Coating Performance on Preservative Treated Wood

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by

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A thesis submitted in conformity with the requirements
for the degree of Doctor of Philosophy

Graduate Department of Forestry
University of Toronto

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2011

Abstract

Wood service life is significantly prolonged by the use of preservatives. Unfortunately, preservative treated wood is still susceptible to weathering degradation (UV and moisture) and subsequent leaching of preserving components. These negative impacts of weathering can be reduced by the application of a coating; however, the effectiveness of the coating depends on its characteristics, especially its compatibility with preservative treated wood.

In this project, the performance characteristics of semitransparent deck stains were evaluated for untreated wood samples and for samples treated with chromated copper arsenate (CCA), alkaline copper quat (ACQ) and copper azole (CA) over three years of natural and three months of accelerated weathering conditions. The parameters measured were water permeability, colour change, general appearance, checking of wood, and the coating's ability to reduce preservative leaching.

Coatings were characterized in terms of glass transition temperature (Tg), solid content, viscosity, density, contact angle, surface tension, and film thickness. Also penetration depth of a polyurethane (PU) coating was examined using Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS).

All the stains evaluated effectively reduced cumulative leaching of preservative components by about 60% on average. An analysis of the preservative gradients and residual soluble components in the ACQ-samples after weathering indicated that preferential leaching of monoethanolamine (Mea) is most likely responsible for the reduced amounts of available copper in coated treated wood samples. Also, a two-week screening test was able to provide accurate predictions of the long-term leaching performance of different coatings.

There was a significant interaction effect between coatings and preservatives: solvent-based coatings showed better water repellency for CCA and untreated wood, but there was no significant difference in water repellent effectiveness between water-based and solvent-based coatings for ACQ or CA-treated wood. Overall, preservative treatments greatly enhanced coating performance. Image analysis of the samples subjected to 3 years weathering showed that coatings reduced surface checking by 30-40%.

Partial least squares regression (PLS-R) modeling was used to correlate measured coating properties with their weathering performance characteristics. The modeling results showed that coatings with low Tg and high viscosity effectively reduce the leaching of preservative components and improved water repellency and visual ratings.

Acknowledgments

First and foremost, I would like to express my heartfelt appreciation to my dear supervisor, Professor Paul Cooper for being there whenever I needed help and guidance. He was the best supervisor that I could ever wish for and it is beyond words to describe how lucky I was to work with him. Also, I would like to thank to my committee members Professors: Mark Kortschot, Ramin Farnood and Ning Yan for their constructive ideas and invaluable advice throughout my research.

Financial support from Natural Resources Canada and NSERC is much appreciated and I like to take this opportunity and thank both academic and administrative staff of the Faculty of Forestry for providing a friendly and pleasant working environment.

I am very grateful to all my colleagues and friends for their help and support, particularly Tony and Dragica which their advice and friendship made graduate study an enjoyable journey for me.

I will remain indebted to my mom for her unconditional love and help especially at the time of writing my thesis, and I am very gratified to my sisters Mitra and Marjan and my brothers Mohammad and Mojtaba, also to Kayena and Kianoush my lovely niece and nephew for believing in me and their spiritual support.

Mainly I owe much gratitude to my husband Babak and to my lovely triplets, Tina, Romina and Sarina for their love and support. Without their help and patience it would be impossible for me to pursue my dream.

I would like to dedicate this thesis to memory of my beloved father, who without his encouragement I would not be here.

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Chapter 1

1 Introduction

1.1 Wood as substrate for coating

Wood is one of the most important building materials in Canada because it is renewable and abundantly available from Canada's rich forests. In comparison to steel and concrete, wood is biodegradable, has low environmental emissions and needs lower energy for processing. Pure beauty and diversity of wooden products in our lives in today's high-tech society is like a precious gift from nature to us.

When the long-term appearance of exterior wooden structures is important to their service life they should be protected from weathering factors such as UV and moisture by application of a suitable coating. However, wood is a biological material which creates many challenges to ensure coating durability in exterior applications. Great care is needed in proper structural design, application, and particularly in coating selection. Dimensional instability of wood during moisture absorption and desorption causes cracking and peeling of the coating from the wood surface. Photo-degradation of wood imposes interface failures in transparent finishes. Resin and extractives found in most types of wood can cause discoloration in light coloured finishes. Also, knots or other irregularities present in wood may interfere with bonding and generate discoloration.

The density of wood is another important factor affecting a coating's durability. Higher density woods shrink and swell more than lower density woods when exposed outdoors [1]. The density of wood varies not only from one species to another, but also within the same tree. For example there is a huge density differences between latewood and earlywood of southern pine lumber

[1]. This characteristic greatly influences coating performance, which is the reason why southern pine is ranked as the worst wood species among softwoods for paint-holdability [2].

Wooden decks are either made of naturally durable species, or non-durable softwood which has been treated with preservative chemicals. Resources of naturally durable species like cedar and redwood are insufficient; therefore, they are more expensive than other softwoods. It should be noted that only the heartwood of these naturally durable species contain high amounts of extractives and is resistant to decay; their sapwoods are not durable [1].

1.2 Preservative treatments and their environmental impacts in service

Pressure treating lumber with preservatives protects the wood from biological degradation by decay fungi and insects. In residential structures water-based preservatives are used rather than oil-based preservatives (e.g. creosote) which are greasy to touch and have strong odours. The oil-based preservatives are also no longer labeled by the Canadian Pest Management Regulatory Agency (PMRA) for residential applications. Chromated copper arsenate (CCA) was the main water-based preservative formulation for residential and industrial applications for decades. However, since January 2004, CCA was also de-listed from residential uses by PMRA. Now Cu-amine based preservatives, such as alkaline copper quaternary ammonium (ACQ) and copper azole (CA), are the predominant preservatives used in Canada for residential applications.

Degree of protection depends not only on preservative type but also on proper penetration. Not all woods can be treated to the same degree; penetration of preservatives into the wood differs even when they are treated under vacuum and pressure. Some species, like spruce and Douglas-fir, are resistant to treatment. Southern pines have very wide treatable sapwood zones and are among the species most easy to treat, although their heartwood is moderately hard to treat [3].

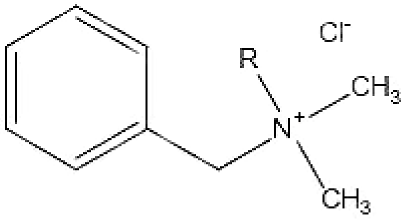
Preservative treatment greatly increases the service life of wood [1], but preservative components leach gradually into the environment [4-14]. The leaching amount varies depending on preservative type, retention (the amount of chemical absorbed per unit volume) and exposure conditions [15-17]. Preservative chemicals, by nature, are toxic to living organisms when they migrate from treated wood to surrounding environments.

The main reason that CCA was replaced by its alternatives in residential applications was that people were concerned about being exposed to toxic arsenic and chromium components of CCA. Although CCA use is now prohibited from residential applications, it still remains the most effective water-based preservative chemical for industrial applications, such as highway construction, utility poles, and pilings. Also, since regulatory agencies have not required that CCA treated residential structures in service be removed, there are still many CCA treated decks, fences and other residential structures in use.

Copper-amine preservatives were developed as arsenic- and chromium-free preservatives for residential structures. The Cu-amine formulations contain copper as fungicide and an organic co-biocide to improve efficacy, especially against copper tolerant decay fungi. The main copper amine based preservatives in use worldwide at this time are: alkaline copper quat (ACQ - copper amine with a quaternary ammonium compound); copper azole (CA - copper amine with tebuconazole); copper HDO (Bis-(N-cyclohexyl-diazeniumdioxy-copper amine) [18] and copper betaine (copper amine with didecyl polyoxyethyl ammonium borate) [19]. Cu-amine preservatives leach copper in relatively high amounts [10]. Although copper has low toxicity to humans, requiring ingestion of more than 15 mg to be toxic (Health Canada), Cu is toxic to aquatic organisms at very low concentrations [20, 21].

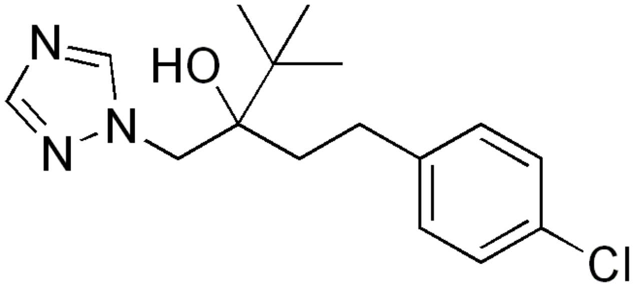
Three different types of CCA with slightly different formulations have been developed for use as wood preservatives over the past several decades. Type A contained more chromium, while type B had more arsenic; these formulations are no longer in use. CCA type C evolved as the predominant type in the market, because of its resistance to leaching and excellent field efficacy. It contains chromium trioxide 47.5%, copper oxide 18.5%, and arsenic pentoxide 34.0%. It is applied at a recommended retention of 4.0 kg/m^3 based on CrO_3, CuO, and As_2O_5 equivalent content for above-ground structures. In CCA formulations, copper acts as fungicide, arsenic as a supplementary fungicide for copper tolerant fungi, and insecticide and chromium oxide to fix the Cu and As inside the wood.

Alkaline copper quat (ACQ) has three different formulations types, with types B, C and D currently incorporated in North American preservative standards. They all contain 66.7% copper oxide and 33.3% of quaternary ammonium compound (quat). ACQ type B and D both use DDAC (didecyldimethylammonium chloride), but type B uses an ammoniacal copper formulation, and type D is based on a monoethanolamine copper formulation. ACQ-C is an amine formulation with ADBAC (alkyldimethylbenzylammonium chloride) as the quat as shown below; this is the formulation registered for use in Canada at this time. In ACQ, copper acts as fungicide for most decay fungi and the quaternary ammonium compound inhibits copper-tolerant fungi and improves insect resistance.



Alkyl dimethyl benzyl ammonium chloride (ADBAC)

Copper azole (CA) has two major types, one of which includes a boron compound as CBA-A with 49% copper, 49% boron as boric acid (H_3BO_3) and 2% tebuconazole. Since boron easily leaches, this formulation is only approved for above ground applications. The other and more widely used copper azole formulation is CA-B with 96.1% copper oxide and 3.9% tebuconazole (TCZ) which is dissolved in a solution of ethanolamine in water. Its recommended retention (1.7 kg/m^3) for above ground exposure is lower than for CCA and ACQ, because of the high efficacy of the TCZ and the fact that the retention is expressed as amount of Cu (not CuO) and TCZ.



Tebuconazole or (3RS)-5-(4-chlorophenyl)-2, 2-Dimethyl-3-1H-[1, 2, 4-triazole methyl]-3-petanol

Preservative effectiveness depends on its type, penetration depth and retention in treated wood. Also it depends on wood species, proportion of sapwood to heartwood and treatment process. Lumber should be kiln dried before treatment to achieve higher penetration and less checking of wood during drying. To attain deeper penetration, lumber may be incised by creating small cuts, usually about 1-2 cm long, before treatment; incisions are especially effective for optimum heartwood treatments. Water-borne preservative treatments must be applied by a vacuum-pressure treating process. Depending on the preservative type, the fixation process is a very important step that affects both leaching rate and wood durability. Fixation can be defined as conversion of water-soluble inorganic components into stabilized, leach-resistant chemicals in wood. Parameters like concentration and pH of the treating solution and ambient relative humidity and temperature are the most important factors affecting fixation [6, 22-23].

While preservative treatment protects wood from decay, it cannot completely protect the wood from weathering effects of UV radiation and moisture. The weathering or discoloration of wood to a gray colour is caused by photochemical reactions. Weathering is a surface phenomenon and the thickness of the gray layer of wood is reported to be only 125 μm. This weathered layer on top of the wood surface acts as a shield to prevent further light penetration [24]. However, free radicals generated by the reaction of wood components, especially lignin with light, are reported to be elevated by the presence of water. Water as a polar liquid can penetrate deeply through wood and cause the swelling of cell walls, which facilitates deeper light penetration and more free radical generation [24]. That is why wood, when exposed outside, should be protected from both UV and moisture.

1.3 Coating types used on exterior wood

In exterior wooden structures the choice of coating differs depending on whether the structure is exposed to direct rain and sun. For a structure that is partially or totally covered, e.g., window joinery and siding, paint is usually a better choice, with longer service life than stains or water repellents [2]. Paints form a thick layer of film on the surface of wood to resist water penetration and are highly pigmented, which completely obscures the substrate underneath. For horizontal surfaces such as decks, paint or film-forming coatings are not advised. In addition to the possible cracking and peeling of paint film on the wood surface, moisture can be trapped and create conditions for decay fungi and mould [25]. Penetrating finishes are the most suitable coatings for decks and fences, because they are less likely to crack and peel from dimensional changes of wood during weathering exposure. While stains are defined as penetrating finishes (in contrast with paints) and non-film forming products [26], solid color stains or water-based semi-transparent stains (especially if %100 acrylic latex) have also been categorized as film forming products [27].

Although there is a high demand for transparent finishes, such as varnishes, and transparent stains for wood structures to show the beauty of the wood grain, UV radiation can pass through transparent finishes and cause degradation of wood underneath. This results in rapid wood discoloration and early failure of film-forming coatings. Therefore, transparent finishes which do not contain effective UV absorbers have shorter service life and are generally not recommended for exterior uses where it is important to retain the colour and prevent peeling.

For decks and fences, semi-transparent penetrating stains that penetrate wood deeply are recommended. These stains should not form enough of a film layer on the surface to crack and peel. Semi-transparent stains contain pigment to some degree to protect the wood from UV rays, but do not hide the beauty of wood grain. Previous literature only considered solvent-based stains as penetrating stains [27]. This could be because, historically, water-based formulations for exterior use were mainly acrylic latexes with large molecular weight resins and high viscosities that could not penetrate significantly into the wood. New alkyd emulsions [28] and polyurethanes (PU) both have low molecular weights and even though they are water-based, readily penetrate into wood.

In terms of resin chemistry, wood coatings can be divided into three main resin types: alkyd, acrylic and polyurethane and their combinations. Also, in terms of technology, they are classified as solvent-based, water-based and UV curing. Since the main focus of this project was on decking applications and basically do-it-yourself projects (DIY) UV curing systems are not considered here.

Alkyd-based coatings are the most common formulations used in exterior wood coatings. Alkyds are mainly oil-modified polyesters (for exterior wood primarily medium to long oil) which are cured by an autoxidation and cross-linking process [29, 30]. The polymer is formed by condensation reaction of polyols (commonly glycerol and pentaerythritol) with fatty acids (usually phthalic anhydride). Most alkyd coatings in the market are solvent-based; however, a few formulations of alkyd emulsions (water-based) stains are also available for decking. Stains formulated with alkyd resins are known to have deep penetration into the wood [31-33]. There is no difference between penetration depths of alkyd solvent-based and alkyd emulsion (water-based) coatings into wood if they have similar viscosity [28].

Acrylics are the result of polymerization reactions of acrylic acid (CH_2=CH-COOH) or its derivatives. In architectural applications acrylic dispersions are usually used. They are synthesized by emulsion polymerization of polymer particles in water. Latex film formation can be described by latex coalescence which, in a simple way, is comprised of a three-stage process: water evaporation, close particle packing and particle deformation by inter-diffusion [34]. Acrylic-based coatings have relatively high molecular weight and thus do not penetrate appreciably into the wood [32]. Acrylic latexes have two main advantages: first they are breathable (or have good water vapour permeability) meaning that they let the moisture inside the wood evaporate from the surface without causing blistering of the coating layer [32] ; second, they are to some extent resistant to UV degradation due to absence of tertiary hydrogen atoms in the methacrylates [35].

Modified alkyd resins with acrylics are more common in exterior formulations than pure acrylic. This hybrid system (alkyd-acrylic) is water-based and fast curing with high gloss retention and exterior durability [36, 37].

Polyurethanes used in exterior wood are usually “two-pack” emulsified in which the isocyanate is temporarily blocked with an amine. After water and amine have evaporated the isocyanate (–NCO) is free to react with a polyol [26]. Polyurethane formulated with aliphatic polyisocyanates has a higher level of performance with high light stability and moisture resistance [26, 38] which is essential for exterior applications.

When formulating a coating for exterior wood, to achieve optimum performance, many factors need be considered e.g., wetting and adhesion, film durability, water repellency and UV resistance. Consideration of these factors can minimize coating failure resulting from both internal and external stresses. There are other important criteria like structural design and applications which could cause coating failure, but the effects of these factors are not investigated in this study.

Wetting is a process whereby a liquid comes into intimate physical contact with the substrate in order to achieve good physical or chemical adhesion. The surface tension of the liquid (coating) should be lower than the surface energy of the solid (wood) for the liquid to spread or wet the surface [32]. If the surface tension of a coating is much lower than the surface energy of the wood, the contact angle will be low and the coating will spread on the surface or penetrate deep into the wood. The surface tension of a coating can be experimentally measured by either the Du Nouy ring method or Wilhelmy plate method, while the surface energy of a solid is more difficult to measure and typically is measured indirectly through contact angle of liquids of known surface tensions. Contact angle of coatings on wood is a fair indicator of good adhesion and sometimes, penetration of coating into the wood (in the case of immediate zero contact angle).

Flexibility of a coating’s film determines how durable the coating polymer will be in service. If a coating has a glass transition temperature (Tg) higher than the average temperature of coated wood in service, it becomes glassy and brittle. Also above the Tg there is a substantial increase in free volume of the coating, making the coating more permeable [32]. Podgorski studied the relationship between Tg and durability of alkyd stains on wood during natural and accelerated weathering and reported that stains with lower Tg had higher durability [39].

1.4 Coated wood performance

Coatings are used for two main reasons: aesthetics and protection. Although coatings cannot protect the wood from decay organisms, they are designed to protect the wood from weathering factors such as UV and moisture.

Water repellency is one of the most important factors affecting the performance of wood coatings outdoors. The average moisture content of wood should remain below 20% in service to avoid decay and mould growth [1, 40]. A coating should act as a membrane on the surface of wood in respect to water (rain, dew, snow) in a way that does not let the water soak into the wood while allowing the moisture vapour inside the wood to escape. In other words, a coating should be water repellent to liquid water, but should also be water vapour permeable. A number of studies measured the ability of coatings to exclude liquid water and their permeability to water vapor on untreated wood samples in the laboratory [41-47]. Pandey et al. showed that wood pressure treated with an aqueous solution of chromium oxide had better water repellency than untreated wood samples during five hour water immersion tests [48]. Nicholas et al. compared water sorption behavior (swelling rate) of CCA treated wood with those of samples treated with four different formulations of alkylammonium compounds; CCA had two times better water repellency compared to Kemanine (the best water repellent formulation among the four quats) [49]. Moisture absorption can also affect both the coating [50] and the bond between wood and coating resulting in interface failure (lack of adhesion) [26, 51] in the coated-wood system.

Wood undergoes chemical degradation when exposed to UV exposure. Therefore, another feature of coatings should be protection of the wood surface from UV radiation. Coatings should contain a pigment, or in clear coatings, a UV stabilizer to provide adequate protection in service. Depending on the application and end user criteria, different types of pigments can be considered (inorganic or organic). Unprotected wood can degrade in a few weeks under UV radiation; for example pine wood darkens in less than a month in service [52] and then turns gray as wood breakdown products are leached from the wood. Continuing exposure of bare wood to light causes the lignin on the surface to be degraded and loosens the fibers (erosion). Wood treated with CCA has been reported to reduce rate of erosion by protecting wood from UV degradation [53]. Evans et al. found that pine veneer treated with aqueous chromium oxide solution restricted weathering and weight loss by modifying lignin to photostable complexes [54]. Copper metal found in the Cu-amine preservative could also protect wood from UV degradation [55].

Another advantage of keeping wood relatively dry is that it reduces stresses caused by swelling and shrinking, thereby reducing checking, splitting and warping of wood. Evans et al. [56] reported CCA-treated pine wood (above ground retention) had longer and wider, but fewer checks in comparison with untreated wood after one year of natural weathering. In addition, improved coating performance and durability on CCA-treated wood compared to untreated wood was shown in previous studies [53, 57]. However, performance of coatings on Cu-amine preservative treated wood is mostly unknown.

Paints and water repellents are reported to reduce dislodgeable arsenic, copper and chromium from CCA and Cu from ACQ-treated wood and reduce preservative leaching [11, 58-61] (more details are discussed in the introduction section of Chapter-5). In May 2005, Health Canada published a fact sheet on CCA treated wood and recommended application of a penetrating stain once a year to reduce risk of exposure to arsenic for existing CCA decks in service. They also suggested that consumers should avoid using film-forming coatings such as paints, because they chip and flake, and scraping and sanding during maintenance could increase risk of exposure to As [62].

Natural weathering is always the best way to evaluate performance of exterior coatings; however, it is time consuming and expensive. Also the results depend strongly on climate conditions of the test site and they are not reproducible [63-65]. That is why researchers seek short-term lab tests that can effectively predict natural exposure results in performance studies.

1.5 Study justification

Most decks in North America are made of pressure treated wood which could last up to 40 years [66]; however, the average service life of decks is less than 20 years [67] because of poor appearance of decks after natural weathering exposure. Until 2004 wooden decks had been treated mainly with chromated copper arsenate (CCA); because people were concerned about leaching of As, the preservative industry voluntary shifted to Cu-amine based preservatives. Since then, most residential lumber has been treated with alkaline copper quat (ACQ) and copper azole (CA) preservatives. Premature removal of treated wood from service due to weathering, including checking, distortion and UV degradation, is a major problem. Application of a compatible coating on treated wood can prolong the high quality appearance period, and decrease environmental concerns related to preservative leaching and early disposal of the treated wood.

Semitransparent penetrating stains are recommended for exterior applications and their average service life is 3-7 years [68]; however, Health Canada recommended reapplication of penetrating stains every year to reduce leaching of As from CCA-treated wood [62]. The application of a penetrating stain every year on treated wood obviously will shift the market to other competitive products like wood plastic composites, which are promoted as requiring little maintenance and would result in increased disposal of CCA and copper amine treated wood in landfills.

Development of criteria to define suitable coating systems that could be applied to wooden structures and ensure long-term weathering protection would promote longer effective life for pressure treated wood products, reduce pressure on landfills and promote health and the environment.

