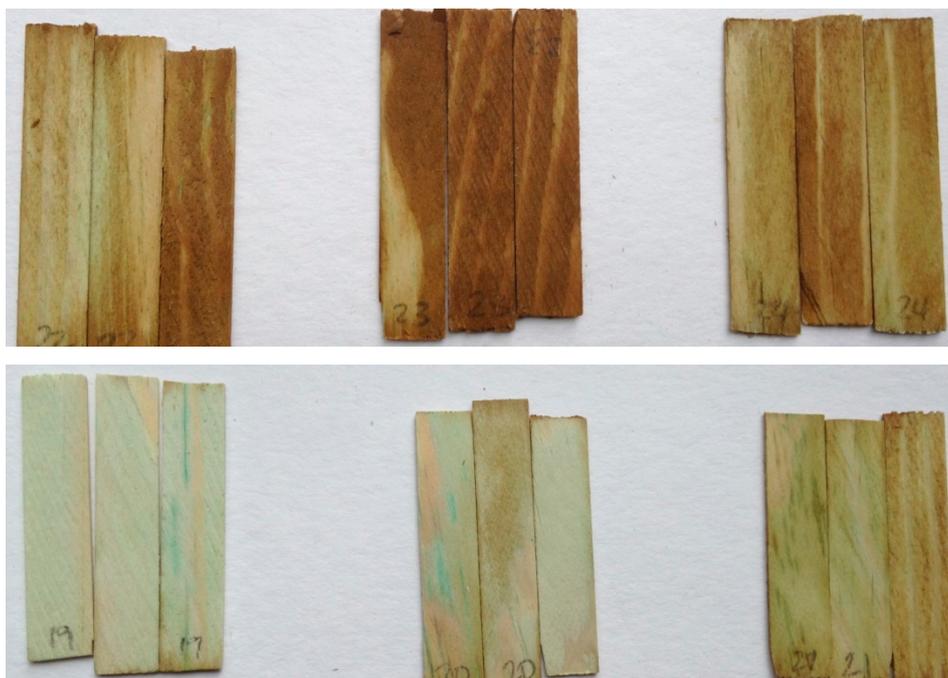


Figure A2. The effect of peroxide solution pH of the color of spruce treated with MBCC (top 20% peroxide, left to right pH 4, pH 6 and pH 8; bottom 10% peroxide, left to right pH 4, pH 6, pH 8).

The effect of storage time was assessed on MBCC-treated samples exposed to 10% hydrogen peroxide (pH 6) (Figure A3). Samples were held wet at different time frames then air dried, left wet or oven dried at 100°C before the hydrogen peroxide was applied. For hold time, a moderate browning was observed in all samples, suggesting that there was no improved color development with a longer storage time.



Figure A3. The effect of wet storage time on the color of spruce treated with MBCC and 10% peroxide (left to right 0 h, 1 h and 22 h hold before oven drying).

There was an impact in color development when different drying methods were employed. Little difference was observed between air drying and oven drying the samples before treating them with hydrogen peroxide, as similar colors were produced with the secondary treatment. However, it was noticed that the initial copper treatment washed off when samples were treated with peroxide while still wet. This was evidenced by the peroxide solution turning brown and the treated samples having a slightly muted brown color (Figure A4).



Figure A4. The effect of oven drying on the color of spruce treated with MBCC and 15% peroxide.

Samples of mixed sapwood and heartwood were treated with 20% peroxide at pH 6 and 8 (Figure A5). The heartwood/sapwood boundary was visually evident in the basic copper carbonate treated samples and remained visible after exposure to peroxide. However, both wood types turned a similar mid-brown color.

Based on these experiments, the optimum conditions were determined to be 20% hydrogen peroxide at pH 6 on dried copper treated samples, producing a consistent rich brown color across the samples. Wet storage time and substrate did not have major effects, while not drying samples before hydrogen peroxide treatments removed some of the copper treatment applied affecting the color produced.



Figure A5. The effect pine sapwood and heartwood on the color of wood treated with MBCC and exposed to 20% hydrogen peroxide at pH 8 (top) and pH 6 (bottom).