1.6 Approach and General Methodology

The study was performed on southern pine because it is the most common wood species for decking in the USA and has a good treatability and poor paint holdability. It was assumed that if a coating performs well on southern pine, it is more likely to perform better on common Canadian decking species. Since semitransparent penetrating stains were recommended for deck application by previous researchers, a number of commercially available semitransparent deck stains were purchased and applied on CCA, ACQ, CA-treated and untreated wood specimens.

Performance of coatings were evaluated under three different exposure conditions: 1) two-weeks (screening) water immersion tests; this comparison included fourteen coatings on all three preservative treatments and untreated wood, 2) three months of accelerated weathering with eight coatings, selected based on screening test results, to represent a broad range of performance and coating formulations and 3) three years of natural weathering with five coatings selected from those eight coatings.

Performance characteristics of coatings were monitored during the above mentioned exposure tests. These included the ability of coatings to reduce wood preservative components leaching, reduce water uptake, minimize colour change and improve visual appearance ratings of treated and untreated wood samples.

In addition, a number of coating properties such as: solid content, viscosity, pH, specific gravity, surface tension, Tg, contact angle, and film thickness were measured to find correlations among coating properties and their weathering performance characteristics.

1.7 Research Questions

Research questions, as initially formulated:

1. Are semitransparent stains effective in reducing leaching (both from CCA and Cu-amine based preservatives)? If so for how long? Can they reduce checking of wood? Reduce water uptake? Improve colour stability?

2. Does resin type and base (water or solvent-base) affect performance? Do coating properties such as viscosity, solids content, surface tension, wettability, pH, Tg and film thickness affect performance? If so, which of these properties are most significant in exterior use?

3. Are there any differences among performance characteristics of coatings on Cu-amine based preservative treated wood compared to their performance on CCA-treated wood?

4. Can a rapid and reproducible laboratory method predict long-term natural weathering performance results?

Additional questions after 3 years of natural weathering tests:

5. Why does leaching of coated samples never reach that of uncoated ones? Did coatings allow time for Cu to be fixed more completely in the wood (in Cu-amine treated wood) during early stages of weathering exposure when coatings effectively reduced leaching?

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Chapter 2

2 Exterior Wood Coatings, Part-1: Performance of Semitransparent Stains on Preservative Treated Wood

Based on paper with the same title submitted to Journal of Coatings Technology and Research, July 2010

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Abstract

Fourteen different commercially available semitransparent deck stains were applied on chromated copper arsenate (CCA), alkaline copper quat (ACQ), copper azole (CA) and untreated wood samples for initial screening of coatings. Five coatings were selected for natural weathering exposure tests based on screening test results. Their abilities to reduce water uptake, colour change, checking of wood, mildew growth and to improve general appearance of preservative treated wood samples were determined during three years of natural weathering in Toronto, Canada.

Overall, Cu-amine treated wood had higher water uptake than CCA treated samples. There was a significant interaction effect among coatings and preservative treatments with some stains performing better on some treatments than the others. Solvent-based coatings had better water repellency performance on CCA treated and untreated wood, but there was no significant difference in water repellent effectiveness between water-based and solvent-based coatings on ACQ or CA-treated wood. All the preservative treated wood had less colour change and better visual ratings than untreated wood samples. Based on image analysis results, for determining

the total area of surface checks on samples after 3 years, preservative treatments had no significant effect on checking of wood while coatings greatly reduced surface checking.

2.1 Introduction

Pressure treated wood is the most common decking material in use in North America. Wood exposed out of doors is vulnerable to biological degradation (decay fungi and insects), and non-durable softwood lumber like pine should be protected by applying a preservative chemical to wood. Prior to 2004, wood decks had been treated mainly with chromated copper arsenate (CCA). CCA contains copper as a fungicide, arsenic as supplementary fungicide for copper tolerant fungi and insecticide and chromium oxide to fix the Cu and As in the wood. Due to concerns about leaching of arsenic and disposal of CCA treated wood removed from service, wood preservative chemical suppliers voluntarily withdrew CCA for residential wood treatment and replaced it with Cu-amine based preservatives. Alkaline copper quat (ACQ) and copper azole (CA) are the two main preservative replacements for CCA in the residential market in North America. These two preservatives contain copper as a fungicide for most decay fungi and a quaternary ammonium compound or tebuconazole (organic co-biocides) to inhibit copper-tolerant fungi and improve insect resistance. Both formulations use monoethanolamine (Mea) as a co-solvent, which temporarily complexes with copper to promote fixation in wood and to facilitate penetration and distribution in wood [1].

Preservative-treated wood can last up to 40 years [2]; however, the early removal of treated wood from service due to weathering degradation, including checking, distortion and UV degradation, reduces the average service life of decks to less than 20 years [3]. Application of a durable coating would reduce the effects of weathering, thus increase the service life of wooden decks. In addition to the recent movement from CCA to Cu-amine preservatives, there has also been a shift from solvent-based coatings to low VOC or water-based coatings [4, 5].

Deck surfaces are among building components where wood is extensively exposed to rain, foot traffic and UV degradation. Therefore, semitransparent penetrating stains are recommended for protection of decks since these finishes do not hide the beauty of wood grain and at the same time have some degree of pigmentation to protect the wood from UV [6-9]. In addition, they penetrate into the wood to some extent and are not considered to be film-forming [10]. Film-forming coatings like paints are not suitable for exterior wood structures such as decks, because they crack and peel from dimensional changes in wood exposed to weathering [10]. Paint cracking, checking and delamination of the film layer from the wood substrate can be enhanced by large differences between the densities of earlywood and latewood in wood species like southern pine.

Performance characteristics of semitransparent stains have been evaluated by a number of studies on untreated wood [11-14] and some studies on treated-wood, which were mainly focused on CCA treatment [15-16]. The performance of semitransparent stains on Cu-amine preservative treated wood is mostly unknown. Gobakken studied mould growth on copper-organic preservative treated wood and found that a semitransparent acrylic waterborne stain had the lowest degree of mould growth after 3.5 years on pine compared with other solvent-based coatings [17]. Podgorski compared paintability and gluability of wood treated with several Cu-amine preservatives with wood treated with CCA and reported better general appearance of transparent coatings on CCA treated wood compared to the Cu-amine preservatives after artificial weathering [18].

With Cu-amine preservatives dominating the residential market, it is essential to study performance of coatings on these treated products. CCA solution is acidic (pH 1.6-2.5), and treated wood remains somewhat acidic while Cu-amine preservatives have pH 9-10 and treated wood remains slightly alkaline after fixation. This pH difference between CCA and Cu-amine treated woods contributes to corrosion of fasteners for the Cu-amine treatments. The pH difference along with other chemical differences could also affect coating performance. For example, CCA treatment makes wood surfaces hydrophobic while Cu-amine preservatives make the wood surface hydrophilic [18].

Chromium in CCA treated wood is reported to react with lignin and form a water insoluble chromate ester [19], which increases water repellency of wood and decreases UV degradation of wood by modifying lignin [15, 20]. Archer reported that there is also some evidence that Cu is able to slow down the photo-degradation of wood by UV radiation [21].

Wood splits and checks in response to dimensional movement from changes in moisture content in exterior exposures. One important role of a coating is to protect the wood surface from absorption of liquid water and as a result, to reduce checking of the wood. Unfortunately, most surfactants used in water-based coatings and the quat component of the ACQ formulation have hydrophilic moieties that can attract water, enhance penetration into wood and cause wood swelling [22, 23].

Another function of a coating is to protect the wood surface from UV degradation. Although weathering of wood is a slow process, the grey discoloration and development of surface checks are the main reasons that people replace their decks [10]. Application of a compatible coating on treated wood can prolong the good appearance period, reduce maintenance requirements and decrease early disposal of the treated wood. This paper evaluates performance characteristics of a number of coating formulations on different preservative treated woods during three years of natural weathering.

2.2 Materials and Methods

Experiments were performed on flat-grain planed sapwood of southern pine (SP). Eight nominal 20mm X 140mm x 4.88m boards were cut in four 20mm X 140mmX 1.22m pieces.

Three pieces were treated, each with a different preservative and one was used as an untreated (control) sample.

Preservatives used were: CCA-C (47.5% CrO_3, 18.5% CuO, and 34% As_2O_5), ACQ-C (66.7% copper oxide, 33.3% quat as alkyl dimethyl benzyl ammonium chloride) and CA-B (96.1% copper, 3.9% tebuconazole). All wood samples were pressure treated to above ground retention (AWPA, 2006) and samples were allowed to fix for one week at 50°C and 95% relative humidity.

Fourteen commercially formulated semitransparent stains tinted to a natural honey brown colour were purchased based on manufacturer recommendations for decks; they covered a broad range of available semitransparent stains formulations in the market for decking in 2006.

A set of small test samples [(3 preservative treatments+ untreated control) x 14 coatings x 3 replicates from different boards] were used for initial coating screening tests. Wood specimens, 7mm X 38mm X 45mm, were brush coated on all sides (only one coat for all coatings except coating-14 where one coat of step-1 (penetrating stain) and one coat of step-2 (UV-blocker) were applied). Coatings were allowed to dry for 48 hours. Two replicates of each were weighed and submerged in 75ml of distilled water for two weeks. Their weights were recorded after one, three and fourteen days and water was replaced with fresh water at those times. Another replicate sample was kept inside the lab and the water immersion test was performed a year later.

According to water uptake values and some of the coating properties, five coatings covering a wide range of chemical and physical properties were selected for the field tests. All treated and untreated wood samples were conditioned to reach constant moisture content (about 12%) prior to coating. The five selected coatings were applied by brush on the top surface (bark side- up) and to the end grain of wood samples (20mm x 140mm x 280mm with 6-8 annual rings). Three replicates for each treatment (CCA, CA, ACQ and untreated control) and coating were exposed to natural weathering and one replicate was kept as a control inside the lab. All coatings were applied only once except coating number 14 applied as three coats, the first two coats of stain and third coat as a UV-blocker after one hour. After air drying for one week, samples were exposed to natural weathering horizontally from May 2006 to May 2009 (Figure 2.1).

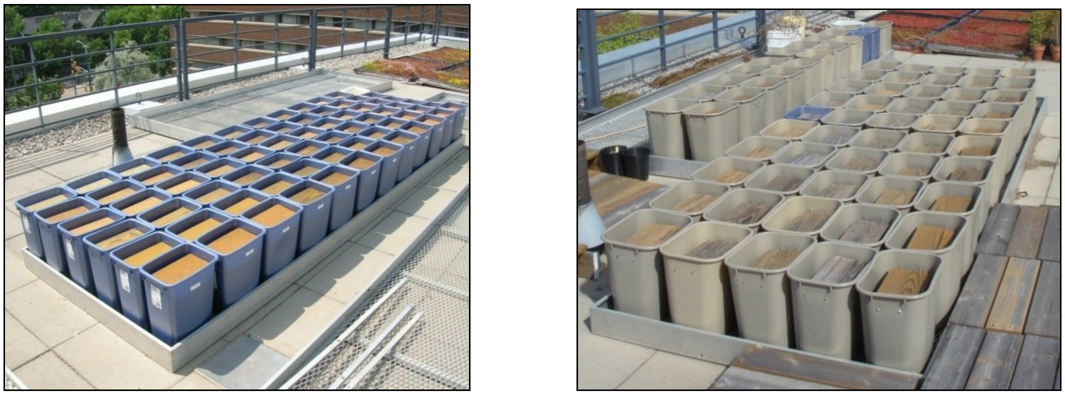


Figure 2.1: Natural weathering samples before and after 3 years of exposure.

Coating solid content and viscosity (by Brookfield viscometer) were measured at room temperature. A more detailed description of coating properties and measurement is discussed in Chapter-3.

Coating Performance

Coating performance, including water repellency, colour change, checking and visual appearance ratings were evaluated.

Water repellency

In the screening test, water repellent effectiveness of each coating on each treated wood sample (WRE) was calculated according to the equation below. Effects of water immersion after 1 day were evaluated because the water uptake values of all samples increased almost at the same rate after 3 and 14 days water immersion.

$$\%WRE = \left(\frac{Wuncoated - Wcoated}{Wuncoated} \right) \times 100$$

Where *W* is water uptake of samples, comparing coated with uncoated samples for each preservative treatment (including untreated samples).

Natural weathering samples were weighed after extended periods of wetting and drying. Moisture contents of samples were calculated based on initial oven dry weight of wood samples estimated based on the wood moisture content when coated (ASTM D4442).

Colour change

Colour change of samples was measured with a Konica Minolta Spectrophotometer (CM-2002) with the CIELab colour system in SCI mode (specular component included). The colour change (ΔE) was determined according to the following equation as outlined in ASTM D2244 and based on the three colour coordinates of L* as lightness, a* as red/green coordinate, and b* as yellow/blue coordinate.

Darker $- \longleftarrow \Delta L \longrightarrow +$ Lighter

Green $- \longleftarrow \Delta a \longrightarrow +$ Red

Blue $- \longleftarrow \Delta b \longrightarrow +$ Yellow

$$\Delta E_{ab} = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

The colour changes of samples were measured after 1, 2, 3, 6, 9, 12 and 36 months. The measurement of each sample included four readings, two on earlywood and two on latewood areas on three replicate specimens for each treatment-coating combination.

Checking of wood

Most general checking appearance evaluations are based on subjective visual assessment. We used image analysis techniques to measure the surface area of checks in a more consistent and reproducible way. Since we were dealing with black and white images for surface checking, we used a modified version of the method used by Robinson et al. for spalted wood [24] using Scion image software, with an important additional step of adjusting the image with Photoshop before using the Scion image.

A high resolution photo of each sample was taken with a Canon SD790 digital camera. Photos were all taken under consistent conditions by positioning samples with the light source directly from above to avoid any edge effects. Images were first adjusted in Photoshop to “auto-colour” and “auto-contrast” in “image-adjustment” and then the brightness/contrast set to the highest level (+100). Images were saved as .tiff files that could be opened in Scion Image software (Figure 2.2 image in right). By loading images, Scion Image produces two images, one original colour, and one grayscale copy. The check area measurements were performed on the gray scale image: first by measuring total area of samples through “analyze-measure” option, and then transforming the image into threshold “option-threshold”. Then use “analyze-measure” again in order to measure only the area of checks this time after threshold transformation. Results can be seen by pressing “analyzed-show results” option. The percentage surface area of checks was calculated by dividing the second number (area of checks) by the first number (total area of the samples).

Figure 2.2: (left) Sample after 3 years of natural weathering and (right) evaluated by image analysis for checks area measurement

Visual Ratings

Samples were ranked visually every year based on their general appearance for coating erosion (ASTM D662), fungal growth (ASTM D3274), and checking and splitting of the wood. Ratings ranged from 10 (perfect condition with no evidence of failure) to 0 (complete failure). For example if there was no sign of coating erosion they ranked as 10 for erosion, and samples were only ranked as 0 for erosion when there was no coating film left on the surface and the wood was completely exposed.

2.3 Results and Discussion

Details about coating types and their bases are shown in Table 2.1, and hereafter only the coating ID number is used. Shaded rows in the Table 2.1 are the stains which were selected for natural weathering tests.

2.3.1 Water repellency

The results of %WRE are presented for the first day of water immersion in Table 2.1.

Table 2.1: Water repellent effectiveness (WRE%) of coated samples after 24 hrs water immersion test, mean (s.d).

Coating-ID	CCA	ACQ	CA	Untreated	Mean	Grouping*
1 – Alkyd (W)**	24(7)	15(10)	15(5)	18(10)	18	DC
2 – Alkyd-Acrylic (W)	22(11)	20(6)	14(9)	15(6)	18	DC
3 – Alkyd (S)	37(10)	30(16)	22(15)	30(15)	30	ABC
4 – Alkyd-Acrylic (W)	60(8)	44(3)	44(10)	13(6)	40	AB
5 – Alkyd (S)	28(14)	19(18)	16(13)	24(10)	22	BCD
6 – Alkyd (S)	30(10)	24(16)	15(15)	39(3)	27	BC
7 – Alkyd (S)	35(10)	24(12)	27(14)	24(13)	28	BC
8 – Alkyd (S)	32(16)	27(15)	19(14)	30(9)	27	BC
9 – Alkyd (S)	57(9)	49(14)	40(19)	51(17)	49	A
10 – Alkyd-Acrylic (W)	34(11)	30(17)	29(10)	17(4)	28	BC
11 – Alkyd (S)	26(11)	22(15)	20(16)	35(13)	26	BC
12 – Alkyd (W)	-5(11)	15(5)	7(3)	0(5)	4	D
13 – Alkyd (S)	56(9)	35(10)	33(19)	35(15)	40	AB
14 – PU (W)	34(19)	56(9)	52(15)	57(18)	50	A

* Results of two-way ANOVA Tukey grouping of coatings comparing means for all preservative treatments; means sharing the same letters are not significantly different.

** W=Water-based S=Solvent-based

The large standard deviations result from the fact that %WRE values of the third replicates tested after one year were different from the first two replicates in some cases. For example %WRE of coating number 14 PU water-based was very high initially, but decreased significantly for the third replicate a year later. On the other hand, water repellent effectiveness of most alkyd solvent-based coatings increased for samples kept in the lab for a year which could be explained by completion of the cure process of alkyd resins [25].

Average WRE of all samples decreased with soaking time from 29% to 17% and then to 13% after 1, 3 and 14 days respectively. Table 2.2 shows the P-value of two-way ANOVA results of coating water repellency during the two-week water immersion test on different treated and untreated woods. Both coating types and preservative treatment types had statistically significant effects on water repellency and there was a significant interaction effect between treatments and coatings.

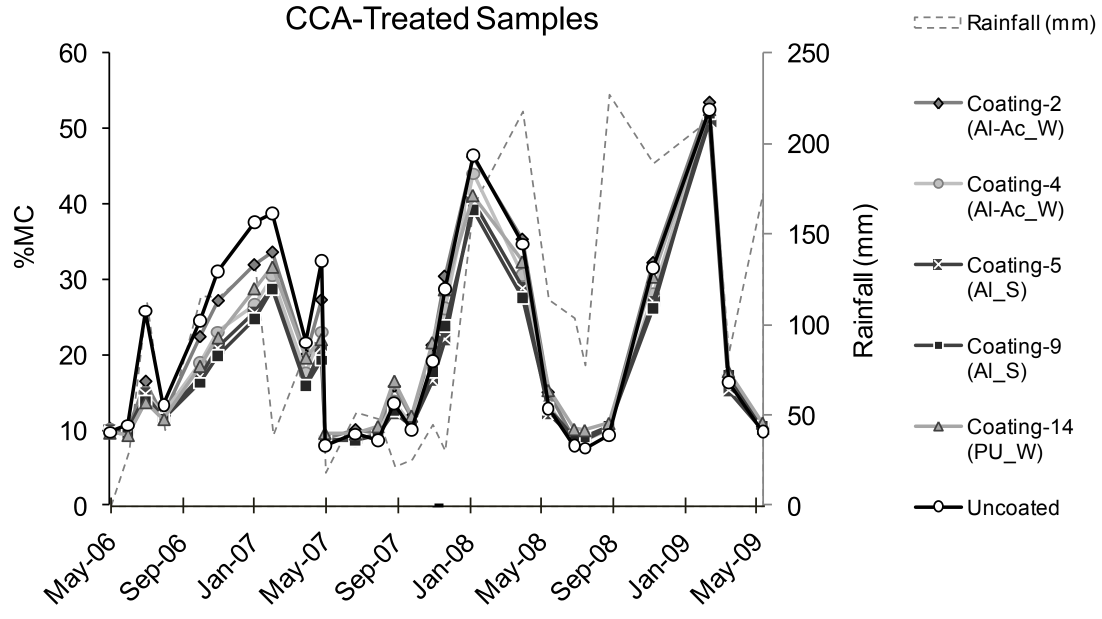
Table 2.2: P-value of two-way ANOVA results of water repellent effectiveness (WRE) of coated samples during two-week water immersion test and interaction effect of preservative treatment with coating (α=0.05).

Source	DF	P_{value}
Treatment	3	0.0463
Coating	13	< 0.0001
Treatment*Coating	39	0.0001

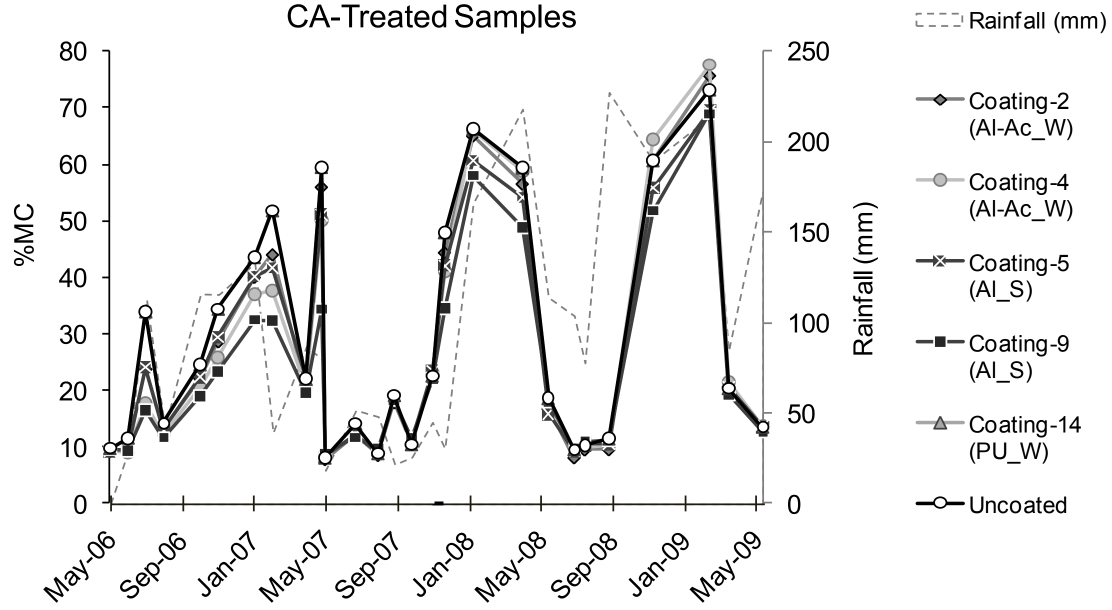
The interaction effect resulted because some coatings performed very well on one or two preservative treatment types, but not as well on the others. For example, coating number 4 showed very good water repellency on CCA treatment, but much lower water repellency on the other treatments; coating number 14 showed poor performance on CCA, but very good performance on the other treatments. Overall, it was observed that CCA-treated wood has higher water repellency than ACQ and CA-treated woods as observed by Nicholas [26] who found that %WRE for radial swelling of pine wood treated with CCA was higher than for samples treated with several alkyl ammonium compounds. He suggested that increased swelling of alkyl ammonium compound treated wood could be an indication of penetration of this compound into the wood cell walls. There was also a significant interaction effect between coating's base and treatment, with solvent-based finishes showing better water repellency on CCA-treated and untreated wood. However water-based coatings performed as well or better on ACQ and CA-treated wood as on CCA-treated and untreated wood. The main reason that most previous studies recommended solvent-based coatings for exterior use, is their good performance on CCA and untreated wood. There was no significant difference between water repellency of water-based (19.2%) and solvent-based (18.0%) coatings on ACQ and CA-treated wood samples and either water- or solvent-based coating systems are appropriate for Cu-amine treated wood. This effect was probably due to high water absorption of Cu-amine treated wood compared with CCA, and change in coating formulations from solvent-based to water-based was not significant.

In terms of water repellency among coatings, alkyd water-based formulations numbers 1 and 12 were the worst as noted before for alkyd emulsion coatings by Ekstedt et al. [27]. On the other hand, high viscosity (124 cP) alkyd solvent-based coating number 9 had the highest water repellency.

Figures 2.3a and b show the moisture content changes in CCA and CA-treated coated and uncoated wood samples during 3 years of natural weathering. Although most coatings had lost their moisture repellency greatly after the first or second year of exposure, coated samples had overall less water uptake than uncoated ones, which is mainly due to high effectiveness of coating in the first year.



(a)



(b)

Figure 2.3: Moisture content change of CCA-treated (a) and CA-treated (b) coated and uncoated samples during 3 years of natural weathering.

During dry periods, all samples reached similar moisture contents, so for coating performance evaluations in statistical analysis, we considered only average moisture content of samples during wet periods (MC above 20%, total of 12 reading times). Figure 2.4 shows the interaction effects among coatings and treatments based on the two-way ANOVA test results.

Overall, both treated and untreated coated wood samples had lower average moisture contents (higher water repellency) than uncoated ones. Surprisingly, the low viscosity alkyd solvent-based coating number 5 had very low water uptake on untreated and CCA-treated wood samples in natural weathering (in contrast to its performance in the screening test). Although this coating had low viscosity (about 10 cP), it had the second highest solid content of 38%, ranked after coating number 9 with solid content of 46%. Coating number 9 was more effective than the other coatings at ensuring low average moisture content for all preservative treatments, but was relatively less effective on untreated wood. ACQ and CA-treated wood specimens had higher moisture contents than those treated with CCA. This effect is also seen by comparing Figures 2.3a and 2.3b. The two solvent-based alkyd coatings (#5 and #9) had higher water repellency on CCA-treated wood, but there was no significant difference between performances of water-based and solvent-based coatings on Cu-amine preservatives treated wood, which was consistent with the two-week screening results.

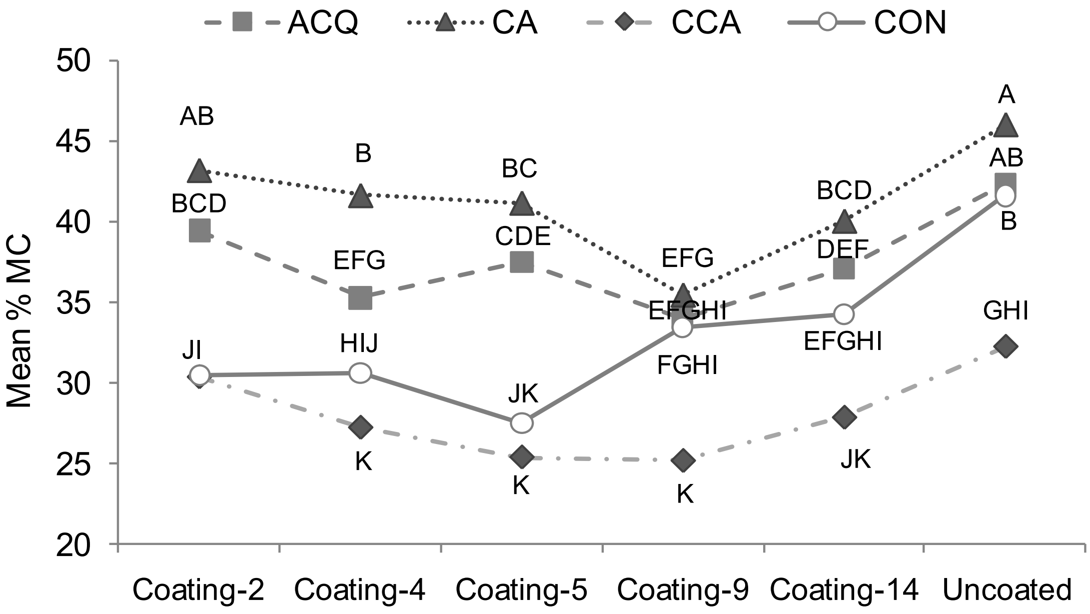


Figure 2.4 : Mean percent moisture content of wood samples during wet periods throughout three years of natural weathering. Different letters represent significant differences among coatings and preservative treatments (α=0.05).

2.3.2 Colour change

The ∆E colour measurement is usually used for determination of photo-degradation in short-term accelerated weathering tests [28-30]. However, during long-term natural weathering when some coating erodes from the wood surface, the exposed weathered wood is compared with the colour of coated-samples measured at the beginning of the test. Also the wood samples exposed to natural weathering are always subjected to mildew growth on the surface which affects the colour measurement. This colour change comparison may not be a good indicator of photo-degradation of coated samples, but can be used for comparing the performances of coatings on different treatments.

∆E colour changes of samples after three years of natural weathering are presented in Table 2.3. Although coatings made of acrylic resin are known to be more transparent to UV light [31], there was no apparent differences between the colour change of acrylic-alkyd coatings (2 and 4) and the other alkyd-based coatings. Average colour change of latewood (22.3) was statistically higher than for earlywood (21.5), which could be because of higher extractive content of latewood or the fact that after three years, most of the coatings had eroded from latewood areas of the coated samples. This effect was especially apparent for coating-14, which with the 3-coat application had a very thick film layer on the top of the wood surface and after 2 years the erosion of coating started exposing first the latewood and later earlywood section of the wood.

Table 2.3: ∆E colour change of samples after 3 years of natural weathering, mean (s.d).

	Wood zone	CCA	ACQ	CA	Untreated
Coating-2	Earlywood	21(0.6)	20(1.2)	19(1.0)	21(4.0)
	Latewood	20(0.0)	20(1.7)	19(0.6)	23(0.6)
Coating-4	Earlywood	19(1.0)	20(1.5)	19(1.0)	20(2.1)
	Latewood	21(1.5)	24(2.6)	20(1.5)	29(1.0)
Coating-5	Earlywood	20(0.1)	20(1.2)	19(0.1)	23(0.1)
	Latewood	20(0.6)	18(0.6)	18(0.6)	26(1.7)
Coating-9	Earlywood	21(0.1)	20(1.0)	20(1.5)	21(1.2)
	Latewood	22(1.0)	23(2.9)	22(1.5)	21(1.5)
Coating-14	Earlywood	25(1.5)	25(2.5)	26(1.5)	28(1.0)
	Latewood	23(0.6)	22(1.5)	26(3.1)	29(1.2)
Untreated	Earlywood	22(0.1)	20(1.2)	20(0.6)	29(1.7)
	Latewood	23(0.1)	20(0.6)	19(0.6)	29(0.6)

Overall, preservative treated wood had significantly lower colour change than untreated wood samples; this could be because chromium and copper modify and stabilize lignin as reported in previous studies [20] or the fact that treated wood overall had lower surface mould than untreated wood samples.

2.3.3 Checking

Although measuring only the surface area of checks of the wood samples is not a complete representation of the checking of wood, it is less subjective than visual assessment ratings. Figure 2.5 shows the average surface area of checks of the natural weathering samples after three years of exposure (image analysis results). Among preservative treatments, only CCA-treated wood had significantly lower surface checking than untreated wood samples. Cu-amine preservative treated wood had on average less checking (1.55%) than untreated woods (1.76%) although the differences were not statistically significant.

All coatings reduced checking of wood by on average 30-40%. Higher viscosity coatings #14 (270 cP) and #9 (124 cP) had considerably lower checking area than lower viscosity coating # 4 (18 cP). Surface checking reduction appeared to be more related to the thickness of the protective film layer on the wood surface than to penetration depth of coatings.

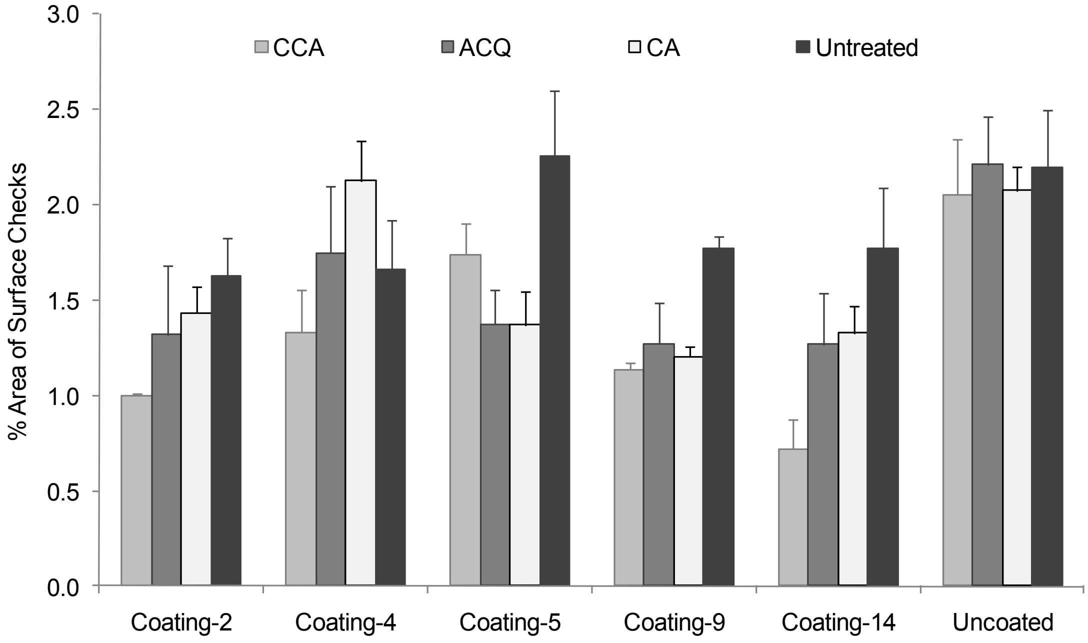


Figure 2.5: Average surface area of checks of samples after 3 years of natural weathering

2.3.4 General appearance ratings

The results of overall visual ranking of samples after 1, 2 and 3 years of natural weathering are presented in Table 2.4. The ranking is based on average ratings for checking, erosion and fungal growth. First year ratings were mainly due to checking of wood for treated samples and mildew growth and checking for untreated wood samples. During the second and third-year, mostly erosion of coatings and mildew growth along with checking of samples contributed to the ratings. Lignin degradation, which causes fiber separation from the surface, was only observed on untreated wood samples.

Table 2.4: Average visual ratings of all samples after 1, 2 and 3 years of natural weathering

ID	**First year**				**Second year**				**Third year**			
	CCA	ACQ	CA	UT*	CCA	ACQ	CA	UT	CCA	ACQ	CA	UT
Coating-2	9.1 (0.3)	8.2 (0.6)	8.2 (0.6)	6.7 (0.0)	7.7 (0.5)	6.6 (0.6)	6.8 (0.2)	6.0 (0.3)	5.6 (0.6)	4.6 (1.0)	4.3 (0.2)	4.0 (0.4)
Coating-4	8.4 (0.3)	7.8 (0.6)	8.0 (0.5)	6.9 (0.3)	8.6 (0.4)	7.7 (0.7)	6.7 (0.5)	4.9 (0.3)	5.6 (0.3)	3.9 (0.1)	4.0 (0.4)	3.4 (0.3)
Coating-5	8.2 (0.5)	7.9 (0.3)	7.9 (0.3)	6.4 (0.3)	6.1 (0.2)	5.6 (0.2)	4.3 (0.3)	3.1 (0.3)	3.7 (1.0)	3.6 (0.3)	3.0 (0.4)	2.0 (0.2)
Coating-9	9.3 (0.0)	8.7 (0.0)	9.1 (0.3)	6.9 (0.6)	8.4 (0.6)	6.8 (0.3)	6.1 (0.3)	4.1 (0.6)	6.3 (0.4)	5.3 (0.3)	4.6 (0.3)	2.8 (0.2)
Coating-14	9.8 (0.3)	9.3 (0.0)	9.3 (0.5)	8.2 (0.3)	8.4 (0.2)	8.0 (0.5)	6.0 (1.7)	4.6 (0.2)	6.1 (0.3)	5.2 (0.1)	4.0 (0.7)	3.7 (0.1)
Uncoated	8.7 (0.0)	7.6 (0.3)	8.2 (0.3)	5.6 (0.3)	7.3 (1.0)	6.5 (0.0)	5.2 (0.8)	2.1 (0.0)	3.4 (0.8)	2.6 (0.4)	2.4 (0.4)	0.8 (0.8)

*UT=Untreated

As observed in previous studies [11, 32], erosion of coatings started on latewood areas after about one year and then expanded to earlywood areas after about two-year. The density of latewood of southern pine is about twice as high as that of earlywood. Since higher density woods undergo greater dimensional changes during moisture changes in the wood [33], coatings on latewood are under more stress than coatings on earlywood. Furthermore, there is less stain penetration in dense latewood contributing to poor adhesion and early failure of coatings [34].

Overall, coatings had the best appearance ratings on CCA-treated wood with least coating surface erosion and fungal growth. Cu-amine preservatives had slightly higher mould growth than CCA, because of the presence of ethanolamine as discussed by Freeman et al. [1]. Alkyd solvent-based coating #5 had the worst appearance ratings of all coatings and statistically ranked similar to uncoated samples. This might be because of its low viscosity and the lack of a film layer on the top of the coated-wood surfaces to protect the wood.

Feist reported improvement of coating performance by CCA-treatment [16]; our results showed that the Cu-amine preservative treatments also enhanced coating performances (e.g., Fig. 2.6). In general, coated preservative treated wood samples had better general appearance ratings than coated untreated wood with less erosion of the coating and less surface checking.

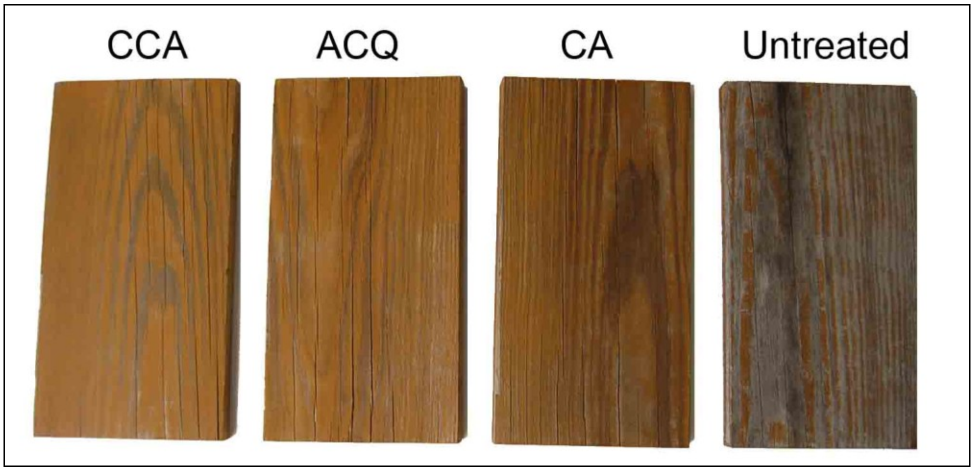


Figure 2.6: Different treated coating-2 samples after three years of natural weathering

2.4 Summary and Conclusions

Coating performance greatly depends on the properties of the substrate. Changes in preservative formulations in the residential market have opened a broad field of research for exterior wood coating performance evaluations. This study evaluated performance of semitransparent stains on two Cu-amine-based preservative treated woods in comparison with traditional CCA-treated and untreated wood. Application of solvent-based coatings for exterior structures is no longer a better option, since there was no improvement of performance by solvent-based coatings compared to water-based coatings on Cu-amine treated wood water repellency and other performance criteria. Cu-amine preservative treatments enhanced the general appearance of coated wood as effectively as CCA. Image analysis of samples after three years showed that coatings reduced surface area of checks on the wood surface by 30-40%.

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2.6 Supporting Information

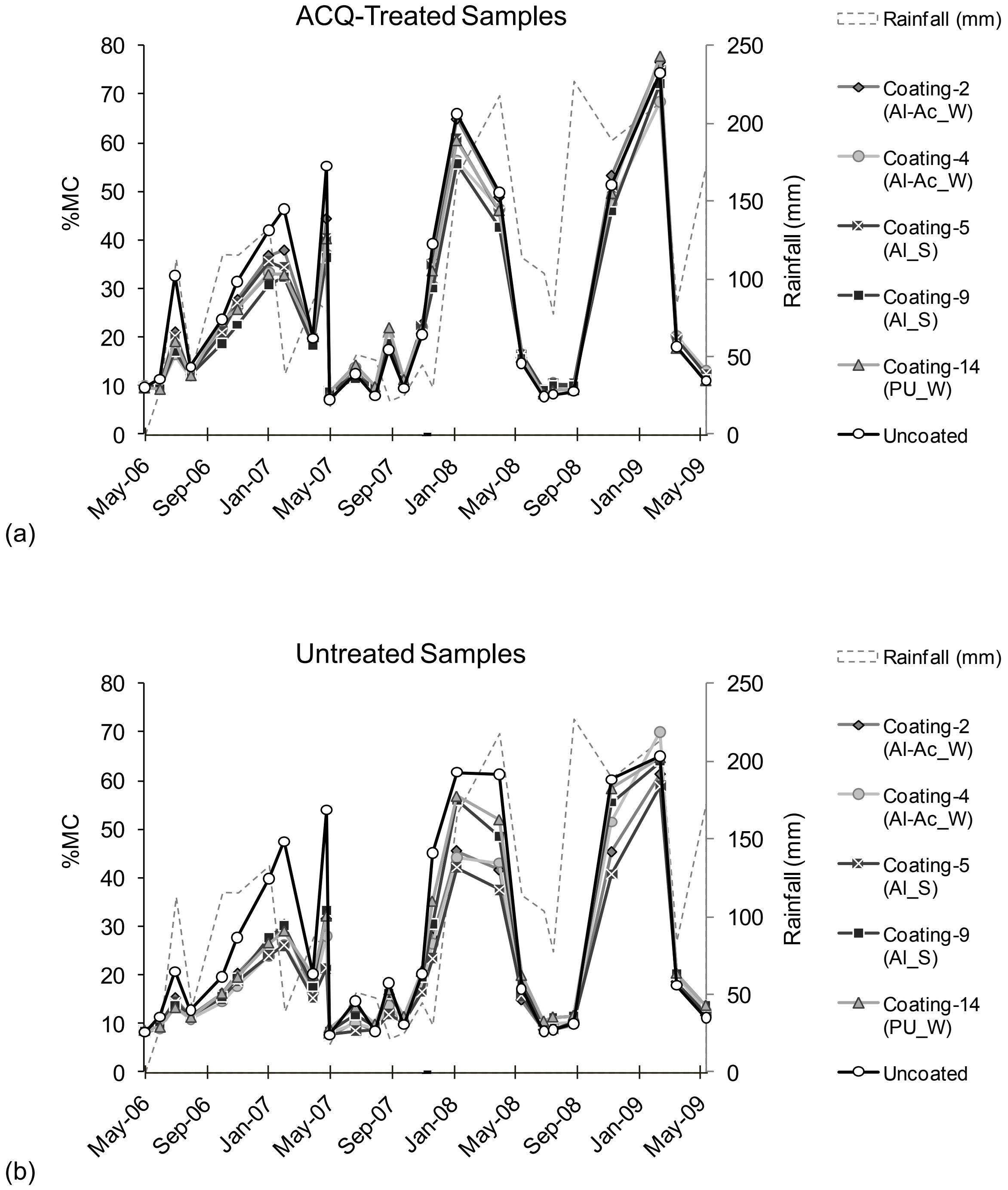


Figure 2.7: Moisture content change of ACQ-treated (a) and untreated (b) coated and uncoated samples during 3 years of natural weathering.

Chapter 3

3 Exterior Wood Coatings, Part 2: Modeling Correlation between Coating Properties and their Weathering Performance

Based on paper with the same title submitted to Journal of Coatings Technology and Research, July 2010

Authors: Mojgan Nejad and Paul Cooper

Abstract

Understanding how a coating's properties are related to its performance will help in the development of new coating formulations. In this study, exterior penetrating wood stains were evaluated for solids contents, viscosities, surface tensions and their contact angles on CCA, ACQ and CA-treated and untreated woods. The glass transition temperatures (Tg) of cured films were determined by differential scanning calorimeter (DSC) and the film thicknesses of cured coatings on wood surfaces were measured by back scattered electron imaging of osmium treated coated samples.

Partial least squares regression (PLS-R) modeling was used to correlate these coating properties with their weathering performance on preservative treated and untreated wood substrates, based on water repellency, colour retention and visual ratings after three years of natural weathering. A PLS model was developed with 77% fitting accuracy and 69% prediction ability. Preservative treatments significantly affect coating performance, and among coating properties, film thickness, viscosity and Tg has the greatest effects on the coatings' performance prediction model.

3.1 Introduction

Many factors affect performance of coatings on exterior exposed wood, including wood properties, structural design, weathering conditions and coating properties. New coating formulations are evaluated for weathering performance either by long-term natural weathering trials or by shorter term accelerated weathering tests. Natural weathering is time-consuming and often not feasible and there is always concern about results of accelerated weathering and how well it represents natural exposure.