References

1. Sandak, A.; Sandak, J.; Dimitriou, A.; Burud, I.; Thiis, T.K.; Gobakken, L.R.; Ormondroyd, G.A.; Kraniotis, D. Assessment and monitoring of aesthetic appearance of building biomaterials during the service life. *WIT Trans. Ecol. Environ.* **2017**, *226*, 527–536. [CrossRef]
2. Evans, P.; Chowdhury, M.J.; Mathews, B.; Schmalzl, K.; Ayer, S.; Kiguchi, M.; Kataoka, Y. Weathering and surface protection of wood. In *Handbook of Environmental Degradation of Materials*; Kutz, M., Ed.; William Andrew Publishing: Norwich, NY, USA, 2005; pp. 277–297. [CrossRef]
3. Feist, W.C. Outdoor wood weathering and protection. In *Archaeological Wood: Properties, Chemistry, and Preservation*; Advances in Chemistry; Rowell, R.M., Barbour, R.J., Eds.; American Chemical Society: Washington, DC, USA, 1990; Volume 225, pp. 263–298. [CrossRef]
4. Blanchard, V.; Blanchet, P. Color stability for wood products during use: Effects of inorganic nanoparticles. *BioResources* **2011**, *6*, 1219–1229.
5. Jin, L.; Archer, K.; Preston, A. Surface Characteristics of Wood Treated with Various AAC, ACQ and CCA Formulations After Weathering. International Research Group on Wood Preservation. Document No. IRG/WP/2369. IRG Secretariat, Stockholm Sweden. 1991. Available online: <https://www.ircg-wp.com/search-ircg-docs.html> (accessed on 20 November 2020).
6. Liu, R.; Ruddick, J.N.R.; Jin, L. The Influence of Copper (II) Chemicals on the Weathering of Treated Wood, 1: ACQ Treatment of Wood on Weathering. International Research Group on Wood Preservation. Document No. IRG/WP/94-30040. IRG Secretariat, Stockholm, Sweden. 1994. Available online: <https://www.ircg-wp.com/search-ircg-docs.html> (accessed on 20 November 2020).
7. Zhang, J.; Kamdem, D.P.; Temiz, A. Weathering of copper-amine treated wood. *Appl. Surf. Sci.* **2009**, *256*, 842–846. [CrossRef]
8. Ozgenc, O.; Hizirolu, S.; Yildiz, U.C. Weathering properties of wood species treated with different coating applications. *BioResources* **2012**, *7*, 4875–4888. [CrossRef]