Formulating a durable coating for exterior applications is not an easy task, especially when the substrate underneath is wood. Since wood is a biological material, it adds extra complexity to coating durability problems, since the failure mode can involve weathering of wood and interface failure in addition to coating degradation. Depending on wood species, coating types and weathering conditions, even small changes in the coating formulation may change the overall performance expectation. Unfortunately there is no defined standard for formulating coatings to achieve optimum exterior performance as there is, for example, for preservative treatment. Protecting wood from decay is based on American Wood Protection Association (AWPA) standards for pressure treating wood with preservative (e.g. alkaline copper quat - ACQ) to a defined retention (e.g. 4 kg/m^3 for above ground application). As long as preservatives penetrate deeply into the wood and fix afterwards, wood is protected from decay for a long time.

There are numerous studies on different aspects of wood coatings including effects of coatings' components on their weathering performance characteristics. These studies suggest that a good performing coating will have the following attributes:

- Low surface tension and low contact angle to provide good wettability and better adhesion [1]

- Low coating glass transition temperature (Tg) to improve film flexibility and enhance durability[1]
- Pigmentation or UV absorbers to protect the wood from UV [3], without hiding the beauty of the wood grain
- Low viscosity to ensure deep penetration [4] and ease of application; deep penetration of coating in the wood improves durability and protection against weathering of wood [5]
- High water repellency to reduce dimensional changes of the wood, thereby reducing coating and interface failure [6, 7]
- Mildew resistance to reduce biological damage and discoloration of the coating and substrate [8]
- Compatibility with a broad range of substrates, including pressure treated and untreated softwoods, hardwoods and composites.

For exterior wood, semitransparent penetrating stains are recommended [9] because they do not crack and peel during exposure when wood shrinks and swells. Among stain formulations, solvent-based coatings are often recommended due to their higher water repellency [6, 10-11], since most water-based coatings incorporate surfactants which make the wood surface more hydrophilic [6, 12] and are more permeable. Resin type is another main factor that affects coating durability; alkyd resins are known to penetrate better into the wood [13, 14], while acrylics provide better UV-protection [15] and polyurethanes generally have high exterior durability [3].

While there are many factors that constitute good performance of a coating on exterior wood products, we believe that the most important criteria for good performance are the following. A good coating should reduce water uptake, minimize colour change in service, and improve the general appearance of the wood (e.g., reduce checking of wood and mildew growth) in comparison with uncoated samples; also, the coating should resist erosion or peeling from the surface. Looking individually at the above mentioned performance criteria is not adequate to evaluate a coating's performance; for example, a coating with a thick film layer may be effective for reducing water uptake of wood over the short term, but may eventually peel from the surface. This failure will both affect appearance and increase maintenance costs due to required surface preparation before re-finishing, and that it is not appealing to end users.

This study was originally designed to measure the ability of coatings to reduce wood preservative leaching. To explain different coatings' performances on different preservative-treated woods, correlations among some of the coating properties and their performances were investigated.

To investigate the correlation, partial least squares regression modeling (PLS-R) was used that can model response variables (e.g., performance characteristics) resulting from many factors (e.g., coatings properties), even when these factors (X variables) are not independent [16, 17]. This study was the first to use PLS to model correlation between coating properties and coating performances (even though many coating properties are strongly correlated with one another).

Part-1 of this paper (Chapter-2) [18] evaluated performance criteria of coatings applied on CCA, ACQ, CA and untreated wood samples during three years of natural weathering in Toronto, Canada. Coatings were evaluated for their ability to reduce water uptake, colour change, checking of wood, mildew growth and other parameters that degraded their appearance during this time.

In this study, a number of coating properties were determined and these properties and the preservative treatment types were related to the coating performance parameters to identify which coating properties and preservative types would most influence coating performance. The results of such a prediction model will be helpful for identifying some of the coating attributes that should be considered when formulating a coating for wooden decks.

3.2 Materials and Methods

Properties of coatings

Fourteen commercially formulated honey-brown coloured stains were purchased based on manufacturer recommendations for deck finishes to investigate the interrelationships among coating properties. Liquid coatings were analyzed for pH by pH meter (Orion SA 520) and viscosities were measured at 20°C by Brookfield dial reading viscometer using spindle #1 @ 20 rpm for most coatings except coatings number 10 and 14 which were measured by spindle #2 @ 20 rpm. Solids contents were determined based on ASTM D2369 test method; coatings were placed on an aluminum pan and heated in an oven at 110°C for 60 minutes. Specific gravities of coatings were measured by hydrometer (G & W instruments) at 20°C. Surface tension of coatings were determined by Sigma 70 Tensiometer at speed 20mm/min, wetting depth 6 mm using Wilhelmy plate (22mmX 50mmX 0.15mm) with average of 10 readings for each samples.

Contact angles of coatings on untreated wood or wood treated with chromated copper arsenate (CCA), alkaline copper quat (ACQ) and copper azole (CA) were analyzed by goniometer after 1 minute with several readings on latewood and earlywood areas of the woods (conditioned at 10% moisture content). In addition dynamic contact angles of a few coatings were measured by axisymmetric drop shape analysis-contact diameter (ADSA-CD) technique [19]. The contact angles of coatings were calculated based on contact diameters of coatings by placing 7µl of coating (with known surface tension) on flat sawn wood samples conditioned at 10% moisture content, and images of the coating sessile drops were obtained from above using a CCD Video Camera (5 images/second).

Glass transition temperatures (Tg) of coatings, were determined on 2ml samples of each stain, cured on an aluminum plate at 100°C for one hour and left to air dry for one month. Tg's of two replicate samples of each cured film were measured by differential scanning calorimeter DSC-Q1000 with temperature increasing at 10°C/min in 2 cycles of heat/cool/heat from -80°C to 80°C.

Film thicknesses were determined for small specimens cut from the replicate kept in the lab as controls (coated–untreated). Three replicate cross sectional samples (5mm X 5mm X 2mm long) of each coated wood sample (only latewood in contact with coatings) were exposed to 1g of osmium tetroxide crystal in a desiccator for 48 hours. Sublimed osmium tetroxide bonds to unsaturated C=C bonds, which are primarily found in the coating layer rather than in the wood. After one week of degassing, 3 replicates of each coated wood sample were embedded in ultra low viscosity epoxy resin from Buehler Epo-thin 20-8140-128 and left overnight at room temperature to cure. The samples were polished with oil-based diamond paste (9 µm particle size followed by 1 µm particle size) using a Logitech LP-30 polisher.

Back scattered electron (BSE) images of carbon coated samples were obtained using a Joel-840 SEM. The images were generated using 15KV accelerating voltage and 1x 10^{-9} amp current beam at a 12 mm working distance for samples. Coating layers in the image were then inverted to black and the rest of the sample to white using Photoshop software. Film thickness of coatings were determined by Image J software; first images were transformed to Binary (Process-Binary-make Binary), then the coating layer was selected and saved as X, Y coordinates (Analyze-Tools-Save XY coordinates). For a given X coordinate the film thickness was calculated based on the difference between maximum Y and minimum Y value in generated files. The average film thickness of the data obtained was based on pixels which were then converted to µm based on the resolution of the image (1024x768).

Evaluation of coating performance

Flat-sawn southern pine sapwood lumber was treated with CCA, ACQ and CA to retentions specified for above ground exposure, or left untreated. Five coatings, covering a wide range of formulations and properties (coatings # 2, 4, 5, 9 and 14 in Table 2) were applied on the top and end surfaces of treated and untreated wood samples (20mm x 140mm x 280mm). Samples were exposed to natural weathering horizontally from May 2006 to May 2009, in Toronto, Canada and water uptake and colour change were measured during this time. Specimens were also ranked based on their general appearance (checking, mildew growth and coating deterioration) using appropriate ASTM tests methods. A Detailed description of treatments and results was given in Chapter-2.

Data Manipulation

All data were scaled to unit variance to avoid domination of one variable over others because of its magnitude. Data were also mean-centered, by which all data were subtracted from their means to improve interpretability of the model. Viscosity and film thickness values were logarithmically transformed to have closer distribution to normality. The X and Y variables that were used in the models and a detailed description of the data preprocessing are given in Table 3.1.

Table 3.1: X and Y variables included in PLS regression modeling, their preprocessing and description.

Variables	Variables ID	Transformation	Description
Xs	Preservative Treatment	Dummy variables (0,1)	(CCA, ACQ, CA and untreated)
	Surface Tension	UV*	
	Contact Angle	UV	
	Viscosity	Log transformation & UV	To overcome positive skewness
	Solid Content	UV	
	Tg	UV	
	Film Thickness	Log transformation & UV	To overcome positive skewness
Ys	Water Repellency	UV	Efficiency of each coating in reducing average water uptake during 3 years compared to uncoated samples
	Colour Retention	UV	Efficiency of each coating in reducing colour change (Max ∆E) during 3 years compared to uncoated samples
	Visual Rating	UV	

*Variables have been transformed to unit variance scaling and mean centered

3.3 Results and Discussion

3.3.1 Coating properties

All measured coating properties are presented in Table 3.2. Contact angles of coatings refer to average contact angles of coatings on untreated wood samples after one minute (average of several readings on latewood and earlywood); coating thicknesses are also for related to coating film thickness measured on untreated wood samples.

Table 3.2: Description of coatings and their measured properties

	Resin Type	Base	Specific gravity	pH	Surface Tension (mN/m)	Contact Angle°	Viscosity (cP)	Solid Content (%Wt)	Tg (°C)	Film Thickness (µm)
1	Alkyd	W	1.02	8.1	32	5	10	17	26	9
2	Alkyd-Acrylic	W	1.02	8.1	31	36	29	27	16	15
3	Alkyd	S	0.98	5.2	25	10	72	47	10	---
4	Alkyd-Acrylic	W	1.03	7.8	30	22	18	28	-11	12
5	Alkyd	S	0.85	4.8	25	0	10	38	17	2
6	Alkyd	S	0.85	4.8	24	0	27	35	-10	---
7	Alkyd	S	0.85	2.7	23	7	41	31	28	12
8	Alkyd	S	0.88	4.7	25	1	33	45	-31	5
9	Alkyd	S	0.92	4.7	25	21	124	46	-7	34
10	Alkyd-Acrylic	W	1.09	8.5	35	39	903	27	2	---
11	Alkyd	S	0.85	5.7	24	0	14	26	-7	---
12	Alkyd	W	1.01	7.3	32	25	60	10	-1	---
13	Alkyd	S	0.95	7.0	25	21	149	42	-10	---
14	Polyurethane	W	1.04	7.9	33	42	270	29	-7	37

Pearson correlation analysis of coatings properties indicated a significant positive correlation between: pH and specific gravity (r=0.91, P_{value}= 0.0001); specific gravity and surface tension (r=0.91, P_{value}= 0.0001); specific gravity and contact angle (r=0.80, P_{value}= 0.01); pH and surface tension (r=0.97, $P_{value} < 0.0001$); pH and contact angle (r=0.73, P_{value}= 0.02), and contact angle and film thickness (r=0.65, P_{value}= 0.04). Solid content was negatively correlated with surface tension (r=-0.78, P_{value}= 0.008) and pH (r=-0.77, P_{value}= 0.009), but was not substantially correlated with any other variables. The water-based formulations generally had higher pH, and so they were also associated with higher specific gravity, surface tension and contact angle and lower solid content, compared to the solvent-based formulations. There was also a strong positive correlation between film thickness and viscosity of the coating (r=0.88, P_{value}=0.004). As expected, coatings with poor wetting properties (large contact angle) and high viscosity resulted in thicker films on the surface.

Contact angles of coatings after one minute measured by goniometer on different preservative treated and untreated wood samples are shown in Figure 3.1. The high standard deviations of samples are mainly related to differences between contact angles of coatings on latewood and earlywood sections of the woods. Lower values indicate better wetting and penetration of the coating in the wood surface. The average contact angle of coatings on latewood was significantly (α=0.05) higher than on earlywood (18.5 vs 14.4) which could be due to large cell cavities and low density of earlywood.

However, based on two-way ANOVA results there were no significant differences among contact angles of coatings on different preservative treatments, indicating that preservative treatment did not change the surface energies of wood samples as mentioned by Cao et al. [22].

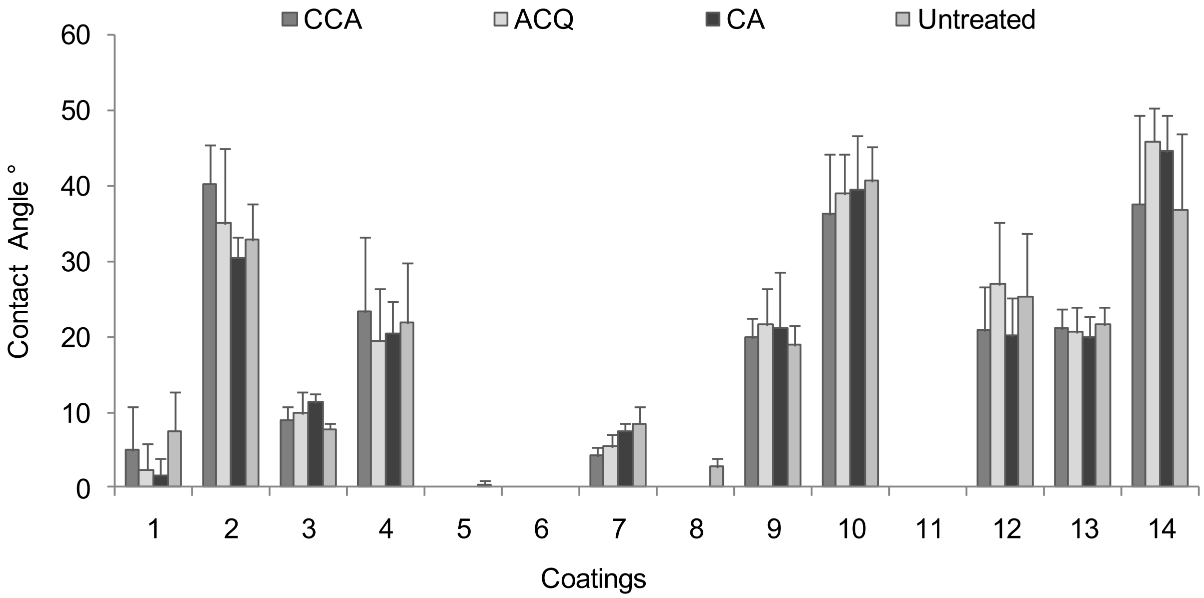
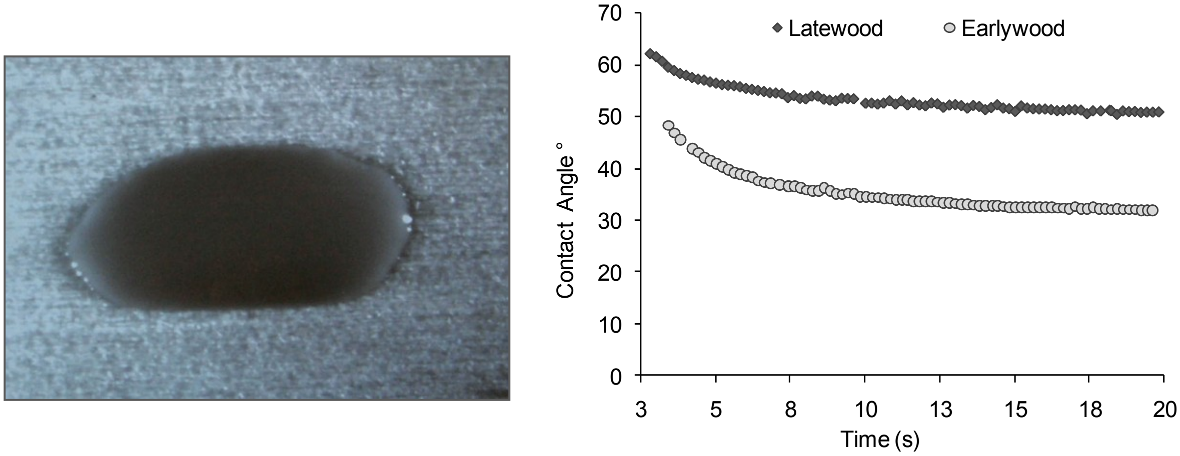


Figure 3.1: Average contact angle of coatings on different preservative treated and untreated wood samples. Values equal to zero indicate immediate penetration of the coating into the wood surface.

An image of a sessile drop of coating-2 on untreated latewood after 20 seconds is shown in Figure 3.2(a) during dynamic contact angle measurement. Spreading of coating along the grain is clearly shown in the image. This effect was even greater on earlywood. Changes in contact angle of coating-2 on untreated wood (tangential direction) during the first 20 seconds are shown in Figure 3.2(b).

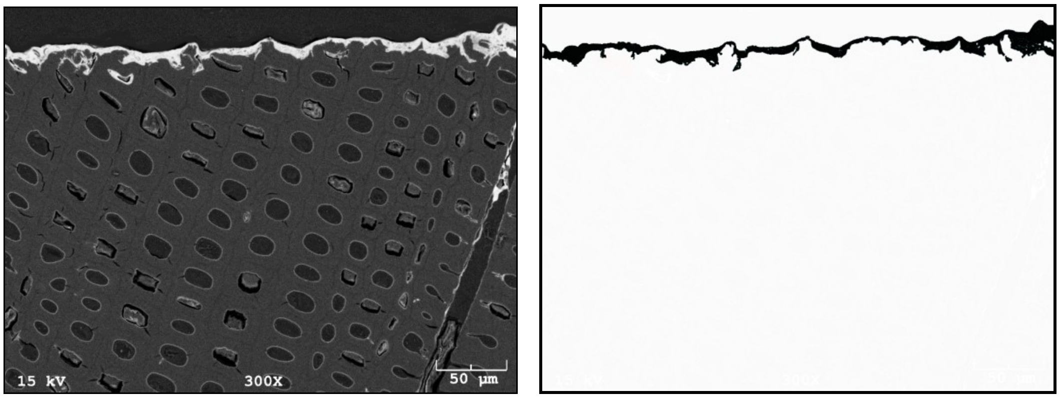


(a) (b)

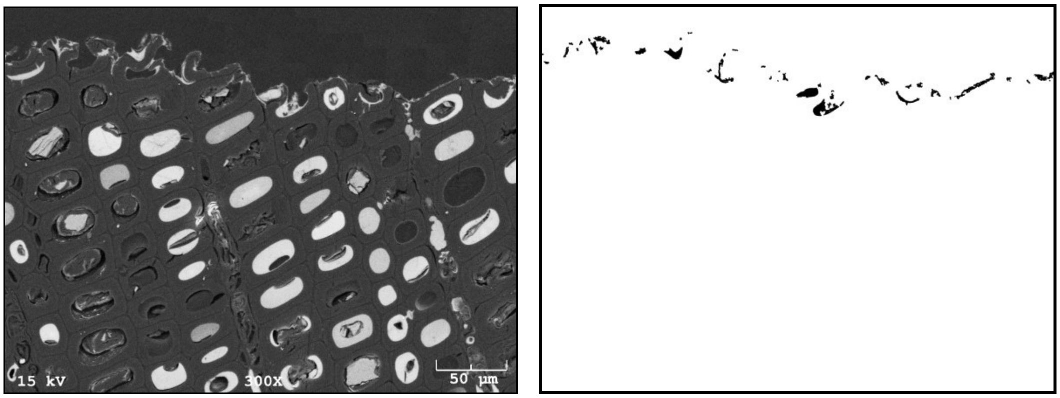
Figure 3.2: (a) Image of coating -2 (alkyd-acrylic water-based) on untreated wood after 20 seconds. (b) Dynamic contact angle of coating- 2 on untreated wood samples.

Examples of images of osmium treated coated wood samples in backscattered mode and transformed Photoshop images for determining coatings' film thicknesses are shown in Figure 3.3. Penetration of coatings deep into rays was clearly visible for all coatings, but penetration and accumulation of coating into cell lumens were only seen for coating number 5, a very low viscosity alkyd solvent-based coating.

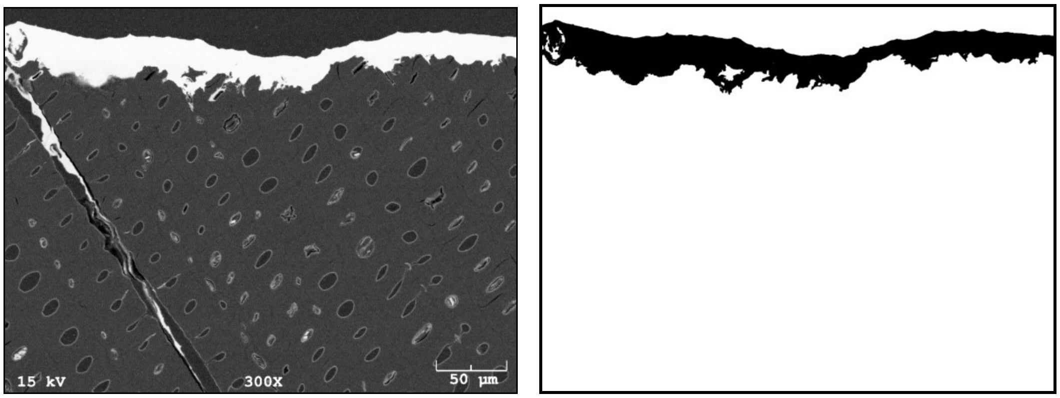
Coatings had different penetration patterns, depending on the resin type, but also within the same resin type. Coatings 5 and 9 were both alkyd solvent-based; however, low viscosity, low contact angle coating #5 penetrated rapidly and completely leaving little visible film (2.4±2 μm, Figure 3.3-b), with obvious resin distribution through the upper cells of wood. Coating # 9 which had higher viscosity and contact angle had greater film thickness (33.7±8 μm image not shown here). The highly viscous coatings, such as polyurethane water-based coating #14, formed a thick film layer (37.1±11 μm) on the surface (Figure 3.3-c).



(a) Coating-4: Alkyd-Acrylic, Water-based



(b) Coating-5: Alkyd, Solvent-based



(c) Coating-14: Polyurethane, Water-based

Figure 3.3: BSE image of osmium treated coated wood and transformed Photoshop images for film thickness estimation.

An example of a coating after weathering is shown in Figure 3.4 (Coating-4). Checking of wood developed mainly through the rays and penetration of coatings through rays might contribute to reduced surface area of checks observed in coated samples compared with uncoated samples after 3 years of weathering [18].

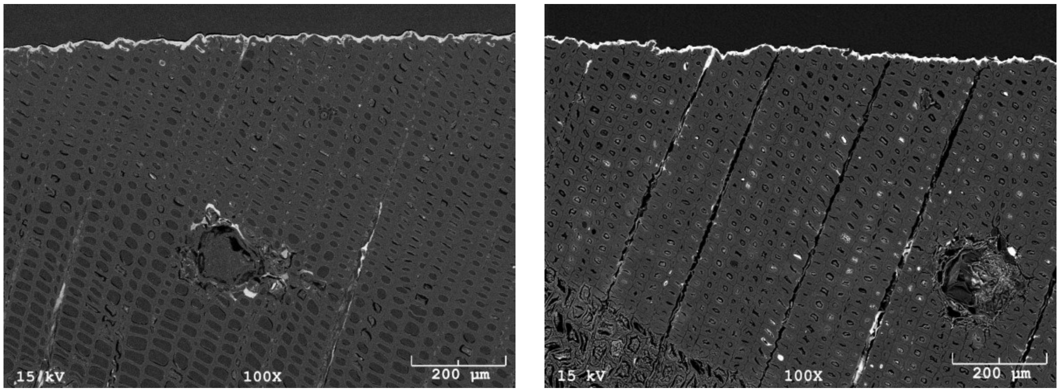


Figure 3.4: BSE image of cross section of unweathered sample left and weathered sample right (Coating-4)

3.3.2 Modeling

The objective of the modeling was to determine whether measured coating properties were related to the durability performance of the coatings on the three defined criteria, colour retention, water repellency and visual rating [18]. The PLS model developed after three PLS components had 77% fitting accuracy (R^2Y = the explained variation) and 69% prediction ability (Q^2Y=the predicted variation) based on a cross validation method. Three PLS components were shown to be optimum for the model [16]. Figure 3.5 plots the components' contributions; light coloured bars represent R^2 as indicator of how well the model fits the measured data for each performance criterion and dark coloured bars show Q^2 as an indicator of how well the model can predict the coating performance for a new coating formulation. Both fitting accuracy and prediction ability of the model were higher for all three modeled criteria were above 60% indicating that the model is good [16]. Small differences between R^2 and Q^2 (less than 0.2) also signified that there were no irrelevant model terms or outliers in the data points [16].

Liquid stain specific gravities and pH values were not included in the model, since they had very little influence on model improvement. This is expected as these two properties are strongly correlated to surface tension and coating base (solvent or water-based). The model presented herein does not include 4 observation samples which were shown to be outliers, mainly because of splitting of those samples during natural weathering.

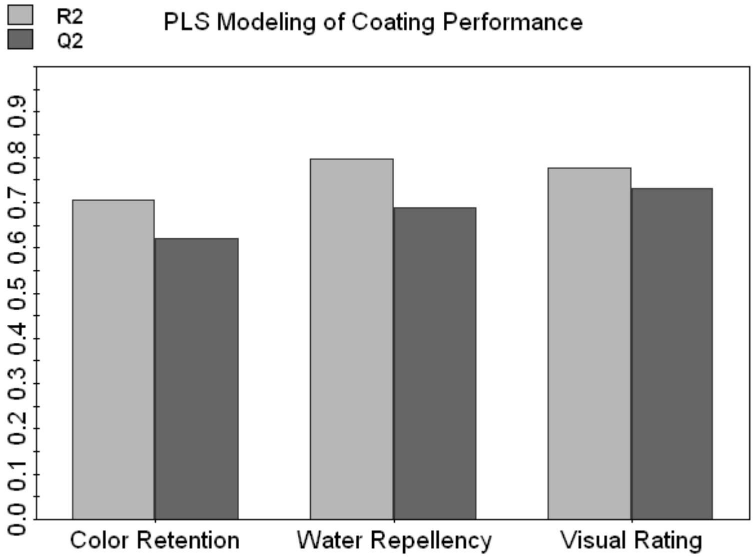


Figure 3.5: Component contribution plot for all response variables (coating performance criteria)

The PLS loadings plot (Figure 3.6) shows the relationship among the factors (treatment type and measured coating properties) and the three response variables (water repellency, colour retention, and visual appearance rating). The further a variable lies from the plot origin, the stronger its influence on the model. Variables close to each other on one side of an axis have a strong positive correlation, but will have a negative correlation with other variables on the opposite side of the axis.

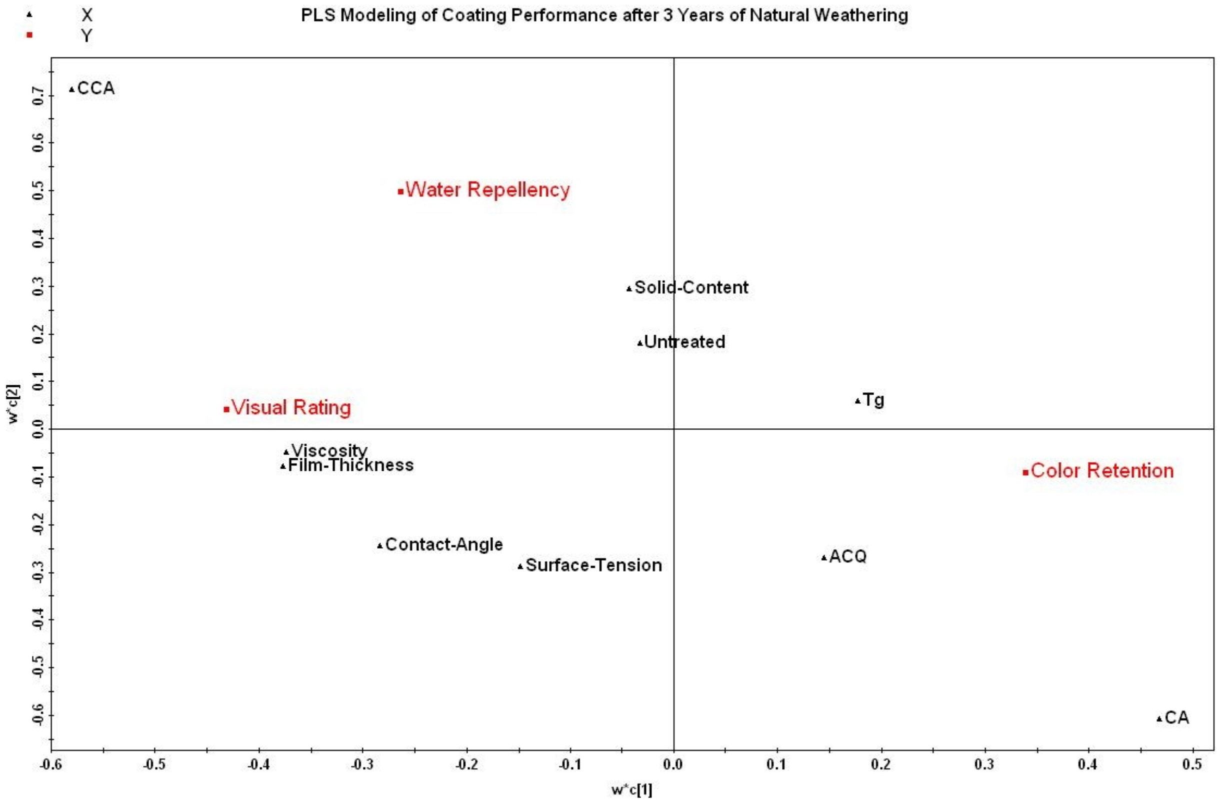


Figure 3.6: Loadings plot of PLS regression modeling of coating performance based on coating properties.

Preservative treatments (CCA, ACQ and CA) significantly affected the modeling results. As can be seen in Fig. 3.6, they are located far from the center. CCA treatment was associated with higher water repellency and visual ratings of samples. ACQ and CA treatments were negatively related to water repellency, and they improved the colour retention of coated samples.

Water repellency imparted by the coatings was positively related to the solid content. Also, coatings which formed a thick flexible film layer on top of the wood surface (higher viscosity, higher film thickness, and lower Tg) had overall better water repellency and visual ratings. However, the erosion of coatings from surfaces of wood, especially in coatings with thicker films, caused the colour retention performance after the three-year exposure to be negatively correlated with film thickness and viscosity.

Although coatings with low contact angles and deep penetration are usually considered advantageous for exterior wood coatings, coating #5 with zero contact angle and no film layer on the surface of wood showed the worst performance in natural weathering consistent with the modeling results.

Future work is needed to measure performance criteria of a wide range of coating formulations with less variability in the wood surfaces caused by species and treatment differences. This will allow a prediction model to be developed that is less influenced by preservative treatments and magnifies the effects of coating properties and will help identify the optimum film thickness that will improve both visual ratings and colour retention.

3.4 Conclusions

A number of coating properties including solids content, pH, specific gravity, surface tension, contact angle, Tg, viscosity and film thickness were measured. Coatings had lower contact angle (better wetting) in earlywood than latewood areas, and there were no significant difference among contact angles of coatings on different preservative treated woods. Back scattered images of osmium treated coated wood samples after weathering showed that checking of wood mainly develops through the rays and since most coatings had deep penetration into the rays, we believe that a surface coating with high flexibility (low Tg), good adhesion and cohesion should reduce checking of wood.

A partial least squares regression (PLS-R) model was developed with 77% fitting accuracy and 69% prediction ability, to correlate measured coating properties with their weathering performances after three years of natural weathering on preservative treated and untreated woods. All predicted performances were highly sensitive to preservative treatment types. CCA treatment greatly enhanced both water repellency and visual ratings. ACQ and CA improved colour retention of coated samples but reduced water repellency. Coatings which formed a thick, flexible layer of film on the top of the wood surface had overall higher water repellency and appearance ratings, but lower colour retention because of erosion of the coating layer from the surface during weathering.

3.5 References

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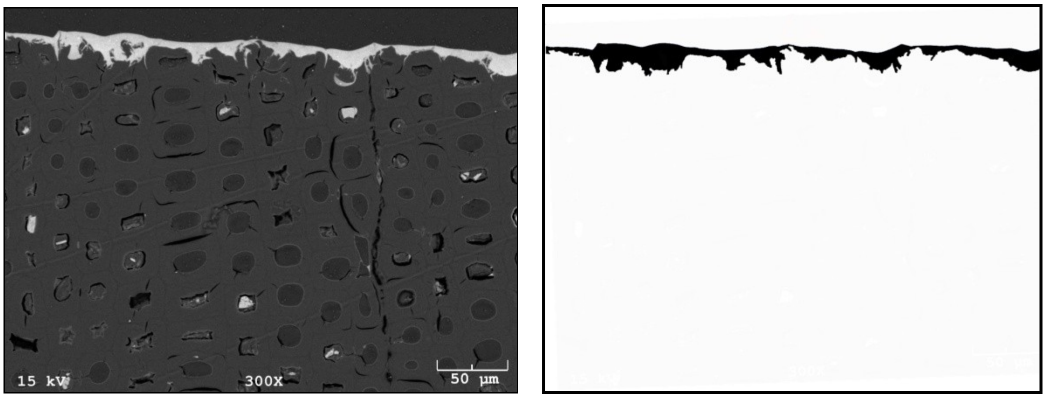
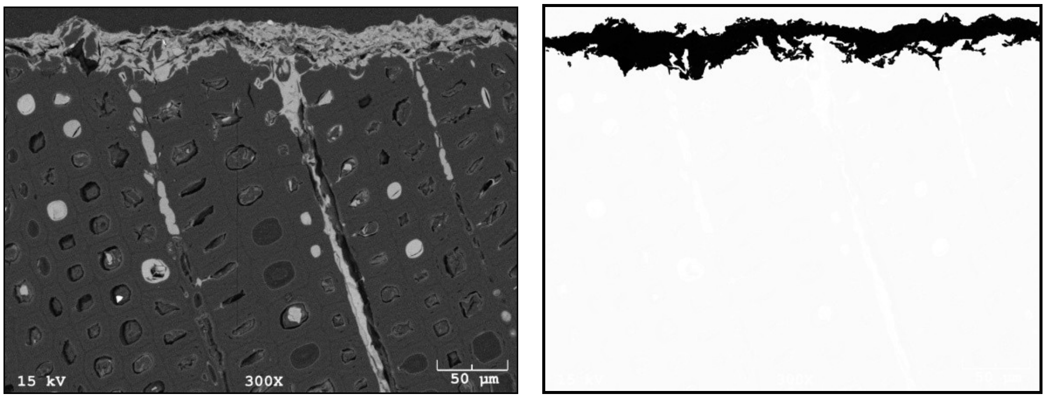
3.6 Supporting Information



(b) Coating-2: Alkyd-Acrylic, Water-based



(b) Coating-9: Alkyd, Solvent-based

Figure 3.7: BSE image of osmium treated coated wood and transformed Photoshop images for film thickness estimation.

Chapter 4

4 Investigation of Imaging ToF-SIMS as a Means to Study Coatings on Wood

Based on paper published online with the same title in Journal of Surface and Interface Analysis, June 22, 2010, Volume 42,DOI: 10.1002/sia.3619

Authors: Mojgan Nejad, Paul Cooper and Rana Sodhi

Abstract

Measuring penetration of coatings into wood may be performed by SEM analysis with samples treated with OsO_4 or other markers used for post-treatment labeling. However, there are indications that Os only binds with the uncured components of the resin. Since these are mainly located at the surface of the coating, the use of Os could thus misinterpret the actual penetration of the coating into the wood surface. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provides a unique means by which the penetration depth of the various components of the coating (resin + pigments) into the wood microstructure can be visualized. This arises from both the high spatial resolution (< 100 nm) and high mass resolution achievable with the technique (albeit not at the same time). The latter feature is of importance to resolve different molecular fragments of similar molecular weight which could be needed as markers for the various components in the complex hydrocarbon systems constituting wood and the coating materials, whilst the former is required to ascertain differences in penetration depth of the components.

In this work, imaging ToF-SIMS spectra are obtained on cross-section of coated wood samples using a bismuth cluster ion source. Coating distribution is followed by identifying fragments

associated more with the coating and with the wood respectively. Sample preparation techniques are of importance and thus results are compared for cross-sections prepared both by microtoming, as well as by mounting in epoxy resin and polishing.

4.1 Introduction

Coatings are applied on the wood surface both for aesthetic reasons and to protect the surfaces from external factors such as moisture, UV degradation and physical wear. Penetrating stains are favored for applications such as exterior decking to reduce effects of weathering such as splitting, warping and UV discoloration.

However, the effectiveness of a coating depends on many factors including the ability of the coating to wet and penetrate the wood surface and the film thickness of the coating on the surface. Higher penetration depth increases mechanical adhesion of a coating within the wood and may increase dimensional stability of the wood. Also, penetration of a coating into cell walls provides adequate anchoring with the wood, which affects the service life of coated wood samples [1, 2]. Conversely, coatings that do not penetrate adequately form a thick film layer on the wood surface, which may provide better physical protection. It is important to be able to quantify the film thickness and coating penetration depth of different coating components so these characteristics can be related to the performance of the coating.

Coating penetration into the wood depends on the molecular weight of the resin (binder) used in the coating, and on the size of the openings in the wood cell walls. For example, acrylic emulsion binders should have a particle size less than 100 nm in order to penetrate into the wood; therefore, enhance better adhesion when used in an exterior wood coating [3].

Extensive research has been carried out on the topic of measuring penetration depth of paint (film-forming coatings) into the wood [2, 4], but the optimum penetration depth of penetrating stains has not yet been determined. Measurement of the penetration of coatings into the wood may be performed by SEM analysis with OsO_4 or other markers used for post-treatment labeling [5]. Since osmium tetroxide reacts with unsaturated carbon–carbon double bonds (C=C), we believe that Os only binds with uncured components of the resin. Since these are mainly located at the surface of the coating, the use of Os could thus misinterpret the actual penetration of the coatings into the wood surface. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) should provide a unique means by which the penetration depths of the various components of the coating (resin + pigments, etc.) into the wood microstructure can be visualized. This arises from both the high spatial resolution (<100 nm) and high mass resolution achievable with the technique (albeit not at the same time). High mass resolution is important to resolve different molecular fragments of similar molecular weight which could be used as markers for the various components in the complex hydrocarbon systems constituting wood and the coating materials. Obtaining images in high spatial resolution mode is required to ascertain differences for measuring penetration depth of different coatings components into the wood cell walls.

In this work, imaging ToF-SIMS spectra are obtained on cross-sections of coated wood samples using a Bi cluster ion source. Penetration (or lack thereof) is followed by identifying fragments associated more with the coating and with the wood, respectively [6, 7]. Sample preparation techniques are of importance and, thus, results are compared for cross-sections prepared both by microtoming, as well as by embedding in epoxy resin and polishing.

4.2 Materials and Methods

The polyurethane coating (2K water-based, commercial stain formulated for deck applications) consisted of two steps; step 1 as a penetrating stain, and step 2 as a UV-blocker. The first step was applied by brush on the top surface of flat-grained sapwood of southern pine (commercial lumber with 6–8 annual rings) with moisture content around 12% and allowed to air dry for one hour prior to the application of the UV-blocker. These samples were subsequently cross-sectioned as described below.

Three different methods were used for sample preparation of coated-wood cross sections. In the first method, a thin layer of wood sample measuring 2 × 2 × 8mm^3 was placed in the sample mount of a Leica EM UC6 Ultra-microtome (Leica Microsystems GmbH, Vienna, Austria) and cut with a diamond knife. The direction of cut was parallel to the wood-coating interface (i.e. blade edge perpendicular to the interface). Embedding the sample in epoxy resin was avoided due to concerns of the interaction of the coating material with the resin. However, for previous SEM analysis, a sample (5 × 5 × 2mm^3) had been prepared by embedding in low viscosity epoxy resin (Buehler # 20-8140-128) and left overnight to cure. This sample was polished with 9 and 1 µm diamond paste using Engis Multispeed and Buehler Metaserv polishing machines. Thus, imaging ToF-SIMS analysis was also performed on this polished sample for comparison with the microtomed samples. Finally, coated surfaces of the wood, as prepared for the first method, were placed face to face and held together in a small custom built vice, milled to a size suitable for the microtome using a Leica EM TXP Target Sectioning System. This sample (about 2mm thick) was then microtomed as before using the diamond trimming knife.

The ToF-SIMS spectra were obtained on a TOFSIMS IV (ION-TOF GmbH, Munster, Germany) equipped with a Bi cluster source. A Bi $^{3++}$ primary ion beam (25 keV, 0.3 pA) was used to generate the spectra in both high spatial and high spectral resolution modes[8]. Charge neutralization was achieved utilizing the pulsed electron flood gun supplied with the instrument. Both positive and negative spectra were collected. Reference spectra (high mass resolution mode) were obtained on the coating and wood alone.

4.3 Results and Discussion

Figures 4.1 and 4.2 show the reference spectra of the wood sample and that of the penetrating stain, respectively. The latter, which forms part of the coating, was obtained by oven drying a few drops placed on a glass dish for one hour and allowing to further cure in air for one month. From this, we should be able to identify characteristic peaks from the coating in order to follow its penetration. Ideally, lignin should be able to provide two good markers for the wood at masses 137 and 151 in the positive spectrum [6]. Unfortunately, as can be seen in Fig. 4.1, these peaks are hardly discernable as compared to spectra shown by Saito et al. [6].This may arise from the presence of a contaminating layer (peaks at 73 and 147 suggest the presence of a siloxane).

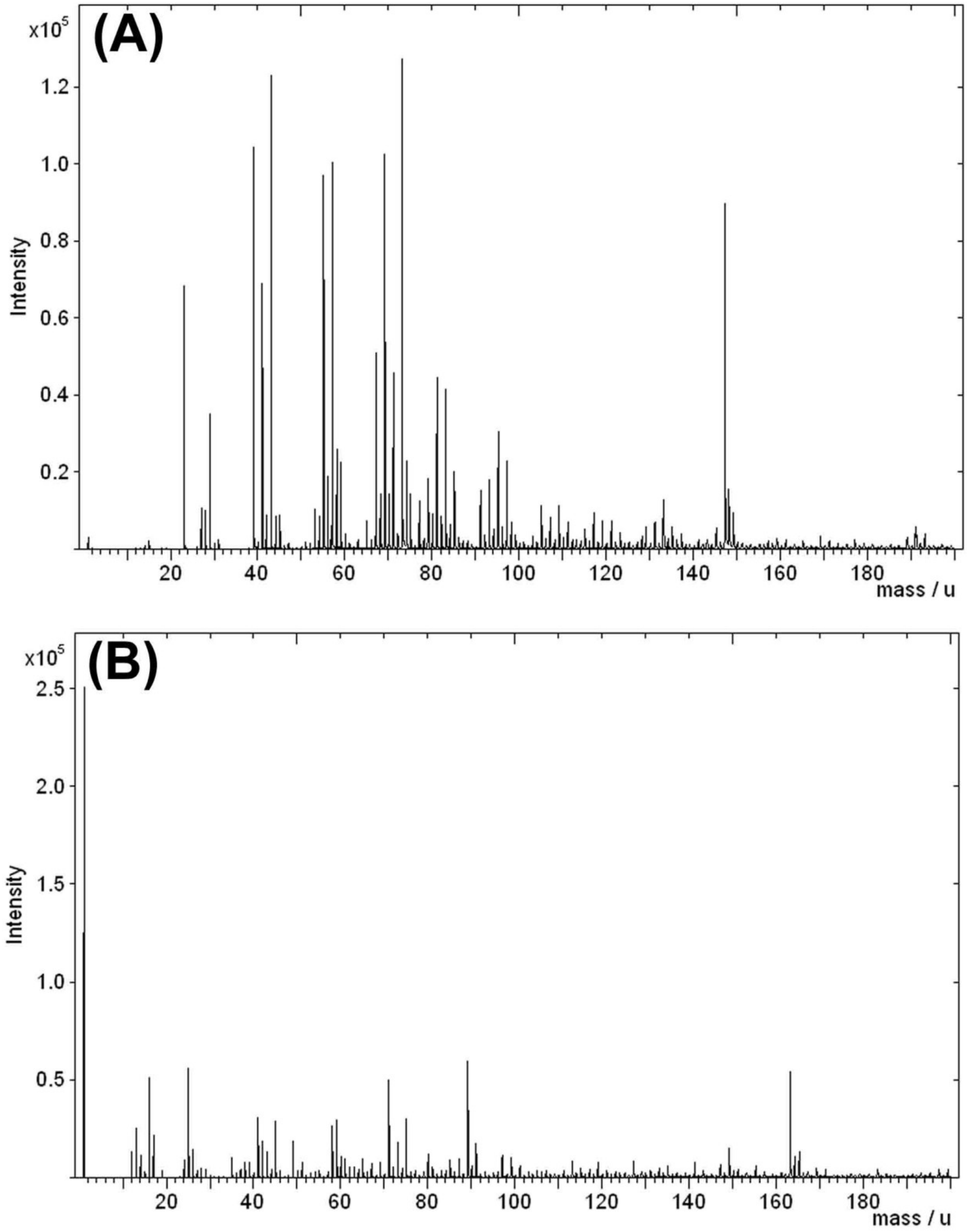


Figure 4.1: ToF-SIMS spectra of pure wood: (A) positive ion spectrum; (B) negative ion spectrum.