9. Zhang, J.; Ziobro, R. Micronized Pigment Technology for Pressure Treatment. Proceedings Canadian Wood Preservation Association, 34, 2013. Available online: <https://www.cwpa.ca/publications/> (accessed on 20 November 2020).
10. Archer, K.; Sturdivant, R.; Schauwecker, C. Pressure Treatment of Lumber with Colorant Additives. Proceedings Canadian Wood Preservation Association, 34, 2013. Available online: <https://www.cwpa.ca/publications/> (accessed on 20 November 2020).
11. Grelier, S.; Castellan, A.; Kamdem, D.P. Photoprotection of copper-amine-treated pine. *Wood Fiber Sci.* **2000**, *32*, 196–202.
12. Auger, S.B. Mineral Stains for Wood and Other Substrates. US Patent 2007/0011820 A1, 12 September 2007.
13. Stirling, R.; Drummond, J.; Zhang, J.; Ziobro, R.J. Micro-Distribution of Micronized Copper in Southern Pine. International Research Group on Wood Protection. Document No. IRG/WP/08-30479. IRG Secretariat, Stockholm, Sweden. 2008. Available online: <https://www.irg-wp.com/search-irg-docs.html> (accessed on 20 November 2020).
14. Matsunaga, H.; Kiguchi, M.; Evans, P.D. Microdistribution of copper-carbonate and iron oxide nanoparticles in treated wood. *J. Nanoparticle Res.* **2009**, *11*, 1087–1098. [[CrossRef](#)]
15. Xue, W.; Kennepohl, P.; Ruddick, J.N.R. Investigation of copper solubilization and reaction in micronized copper treated wood by electron paramagnetic resonance (EPR) spectroscopy. *Holzforschung* **2012**, *66*, 889–895. [[CrossRef](#)]
16. ASTM G-155 Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials; ASTM International: West Conshohocken, PA, USA, 2013.
17. Stirling, R.; Uzunovic, A.; Morris, P.I. Control of black stain fungi with biocides in semitransparent wood coatings. *For. Prod. J.* **2011**, *61*, 359–364. [[CrossRef](#)]
18. AWP A E24-16 Laboratory Method for Evaluating the Mold Resistance of Wood-Based Materials: Mold Chamber Test; American Wood Protection Association: Birmingham, AL, USA, 2016.
19. OECD Guidance on the Estimation of Emissions from Wood Preservative—Treated Wood to the Environment: For Wood held in Storage After Treatment and for Wooden Commodities that are not covered and are not in Contact with Ground. Organization for Economic Co-operation and Development, Paris, France. 2008. Available online: https://echa.europa.eu/documents/10162/16908203/pt8_oecd_guidance_emission_estimation_treated_wood_en.pdf/97bc4a98-abf6-4a3a-a448-88681a17dd52 (accessed on 23 July 2009).
20. AWP A A9-16. Standard Method for Analysis of Treated Wood and Treating Solutions by X-ray Spectroscopy; American Wood Protection Association: Birmingham, AL, USA, 2016.
21. Xue, W.; Kennepohl, P.; Ruddick, J.N.R. Quantification of mobilized copper (II) levels in micronized copper-treated wood by electron paramagnetic resonance (EPR) spectroscopy. *Holzforschung* **2013**, *67*, 815–823. [[CrossRef](#)]
22. Deka, M.; Humar, M.; Rep, G.; Kričej, B.; Šentjurc, M.; Petrič, M. Effects of UV light irradiation on colour stability of thermally modified, copper ethanolamine treated and non-modified wood: EPR and DRIFT spectroscopic studies. *Wood Sci. Technol.* **2008**, *42*, 5–20. [[CrossRef](#)]
23. Stirling, R.; Wong, D. The Impact of Coatings on the Service Life of Wood Decking. International Research Group on Wood Protection. Document No. IRG/WP/18-20635. IRG Secretariat, Stockholm, Sweden. 2008. Available online: <https://www.irg-wp.com/search-irg-docs.html> (accessed on 20 November 2020).
24. Zhang, J.; Ziobro, R.J. Micronized Copper Preservative Systems: Observations on the Release of Cupric ion (Cu²⁺) from Treated Wood and Performance against Wood Decay Fungi. International Research Group on Wood Protection. Document No. IRG/WP/09-30519. IRG Secretariat, Stockholm, Sweden. 2009. Available online: <https://www.irg-wp.com/search-irg-docs.html> (accessed on 20 November 2020).
25. Xue, W.; Kennepohl, P.; Ruddick, J.N.R. Reacted copper (II) concentrations in earlywood and latewood of micronized copper-treated Canadian softwood species. *Holzforschung* **2015**, *69*, 509–512. [[CrossRef](#)]
26. Kadla, J.F.; Chang, H.M. The reactions of peroxides with lignin and lignin model compounds. In *Oxidative Delignification Chemistry, ACS Symposium Series 785*; American Chemical Society: Washington DC, USA, 2001; pp. 108–129. [[CrossRef](#)]
27. Gascón-Garrido, P.; Thévenon, M.F.; Mainusch, N.; Militz, H.; Viöl, W.; Mai, C. Siloxane-treated and copper-plasma-coated wood: Resistance to the blue stain fungus *Aureobasidium pullulans* and the termite *Reticulitermes flavipes*. *Int. Biodeterior. Biodegrad.* **2017**, *120*, 84–90. [[CrossRef](#)]

28. Gadd, G.M. Effect of copper on *Aureobasidium pullulans* in solid medium: Adaptation not necessary for tolerant behaviour. *Trans. Br. Mycol. Soc.* **1984**, *82*, 546–549. [[CrossRef](#)]
29. Gress, J.; De Oliveira, L.M.; Da Silva, E.B.; Lessl, J.M.; Wilson, P.C.; Townsend, T.; Ma, L.Q. Cleaning-induced arsenic mobilization and chromium oxidation from CCA-wood deck: Potential risk to children. *Environ. Int.* **2015**, *82*, 35–40. [[CrossRef](#)] [[PubMed](#)]
30. Xu, G.; Cappellazzi, J.; Konkler, M.J.; Morrell, J.J. Effect of Multiple Leaching Cycles on Decay Resistance of Micronized Copper Azole-Treated Southern Pine Sapwood. *For. Prod. J.* **2020**, *70*, 178–181. [[CrossRef](#)]
31. Xue, W.; Ruddick, J.N.R.; Kennepohl, P. Solubilisation and chemical fixation of copper(II) in micronized copper treated wood. *Dalton Trans.* **2016**, *45*, 3679–3686. [[CrossRef](#)] [[PubMed](#)]
32. Peisach, J.; Blumberg, W.E. Structural implications derived from the analysis of electron paramagnetic resonance spectra of natural and artificial copper proteins. *Arch. Biochem. Biophys.* **1974**, *165*, 691–708. [[CrossRef](#)]

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