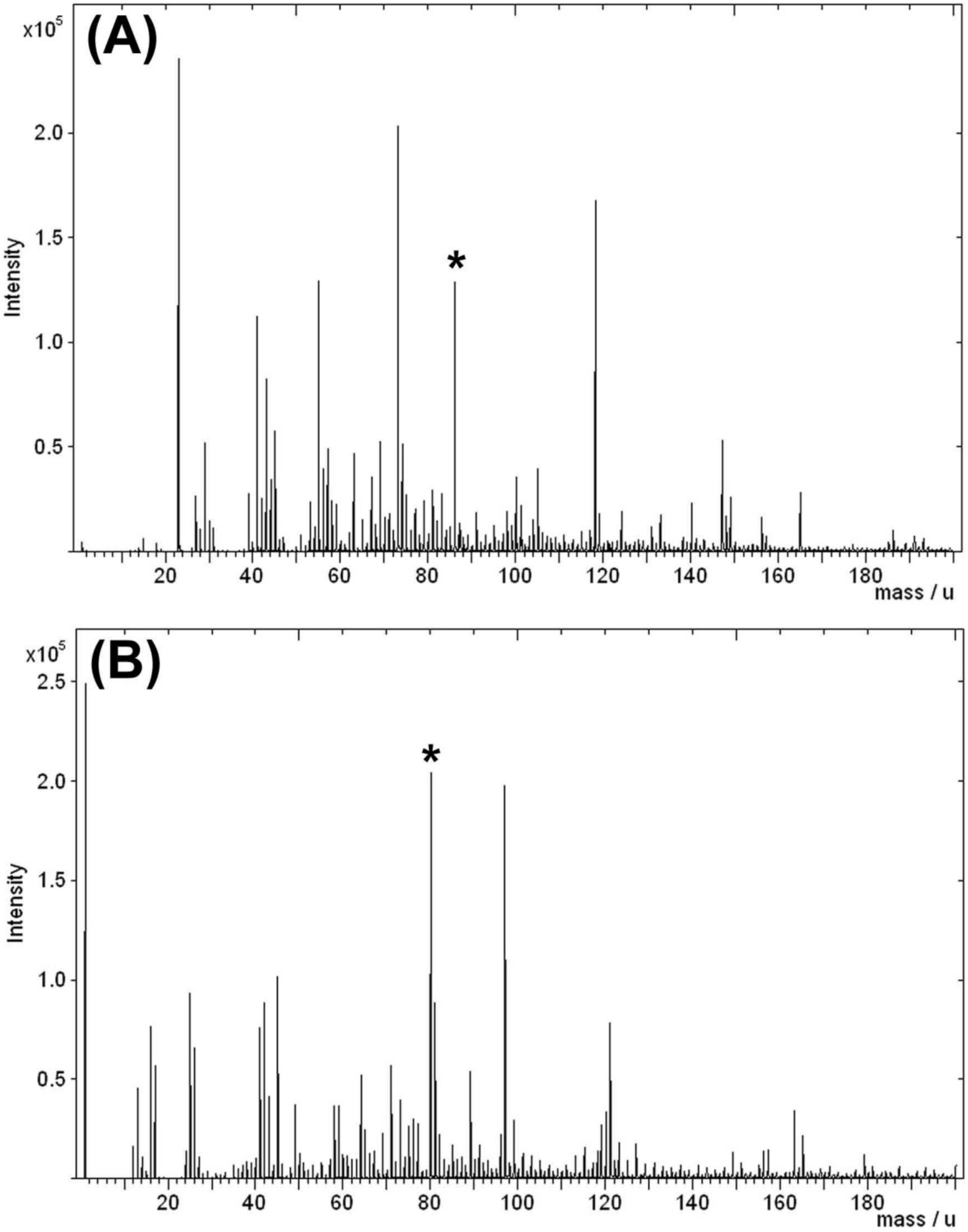


Figure 4.2: ToF-SIMS spectra of pure coating (stain): (A) positive ion spectrum; (B) negative ion spectrum. Peaks used to follow coating are labeled with an asterisk (∗).

However, in the actual cross-sections (Fig. 4.3), the siloxane features were greatly reduced and the lignin peaks are clearly present (albeit still weak) in the wood part of the sample, and absent in the coating part. Thus, the sum of these two peaks was used as a marker for the wood. Masses 86 and 80 were used to represent the coating for the positive and negative spectra, respectively, as seen by their prominence in the coating spectra (Fig. 4.2) and relative absence or weakness in the wood spectra (Fig. 4.1)

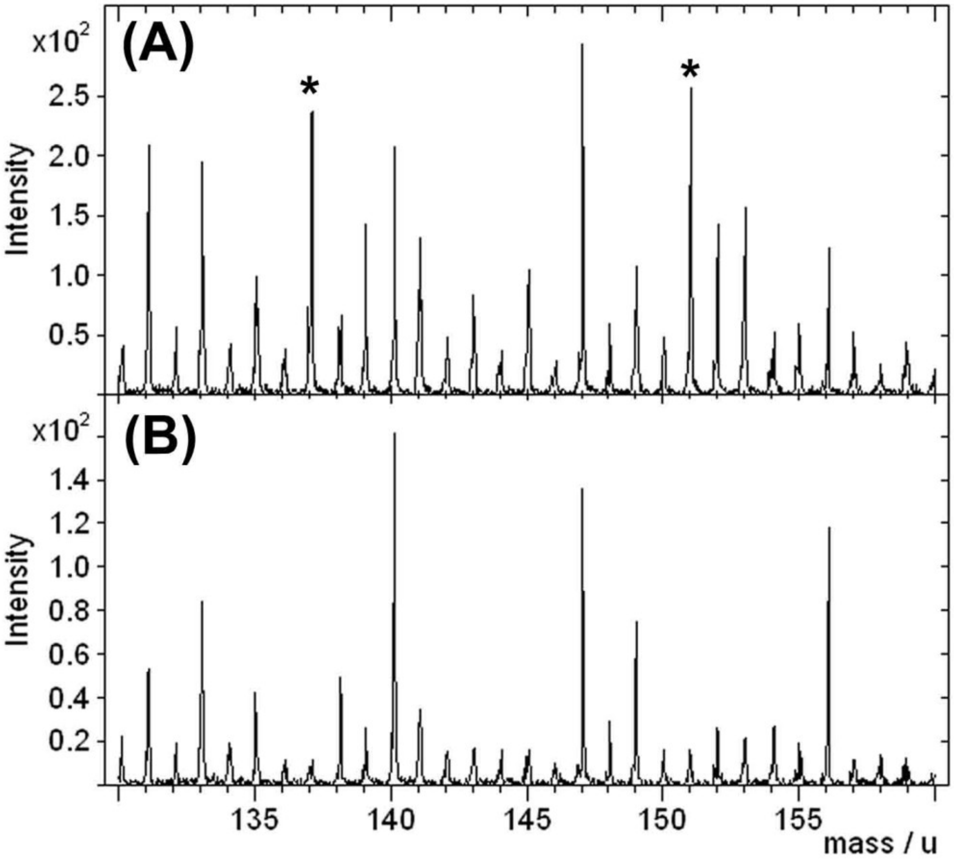


Figure 4.3: Detail of mass range 130–160 amu for the positive spectra of (A) wood region, and (B) coating region obtained from the microtomed sample. Peaks associated with lignin (137 and 151) [6] are labeled (∗) and are clearly associated with the wood.

In addition to identifying characteristic peaks to follow penetration, sample preparation to produce a smooth surface is extremely important. Ideally, preparation of the cross-section should be on the wood alone. This avoids possible interaction between the PU coating and the epoxy resin. However, the coating is a thin layer at the side of the wood sample, and hence, good images were difficult to obtain with ToF-SIMS due to field effects.

To measure coating‘s film thickness, a sample was embedded in epoxy resin and polished. This alleviated the edge effects and produced a good surface for imaging. Although this is fine to determine topographic information e.g., by SEM, it can pose difficulties for techniques such as ToF-SIMS where chemical information and distribution are often required. Problems can arise from smearing, and in this case, possible interactions between the supporting epoxy resin and the coating. Figure 4.4 shows the polished cross section of a coated sample embedded in epoxy. The presence of the coating layer is clearly seen from the contrast between the epoxy, coating and wood layers. There does appear to be some interaction between the coating and the epoxy – suggesting an intermediate region between the pure epoxy and the ‘‘pure’’ coating. Also shown in Fig. 4.4 are overlays of lignin (red in figure) and mass 86 (green in figure) in the positive spectrum and similar plots for fragments 45 (red) and 80 (green) in the negative spectra. The ‘‘red’’ fragments are representative more of the wood, whilst the ‘‘green’’ fragments are representative of the epoxy/coating. Smearing of the ‘‘green’’ components is clearly evident. While epoxy/coating interaction remains a problem, removal of the smeared overlayer by sputter cleaning remains a possibility, especially if a C60 source is employed and providing that the molecular information is indeed retained. This is currently under investigation.

Microtoming of the dry sample is preferable to working with samples embedded in epoxy resin. As noted earlier, difficulties exist in obtaining good cross-sectional images of the coated wood due to low film thickness of coating and to the field edge effects. To counter the edge effects, coated faces were placed together and held in a vise. This was then milled down to size and the surface was microtomed simply with the diamond trimming knife. Since the coating now constituted the ‘‘filling’’ in a ‘‘sandwich’’, the edge effects were mitigated. Figure 4.5 shows images from this prepared surface. The coating layer is clear discernable, especially from the overlays which are also included in the Figures. As before, the lignin peaks and mass 86 were chosen to represent the wood and coating respectively for the positive sample whilst masses 45 (wood) and 80 (coating) were chosen for the negative spectra.

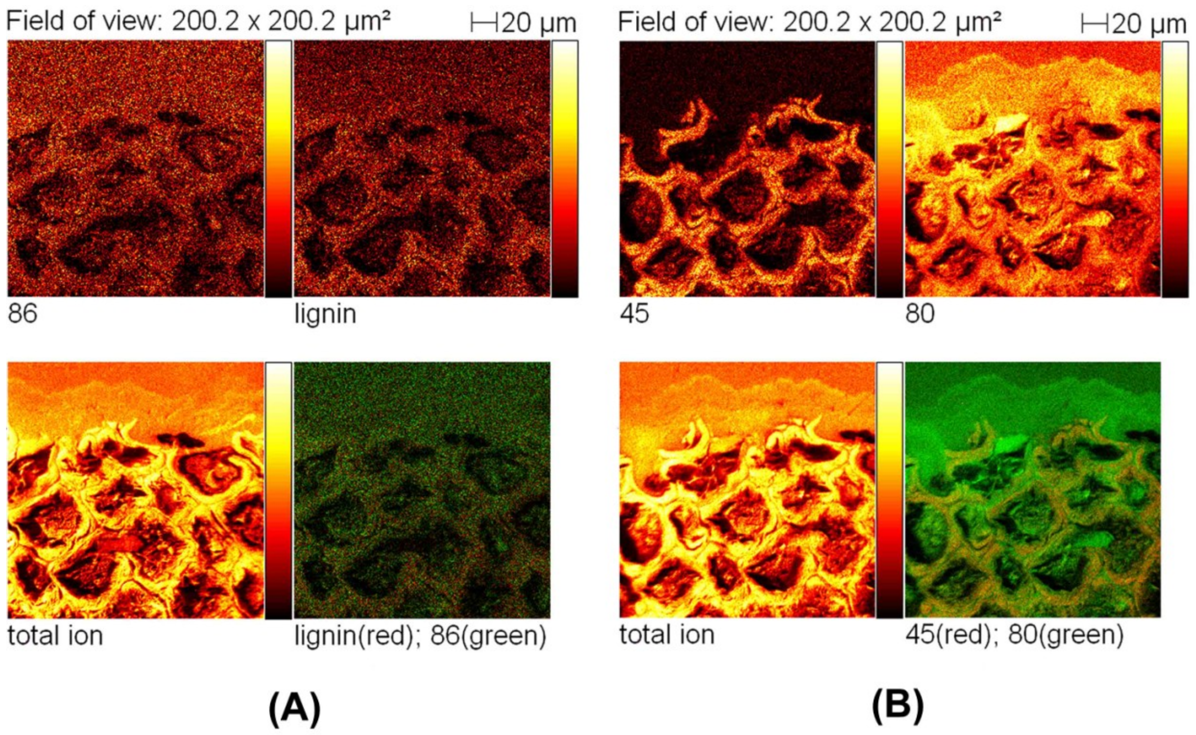


Figure 4.4: Cross-section of wood embedded in epoxy and polished (earlywood area). Coating at top (A) Positive ions: Lignin (masses 137 and 151 colour) represent the wood region, while mass 86 represents the coating. (B) Negative ions: mass 45 represents the wood and mass 80 the coating.

Penetration of the coating into the openings of the wood is clearly evident from the distribution of masses 86 and 80 in the positive and negative overlays (Fig. 4.5 – green in the combined Figure). A more detailed examination was performed at a portion where there was good adhesion. However, there was difficulty in obtaining a good image of the coating, suggesting that in spite of the improvement in specimen preparation technique, further improvements are necessary - probably due to the lack of a perfect face-to-face fit, and hence effective field compensation was not obtained when going to the smaller area. We are still working on improving this.

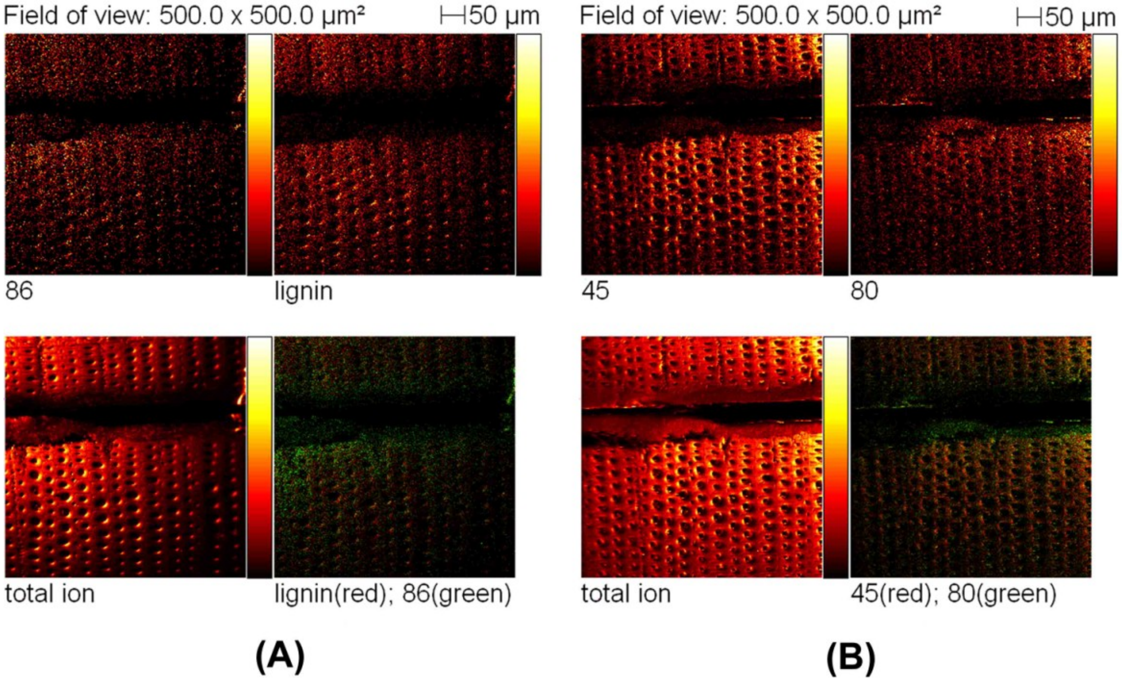


Figure 4.5: Cross-section of microtomed wood sample (latewood area, coating face-to-face in middle) (A) Positive ions: Lignin (masses 137 and 151 colour Figure) represent the wood region, while mass 86 represents the coating. (B) Negative ions: mass 45 represents the wood and mass 80 the coating.

4.4 Conclusions

It is seen that imaging ToF-SIMS is able to distinguish between a wood surface and an applied coating layer. Sample preparation is important, and microtoming of a nonembedded surface is preferable over that of a polished surface where smearing of the sample can cause problems.

Further, ‘sandwiching’ of the coating allows a means to avoid edge effects and provides a simple way to obtain an image of the coating layer. From the above results, the coating seems to form a sharp interface with penetration apparent into openings in the wood. The relative weaknesses of various fragments in the spectra from the coated and noncoated regions make it difficult to identify definitive markers and; thus a more detailed look at the interface using multivariate techniques may be warranted.

4.5 References

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4.6 Additional Note

Both principle component analysis (PCA) of high resolution spectra data, and PCA image analysis with MATLAB software for high resolution obtained images were used; however, multivariate analysis results were not satisfactory. This was because samples were run for too short a period of time to obtain appropriate peak intensities. Another set of samples was prepared and ongoing collaboration between the Faculty of Forestry and the Surface Interface Ontario (Chemical Engineering Department) will be continued to achieve better results identifying differences in penetration depth of different coating components such as pigment and resin into the wood.

Chapter 5

5 Coatings to Reduce Wood Preservative Leaching

Based on paper with the same title published on line in Journal of Environmental Sciences and Technology, DOI: 10.1021/es101138v, July 16, 2010

Authors: Mojgan Nejad and Paul Cooper

Abstract

The efficiency of semitransparent penetrating stains to reduce leaching of wood preservative components was evaluated. Five commercial wood deck finishes were applied to untreated and chromated copper arsenate (CCA), alkaline copper quat (ACQ), and copper azole (CA) treated wood, and leachates were collected and analyzed during 3 years of natural weathering exposure in Toronto, Canada. All stains evaluated effectively reduced the cumulative leaching of all inorganic preservative components by about 60% on average. Although most coatings showed significant film degradation starting around 12 months, the reduced leaching persisted even after 3 years. This suggests that temporary protection of wood with a coating during the early stages of use resulted in long-term reduction in preservative leaching potential. A two-week screening leaching test was able to predict the long-term leaching performance of different coatings reasonably well. Cured coating glass transition temperature (Tg) and liquid coating viscosity were the most important variables affecting a leaching prediction model. To effectively reduce leaching of preservative components from treated wood, coatings should have Tg low enough to withstand stresses caused by freezing in winter and have adequate viscosity to form a barrier film layer on the wood surface.

5.1 Introduction

Most decks and other exterior structures in North America are constructed using nondurable softwood lumber which is pressure-treated with a wood preservative to render it decay-resistant. Prior to December 2003, most lumber for residential construction was treated with chromated copper arsenate (CCA); however, concern about leaching of arsenic (As) from CCA treated wood led to the replacement of CCA by copper(Cu)-amine based preservatives for residential applications [1, 2]. The two main Cu-amine based preservatives that replaced CCA for these uses in the North American market are as follows: alkaline copper quat (ACQ) and copper azole (CA), which do not contain arsenic but contain a quaternary ammonium compound and tebuconazole respectively as organic cobiocides with the copper. Both have high copper contents and leach Cu in relatively high amounts [3, 4] which could be toxic in aquatic environments [5, 6].

The ability of some coating formulations to reduce preservative availability was reported in 1987 by Kizer using wipe test sampling [7]. Other studies confirmed the ability of paint and solid stain to reduce CCA leaching [8, 9]; however, these types of coatings form a thick film layer on the wood surface which cracks and peels during weathering due to dimensional changes of the wood. Water repellents and water-repellent additives also effectively reduce CCA and ACQ component leaching [10-14], but water repellents do not provide adequate UV protection for wood in exterior use [15-16].

Semitransparent penetrating stains are recommended for exterior applications [15-17], but there is little information on the ability of these stains to reduce preservative component leaching, except for a few studies based on short-term simulated rainfall tests on CCA treated wood [18-19].

There is no information on the effectiveness of penetrating stains to reduce Cu leaching from ACQ and CA treated wood. In 2005, the US Environmental Protection Agency (EPA) published a report on the efficacy of a number of coatings in reducing dislodgeable CCA components [18]. They included four stains (three clear and one semitransparent) in that study but used a wipe test procedure which estimated preservative that could be dislodged from the surface and did not evaluate the leaching of preservative components to the surrounding environment.

For existing CCA decks in service, Health Canada suggests application of a penetrating stain at least once a year [20]. This solution would make CCA decks high maintenance products, which could encourage people to remove their sound decks from service and eventually add to landfill issues with CCA disposal.

Two issues addressed in this paper are effectiveness of penetrating stains to reduce Cu and other inorganic components leaching from preservative-treated wood and effects of coating failure on leaching rates. The efficiency of several commercial deck stains to reduce leaching from CCA, ACQ, and CA treated wood exposed to natural weathering for 3 years was evaluated. A partial least squares regression (PLS_R) model was used to correlate liquid and cured coating properties with their ability to reduce leaching.

5.2 Materials and Methods

The study was performed on southern pine (*Pinus* species group) due to its low paint-holding ability [15] and excellent preservative treatability [2]. Flat grained southern pine (SP) sapwood boards (20mm×140mm× 4.88 m) were cut in four 1.22m lengths. Three of these end-matched pieces were treated, each with a different preservative, and one was used as an untreated (control) sample. Preservative solutions used had the following mass balances for actives: CCA-C (47.5% CrO_3, 18.5% CuO, and 34.0% As_2O_5), ACQ-C (66.7% copper oxide, 33.3% quat as alkyl dimethyl benzylammoniumchloride), and CA-B (96.1% copper, 3.9% tebuconazole). The copper components of ACQ and CA were solubilized with monoethanolamine.

Preservative treatment retentions were targeted for above ground applications according to AWPA standards [21], i.e., CCA and ACQ 4.0 kg/m_3 and CA 1.7 kg/m_3. In order to achieve consistent preservative fixation in wood, samples were kept in a high humidity chamber (95% relative humidity) at 50°C for one week. Cross sections of treated wood samples were digested based on AWPA A7-04 [22] and analyzed for actual retentions of inorganic components by Inductively Coupled Plasma-Optic Emission Spectrometer (ICP-OES), Optima7300 DV. The detection limits were 6 *μ*g/L for As and 1 *μ*g/L for Cr and Cu in axial mode, and concentrations in the analyzed samples were always above the detection limit.

Fourteen coatings recommended for decking applications were purchased based on a literature search and discussion with manufacturers. Preservative treated and untreated control wood specimens, 7mm×38mm×45mm,were brush coated on all sides with each of the 14 stains, and the coating was allowed to cure for 48 h. Specimens (2 replicates of each) were submerged in 75mL of distilled water, and water was replaced after 1, 3, and 14 days. At each time, the amounts of inorganic components leached were determined by ICP.

Based on these initial screening results and some of the coating properties such as resin type and coatings base (water or solvent), five coatings covering a broad range of commercially available formulations and performance characteristics were selected for the natural weathering exposure to provide a range in expected performance (Table 5.1).

The five selected coatings were applied on the top and end surfaces of wood samples (20mm×140mm×280mm long). Three replicates of each treatment (CCA, ACQ, CA and untreated control) and coating were exposed to natural weathering in Toronto, Canada from May 2006 to May 2009 (Figure 5.1). Samples were positioned on four deck screws mounted

12cm below the surface of plastic containers (20 L containers measuring 200 mm × 325 mm × 375 mm). Rainfall leachate was collected after one, two, and three months, and every three months thereafter, and for each sample the volume of leachate was recorded and the concentration of inorganic preservative components determined. Leachates were collected at other times as needed to avoid overflow or contact of leachate water with wood and whenever there was at least 1 L of leachate during dry periods to reduce the effects of evaporative loss. The amounts of components leached at each measurement time, based on the leachate volumes and concentrations, were determined and expressed as % of total added to the wood and as flux (mg/m^2) values which were plotted as cumulative losses against exposure time. During the winter the leachate froze, damaging the plastic buckets, so the wood samples were left outside without leaching collection during these periods.

Because of the low temperatures and the fact that precipitation was mainly snow, leaching losses during this exposure are very low [23]. Specimens were weighed after significant wetting and drying periods and the moisture contents determined as a measure of the coatings' abilities to exclude moisture.

Solid content, specific gravity, pH, and viscosity (by Brookfield viscometer) of each liquid coating were measured. Also surface tension of coating was determined using a Sigma 70 Tensiometer. As a measure of coating flexibility, the glass transition temperature (Tg) of each stain (oven-dried film) was determined by differential scanning calorimeter (DSCQ1000) at a heating rate of 10 deg-min-1. Below the Tg, a polymer goes from a soft and flexible state to a hard and glassy state; when the average coating temperature is below its Tg, the coating becomes brittle and fractures, allowing it to flake or erode from the surface.

Partial least squares regression (PLS_R) modeling is used to find any correlations between coating properties and their efficiency in leaching reduction. PLS can handle collinearity between X and Y variables. Coating properties including resin type, viscosity, pH, solid content, surface tension, Tg, specific gravity, and treatment types and elements were considered as input variables, and efficiency of coating to reduce cumulative percentage leached after 3 years of natural weathering was considered as the output variable. Most data mining techniques and modeling of results need data preprocessing for model improvement. For this model, all data were mean-centered and scaled to unit variance [24]. In addition, viscosity was transformed logarithmically to have a distribution closer to normality. Qualitative (categorical) variables in the regression model such as treatment types and elements were transformed to zero and one. For instance, for CCA treatment, the CCA value is one and ACQ and CA values are zero.

Figure 5.1: Natural weathering setup- Treated coated and uncoated samples were exposed to natural weathering, in Toronto, Canada

5.3 Results and Discussion

The average preservative retentions of samples, based on digestion and ICP results, were higher than targeted; measured retentions were CCA 5.3 kg/m^3, ACQ 4.9 kg/m^3, and CA 2.0 kg/m^3. All five penetrating stains evaluated significantly reduced leaching (α=0.05) of all inorganic preservative components over the 3-year natural exposure period (Table 5.1 and Figure 5.2).

Table 5.1: Cumulative Leaching after 3 Years of Natural Weathering As Percentage Leached and Cumulative Flux (mg/m^2) - Average of Three Replicates *b*

ID	Coating Type	Leaching Flux mg/m^2					% Leaching				
		CCA			ACQ	CA	CCA			ACQ	CA
		As	Cu	Cr	Cu	Cu	As	Cu	Cr	Cu	Cu
2	Alkyd-Acrylic(W)*	311 (27)	403 (66)	78 (8)	4431 (1390)	3291 (904)	1.4 (0.1)	1.5 (0.2)	0.2 (0.02)	6.0 (1.4)	5.7 (1.2)
4	Alkyd-Acrylic(W)	237 (17)	283 (33)	71 (3)	3178 (847)	2308 (172)	1.0 (0.1)	1.1 (0.2)	0.2 (0.01)	4.7 (1.0)	4.1 (0.1)
5	Alkyd(S)*	327 (26)	456 (54)	106 (4)	3219 (666)	2946 (645)	1.5 (0.2)	1.8 (0.2)	0.3 (0.02)	4.4 (0.6)	5.4 (1.2)
9	Alkyd(S)	246 (11)	368 (38)	67 (7)	2519 (109)	2038 (539)	1.1 (0.2)	1.5 (0.2)	0.2 (0.02)	3.5 (0.1)	3.3 (0.6)
14	Polyurethane(W)	293 (27)	176 (51)	56 (7)	2619 (330)	2714 (376)	1.3 (0.2)	0.7 (0.2)	0.1 (0.01)	3.6 (0.4)	4.8 (0.7)
Uncoated		514 (4)	591 (70)	161 (25)	7894 (2078)	6676 (1898)	2.3 (0.2)	2.4 (0.1)	0.4 (0.03)	11.2 (2.4)	11.6 (3.1)

a W= water-based, S=solvent-based. *b* Standard deviations in brackets.

Figure 5.2 summarizes the coatings' efficiencies to reduce total leaching after 3 years of natural weathering. Considering that coating performance was evaluated on southern pine, which is a high density wood with large density differences between latewood and earlywood within each annual growth ring, coatings were subjected to much higher stresses compared to other typical decking species like spruce and fir. Furthermore, samples were exposed to natural weathering in Toronto, Canada which has 50 °C difference in average temperature from summer to winter, resulting in a severe condition for testing coatings' flexibilities. Despite these factors, the penetrating stains evaluated reduced leaching after 3 years exposure by 30 to 79% depending on the preservative component and coating. Coatings effectively reduced leaching of As by 50%

((6.3%) on average, Cr by 57% ((3.4%), Cu from CCA by 48% ((7.4), and Cu from ACQ and CA on average about 70% ((5.1%).

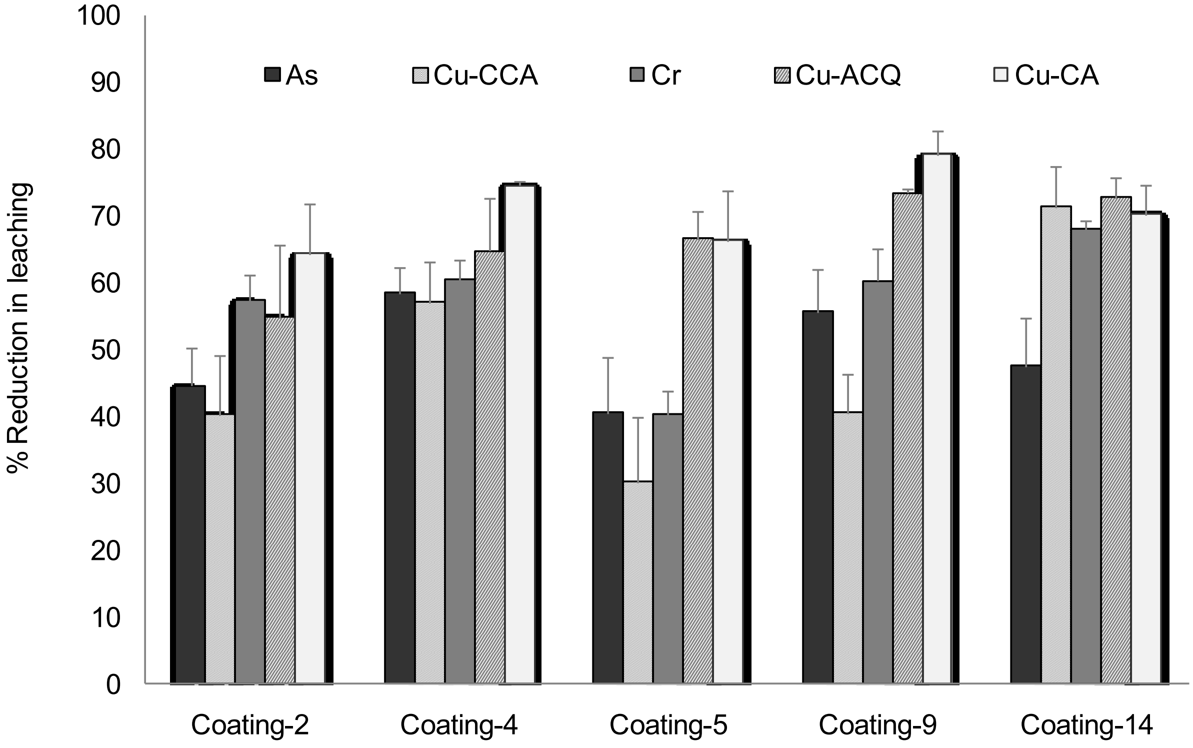

Figure 5.2: Efficiency of different coatings in leaching reduction based on cumulative % leached after 3 years of natural weathering (the error bars represent s.d.).

In absolute terms, in each case, the best coating reduced As leaching from about 510 mg/m^2 to about 240 mg/m^2 and Cr from 160 mg/m^2 to 56 mg/m^2 relative to the uncoated samples. Cu leaching was reduced more effectively from ACQ and CA preservative treated wood than from CCA treated samples. The best coating (coating 9) reduced copper leaching from ACQ samples from about 7900mg/m^2 in uncoated wood to about 2500 mg/m^2; for CA treated wood, the reduction was from about 6700 mg/m^2 to about 2000 mg/m^2.

Based on Tukey grouping in two-way ANOVA tests of leaching data, coatings 4, 9, and 14 had better performance than coatings 2 and 5. It was assumed that coatings would reduce leaching, and water uptake by acting as a moisture barrier and remain effective only as long as they were intact. However, all coatings were significantly degraded after about 12 months of exposure, with erosion of coating from the top surface and exposure of bare wood, especially in the latewood portions of the annual growth layers. As a result, the coated samples had lower wood moisture contents after wet periods during the first year of exposure, but coatings had little ability to exclude moisture during the third year in service (Table 5.2).

Table 5.2: Average % moisture content of samples during wet periods during the first year and third year – mean (s.d.).

Coating ID	% Average moisture content of samples during wet periods							
	CCA		ACQ		CA		Untreated	
	1	3	1	3	1	3	1	3
Coating-2	25 (2)	29 (0.4)	28 (2)	42 (2)	30 (2)	43 (5)	21 (1)	34 (5)
Coating-4	22 (1)	27 (1)	25 (2)	38 (2)	27 (2)	45 (6)	19 (1)	39 (6)
Coating-5	21 (0.3)	26 (0.5)	26 (2)	40 (4)	30 (1)	40 (0.5)	19 (0.4)	33 (1)
Coating-9	20 (0.6)	27 (0.5)	23 (1)	38 (2)	24 (1)	39 (2)	21 (1)	39 (2)
Coating-14	22 (1)	29 (0.5)	26 (1)	40 (2)	28 (2)	42 (2)	21 (1)	41 (4)
Uncoated	30 (1)	33 (1)	33 (1)	40 (2)	35 (1)	43 (1)	29 (1)	40 (4)

It was noted that ACQ and CA treated samples had higher water uptake than CCA and untreated wood samples which may be attributed to the presence of surfactants [25] in the formulations (quat in ACQ and emulsifiers in CA). Surfactants such as quat reduce the contact angle of rainwater drops on the wood surface to increase wetting and water absorption.

There was not the expected correlation between average moisture absorption and average leaching characteristics. For example, coating 14 had similar water absorption compared to coatings 2 and 5 but generally had much lower preservative component leaching than either coating.

Despite the observed early coating failure, leaching rates did not accelerate after the coatings broke down and cumulative leaching never reached that of uncoated samples as seen for arsenic leaching from CCA treated wood (Figure 5.3) and for copper leaching from ACQ treated wood (Figure 5.4). Cumulative leaching of As was highly correlated with the cumulative rainfall (Figure 5.3), and leaching was higher during the time when samples remained wet for extended periods.

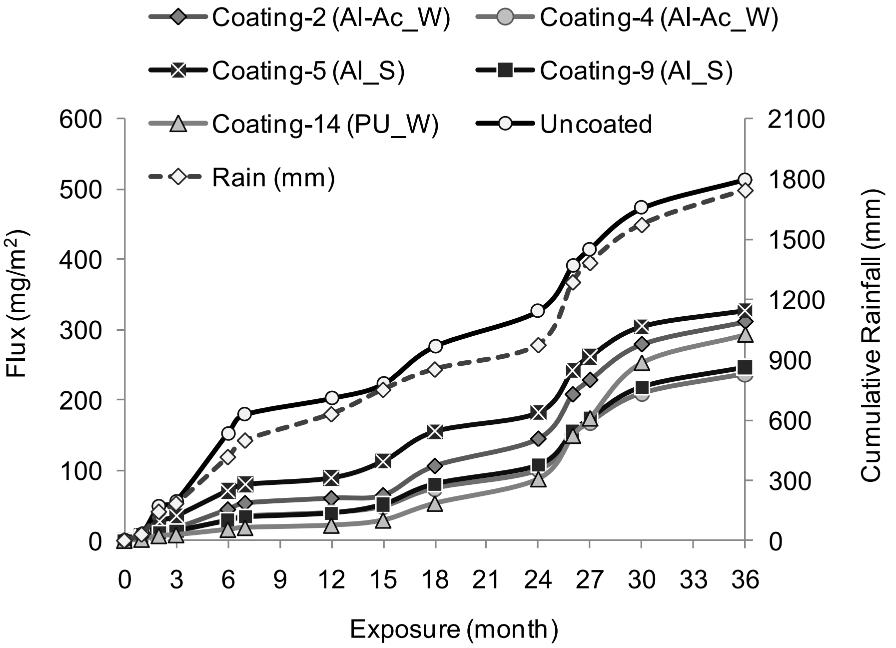

Figure 5.3: Cumulative leaching of As (mg/m^2) from CCA treated samples during 3 years of natural weathering

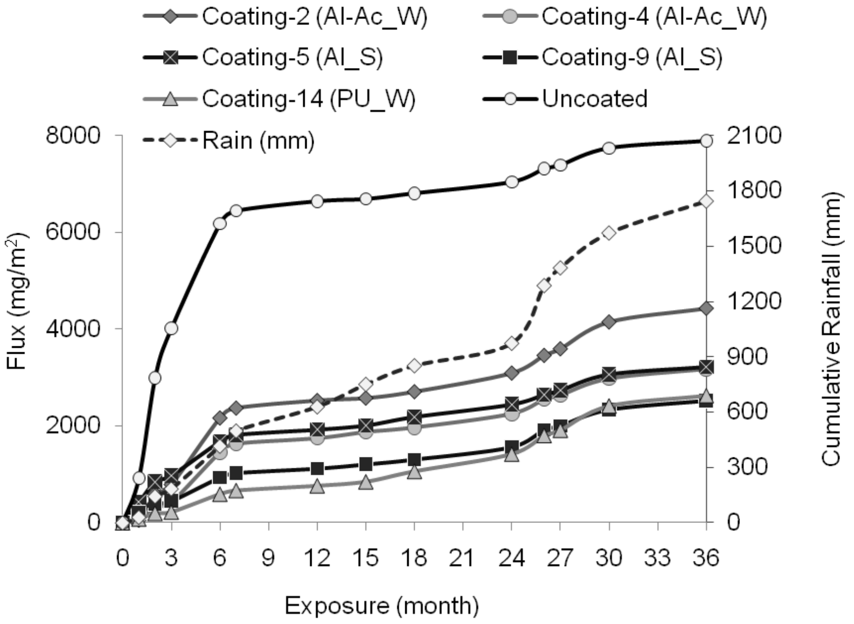

Figure 5.4: Cumulative leaching of Cu (mg/m^2) from ACQ treated samples during 3 years of natural weathering

For example each year between August and November (between 3-6, 15-18, and 27-30 months, Figure 5.3) there was a sharp increase in As leaching compared to the other times. Chromium leaching showed a similar pattern but with lower amounts leached. The CCA copper leaching (shown in the SI) was slightly higher than arsenic, and the coatings were generally less effective at reducing leaching. The shapes of the cumulative leaching curves were different than for As and Cr and more similar to those of copper leaching from ACQ and CA discussed below. This is attributed to the similarities in mechanisms of copper fixation in all treatments (ion exchange and other complexation reactions with acetyl and phenolic acid groups in wood).

Additionally there was a significant increase in leaching of all elements in the last summer in 2008 (24-27 months), when the average rainfall was three times higher than for 2007 (12-15 months), and two times higher than for 2006 (1-3 months). A similar correlation between higher rainfall and higher As leaching was observed by Taylor and Cooper [23]. The polyurethane coating (number 14) performed very well for the first two years, but its performance drastically declined during the third year. Since this coating was applied as recommended with three coats, there was a thick layer of film on the top of the wood surface. This could be the main cause of this coating's failure and peeling from the surface.

The coating started to peel from the latewood area, and after about two years the peeling extended to the earlywood areas. Overall water-based coatings (with efficiency of 50.3%) were more effective in reducing CCA elemental leaching than solvent-based coating (efficiency of 44.6%, $\alpha=0.05$).

The cumulative Cu leaching curves for ACQ treated samples (Figure 5.4) and CA samples (not shown) were similar in shape and total leaching amounts; however, unlike As and Cr in CCA, the copper leaching rates were not well correlated with cumulative rainfall. Cu leached at a high rate at the beginning of the exposure and the leaching rate leveled off after 6 months. Despite the heavy rainfall during the time between 24 to 30 months, there was only a gradual increase in leaching rates of Cu from both coated and uncoated ACQ and CA boards. We have observed [3] that after treatment and conditioning of southern pine treated with ACQ, the Cu solubility is about 34%. It is evident in Figure 5.4 that the in service leaching will not reach this level in the uncoated wood (currently averaging 11.2%). This suggests that during the weathering exposure, some of the soluble copper became less available. Even though the coatings were failing after one year based on their appearance and water uptake results, cumulative copper leaching from coated samples remained low compared to uncoated samples.

There are a number of possible explanations for the observed results. First, despite visible degradation of the coatings, they could continue to provide protection against leaching, especially in the earlywood tissue where the highest retentions of preservative components are expected. Second, there could be preferential leaching of the monoethanolamine solvent from wood in service allowing precipitation of copper compounds. Third, the preservative components could undergo other long-term fixation processes while being protected by the coating. We investigated the above effects to determine the causes of long-term reduction in total leaching in coated samples (chapter-6).

Whatever the cause, it is evident that the application of even low efficiency penetrating stains to treated wood can significantly reduce emissions of all preservatives evaluated over the long-term. With the recommended maintenance and refinishing of treated wood decking and other products with such finishes when they start to fail, the impacts of such treatments on the environment will be significantly reduced over the life of the structure.

Figures 5.5 and 5.6 compare screening test results of cumulative % leached with natural leaching data after 3 years. There is a relatively strong correlation between leaching after the two week lab tests and leaching after 3 years of natural weathering exposure. Since it is more convenient to perform a two-week lab test for prediction of long-term natural exposure, we recommend this short-term test for predicting the ability of new coating formulations to reduce leaching.

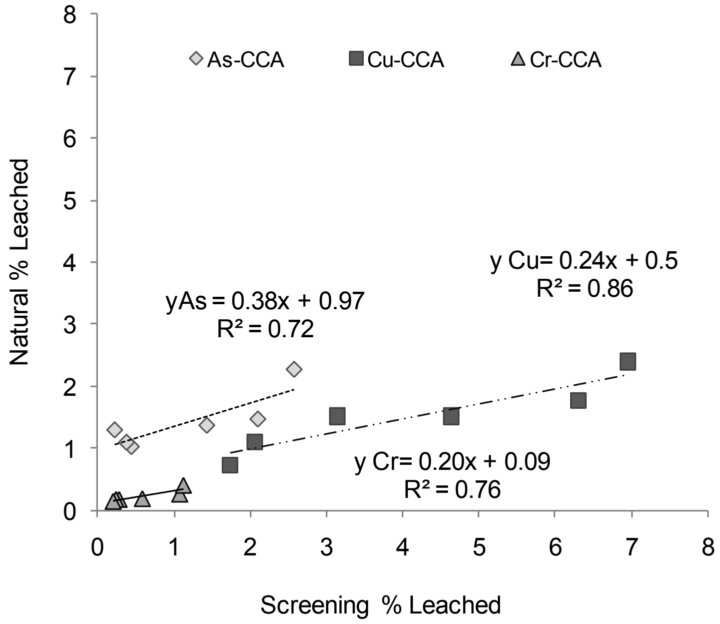

Figure 5.5: Percentage leached from screening samples compared with cumulative leaching of natural weathering after 3 years from all CCA components.

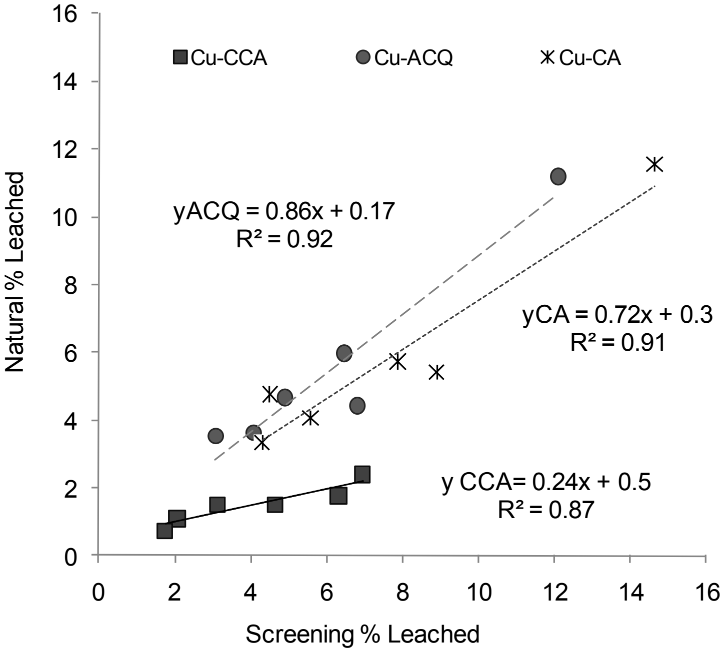

Figure 5.6: Cumulative percentage leached from screening samples compared with cumulative leaching of natural weathering after 3 years- Cu of all treatments

It should be noted that there is an interaction with preservative type, i.e. the screening test shows relatively high Cu leaching, similar to 3 years natural weathering for CA and ACQ, but for CCA components, the screening test over-predicts leaching in service. This emphasizes that short-term accelerated leaching protocols, used to compare leaching characteristics of different wood preservatives, may not provide comparable results among different preservatives.

Relationship between Coatings Properties and Natural Leaching Results

Table 5.3 shows some of the coatings properties that were measured and used to model leaching. The leaching prediction model is influenced by treatment type and leached elements considerably, and Tg of coating and viscosity were the two main coating parameters that affected the model significantly.

Table 5.3: Coating properties measured in the laboratory

ID	Resin Type & Based	Specific gravity	pH	Viscosity cP	Solid content (%Wt)	Surface Tension (mN/m)	Tg °C
2	Alkyd-Acrylic (W)	1.02	8.1	29	27	31	16
4	Alkyd-Acrylic (W)	1.03	7.8	18	28	30	-11
5	Alkyd (S)	0.85	4.8	10	38	25	17
9	Alkyd (S)	0.92	4.7	124	46	25	-7
14	PU (W)	1.04	7.9	270	29	33	-7

Based on the loadings plot (Figure 5.7) lower cured coating Tg and higher liquid coating viscosity were associated with higher leaching reduction. This suggests that the film should be flexible enough (low Tg) to withstand stresses caused by large temperature variations and wood swelling and shrinking. Also, high viscosity coatings do not penetrate the wood as much, leaving a thicker film layer to reduce leaching. Leaching reduction was also more strongly associated with ACQ and CA compared to CCA components as confirmed in Figure 5.2.

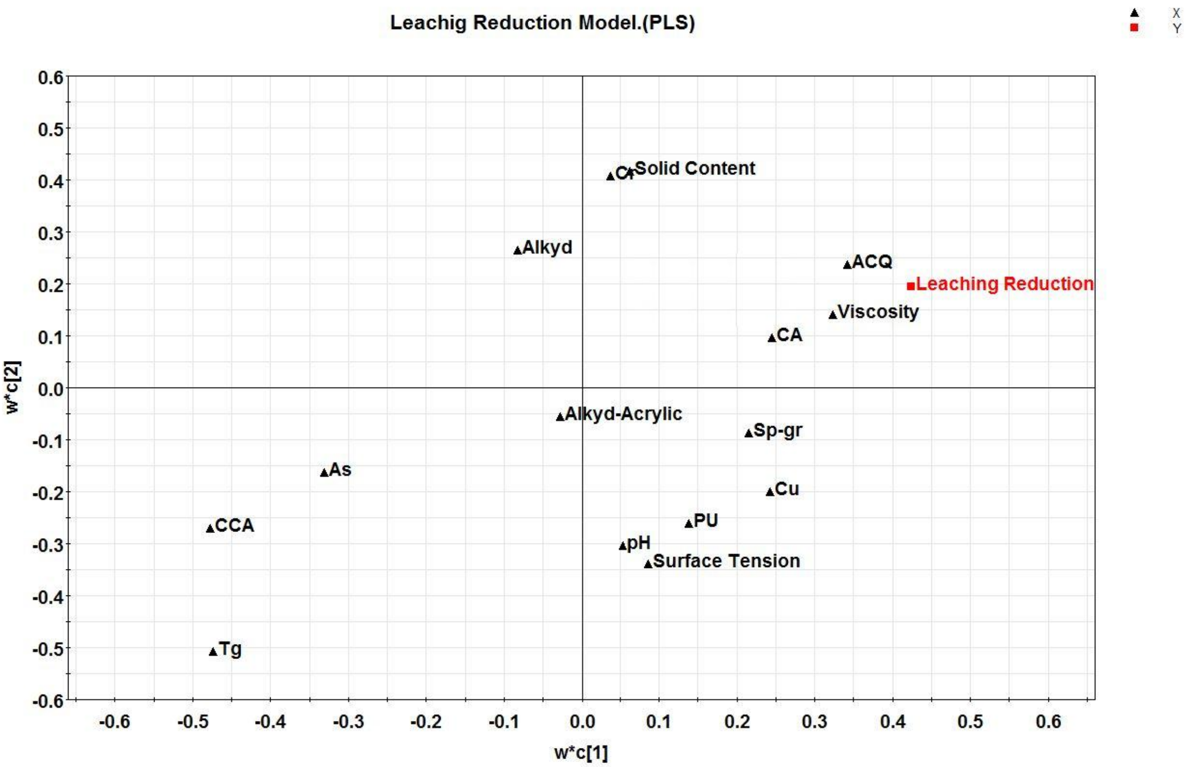

Figure 5.7: Loadings plot of PLS prediction model of leaching reduction based on coatings properties

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5.5 Supporting Information

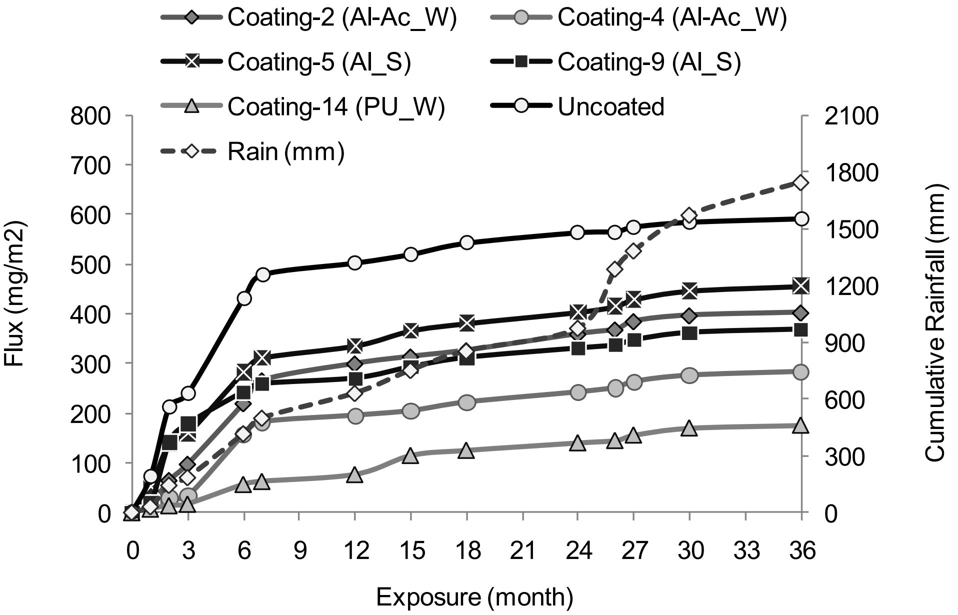

Figure 5.8: Cumulative leaching of Cu (mg/m^2) from CCA treated samples during 3 years of natural weathering

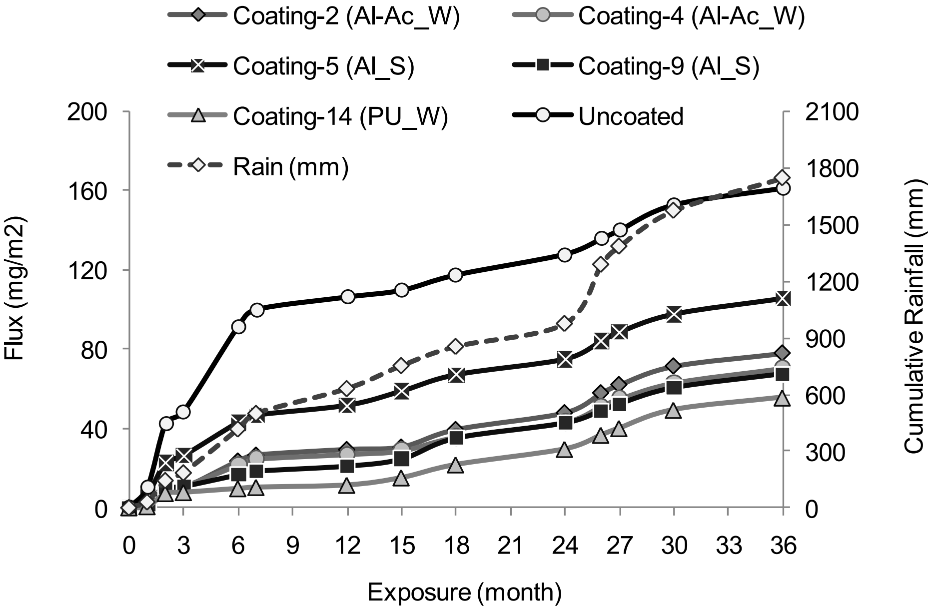

Figure 5.9: Cumulative leaching of Cr (mg/m^2) from CCA treated samples during 3 years of natural weathering

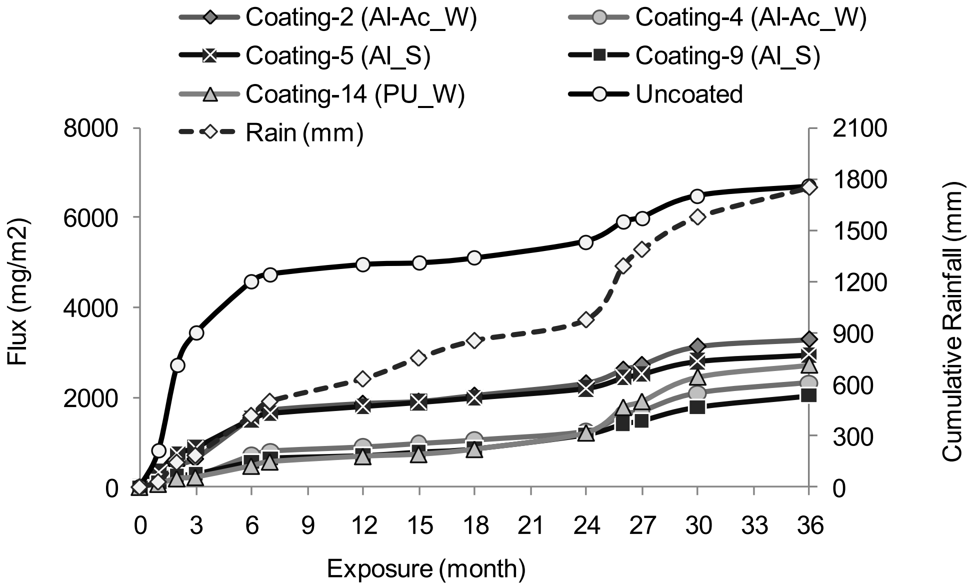

Figure 5.10: Cumulative leaching of Cu (mg/m^2) from CA-treated samples during 3 years of natural weathering

Chapter 6

6 Comparison of Preservative Leaching and Water Absorption in Coated Samples by Laboratory and Natural Weathering Tests

For submission to Journal of Wood Science and Technology

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Abstract

Fourteen commercial stains were tested in the laboratory to compare water uptake and leaching reduction from chromated copper arsenate (CCA), alkaline copper quat (ACQ) and copper azole (CA) treated wood. Based on results of a two-week screening test, eight stains were selected to be evaluated over three months of accelerated weathering and from these, five stains were evaluated over three years of natural weathering exposure in Toronto, Canada. These comparisons were made to try to identify a fast method for replacing natural exposure tests to evaluate finishes.

Comparison of different weathering techniques showed significant correlations between lab tests and leaching results of natural weathering; also there was a good correlation between water uptake of ACQ and CA-treated wood in lab tests and in samples exposed to 3 years natural weathering. Modeling of the relationship between coating properties and their performances after three months of accelerated tests showed that coatings which form a flexible thick layer of film on the surface of wood have better water repellency performance and higher efficiency to reduce preservative components leaching.

6.1 Introduction

Development of laboratory tests to quickly obtain coating performance results comparable to natural weathering exposure is essential for the development of new coatings. To get adequate acceleration and good correlation to natural weathering, artificial weathering tests for coatings should include UV cycles to simulate the photo-degradation by sunlight, condensation to simulate moisture absorption, water spray to remove degraded material from the wood surface [1], and freezing after wet cycles to accelerate development of cracks in the coating and checks in the coated wood specimens [2].

Since sunlight only contains 5-7% UV-light and there is only small amount of UVB radiation [3], to truly simulate the effect of sunlight without resulting in severe polymer damage, accelerated weathering devices should contain UV lamps in the UVA region (400 to 320nm) [2, 4].

Moisture is another important factor in coating failure studies, particularly when the substrate underneath is wood. Increase in moisture content of coated wood samples under natural weathering is due to dew or condensation, rain, or melting snow or ice [3]. The stresses caused by a moisture gradient between the surface and interior of the wood, results in surface checking, and sometimes interface failure. In any artificial procedure, it is essential to have wet and dry cycles so water can wash off the degraded material from the surface of coated wood after each UV cycle.

The principle objective of this project was to assess the ability of coatings to reduce wood preservative leaching from CCA preservative treated wood and from wood treated with Cu-amine systems which are used in place of CCA for residential uses. Although CCA-treated wood is no longer in use for residential applications, CCA decks and fences built prior to December 2003 are still in service. Health Canada has suggested application of semitransparent stains every year to reduce leaching of As from CCA-treated wood [5]. Cu-amine preservatives leach Cu in high amounts which is not toxic to humans, but could cause problems in aquatic environments [6]. Developing a short reliable laboratory test will help both preservative and coating industries by reducing the evaluation time for the development of new formulations to seal preservative treated wood.

Several studies performed water immersion tests for quick leaching evaluation using a range of exposure time (14-32 days) [7-9]; this paper uses the cumulative percentage leached during three years of natural weathering to validate data obtained from two-week water immersion tests and three months of accelerated weathering. Also, the average moisture contents of samples during wet periods are compared for the different laboratory tests with natural weathering.

To investigate which coating properties affect coating performances, partial least squares regression modeling was used to find coating properties that affected the prediction model the most. This model should be helpful for coating formulators in their future development when the goal is to formulate a coating with high water repellency for application on pressure treated wood.

6.2 Materials and Methods

A set of small wood samples (38mm x 7mm x 45mm) was used for two-week lab tests, comparing three preservative treatments + untreated control x fourteen coatings x two replicates for leaching and three replicates for water uptake. All coatings were applied only once following manufacturers' recommendations, except coating number 14 for which two coats were applied (one coat of step one penetrating stain and one coat of step two as UV blocker). Samples were coated on all sides and after 48 hours of air drying, submerged in 75 ml of distilled water for two weeks. The water was removed for analysis and replaced with fresh water after one, three and fourteen days. Samples were weighed at each water change and moisture contents of samples were calculated.

According to screening test results and some of the coating properties such as: resin type and coatings base (water or solvent) eight stains (covering a wide range of performance) were selected for accelerated weathering tests, and five of these coatings were selected for the field tests.

Accelerated weathering was conducted on 20mm x 140mm x 110mm long samples with the coating applied on all sides. The test included 12 one-week cycles, according to a modified version of the prEN-927-6 test [10]. The one-week testing cycles included three-days UV-A radiation (340nm lamp, with intensity of 1.06 mW/cm^2 at 7cm distance from light source), one-day water spray (15 minutes water spray every four hours providing an average of 37mm of rain per day) in a conditioning chamber with adjusted temperature at 35°C and three-days freezing at -12°C. Since samples were small and coated on all sides, in order to have a detectable amount of elements in leachate, three replicates of each coated-treated samples were set in one plastic container (27cm x 36cm x 23cm). They were placed on plastic mesh adjusted 6 cm below the container opening for the water spray cycle. Leachates were collected and analyzed by Inductively Coupled Plasma-Optic Emission Spectrometer (ICP-OES) Optima 7300 DV every week.

The moisture uptake and leaching performance of coated (5 selected coatings) and uncoated treated and untreated wood samples was evaluated during three years of weathering in Toronto, Canada from May 2006 to May 2009 [11]. Specimen dimensions were 20mm × 140mm × 280mm long and samples were coated only on the top surface and the end grain.

Coating properties, including viscosity, solid content, pH, surface tension, contact angle (after 1 minute), glass transition temperature (Tg, by DSC) and film thickness (by SEM) were determined [12]. Partial least squares regression modeling was used to investigate correlations between results of coating performance in the accelerated weathering test and coating properties. More details about the modeling technique and methods used to measure coating properties are presented in chapter-3 [12].

6.3 Results and Discussion

Measured coating properties are summarized in Table 6.1; coatings with shaded background were selected for accelerated weathering tests and the five darker shaded coatings were used for the natural weathering exposure. Coatings were selected to ensure a broad range of coating resin type, base and performance for finishes available in the market in 2006.

Table 6.1: Coatings measured properties, and general information.

ID	Resin Type	Base	Specific gravity	pH	Surface Tension (mN/m)	Contact Angle°	Viscosity (cP)	Solid Content (%Wt)	Tg (°C)	Film Thickness (µm)
1	Alkyd	W	1.02	8.1	32	5	10	17	26	9
2	Alkyd-Acrylic	W	1.02	8.1	31	36	29	27	16	15
3	Alkyd	S	0.98	5.2	25	10	72	47	10	---
4	Alkyd-Acrylic	W	1.03	7.8	30	22	18	28	-11	12
5	Alkyd	S	0.85	4.8	25	0	10	38	17	2
6	Alkyd	S	0.85	4.8	24	0	27	35	-10	---
7	Alkyd	S	0.85	3	23	7	41	31	2	12
8	Alkyd	S	0.88	4.7	25	1	33	45	-31	4
9	Alkyd	S	0.92	4.7	25	21	124	46	-7	34
10	Alkyd-Acrylic	W	1.09	8.5	35	39	903	27	2	---
11	Alkyd	S	0.85	5.7	24	0	14	26	-7	---
12	Alkyd	W	1.01	7.3	32	25	60	10	-1	---
13	Alkyd	S	0.95	7.0	25	21	149	42	-10	---
14	Polyurethane	W	1.04	7.9	33	42	270	29	-6.6	37

6.3.1 Screening results:

Table 6.2 shows the results of moisture contents of screening specimens averaged for 1, 3 and 14-day water immersion tests, and the cumulative amounts of components leached, expressed as percentage of initial retention, after 14 days in test.

The two-way ANOVA showed water-based coatings were significantly more efficient in reducing CCA elemental leaching than solvent-based coatings (α=0.05). Also, there was a strong positive correlation between average moisture contents of samples during 14 days and cumulative components leached. Based on the Pearson correlation, the correlation was the strongest for CA-treated wood (r=0.92) and the lowest for Cu from CCA-treated wood (r=0.72), with all the correlations being highly significant at the 95% confidence level.

Table 6.2: Average % Moisture content of samples during 14-day water immersion (three replicates) and cumulative percentage leached from screening samples after 14 days (two replicates).

Screening	Ave. % Moisture Contents during - 14 days				Cumulative % leached – 14 days				
Coating ID	CCA	ACQ	CA	Untreated	CCA			ACQ	CA
					As	Cu	Cr	Cu	Cu
1	62(3)	59(6)	57(6)	58(4)	2.1	4.0	0.9	7.0	8.6
2	55(2)	50(6)	57(2)	55(3)	1.4	4.6	0.6	6.5	7.9
3	50(5)	54(4)	55(5)	48(6)	1.7	6.2	0.8	5.5	7.7
4	44(4)	51(4)	49(1)	57(2)	0.4	2.1	0.3	4.9	5.6
5	58(6)	60(5)	61(3)	51(4)	2.4	6.3	1.1	8.4	10.9
6	56(6)	57(7)	60(6)	45(1)	2.0	6.2	0.8	6.9	9.2
7	53(6)	55(7)	56(8)	49(4)	1.2	4.3	0.6	7.3	8.2
8	53(6)	52(5)	58(7)	49(4)	2.0	7.3	0.8	6.6	8.6
9	41(4)	45(1)	49(8)	44(6)	0.4	3.1	0.2	3.1	4.3
10	52(7)	55(4)	52(1)	56(2)	0.6	3.2	0.7	6.6	8.9
11	59(4)	58(6)	60(7)	47(4)	1.9	6.8	0.9	8.7	9.6
12	64(5)	58(1)	64(3)	62(1)	1.3	6.2	0.9	11.1	11.9
13	42(3)	50(6)	49(3)	48(4)	0.4	2.0	0.2	5.9	6.6
14	46(10)	46(9)	44(6)	43(4)	0.2	1.7	0.2	4.1	3.5
Uncoated	63(1)	66(5)	67(2)	63(2)	2.6	6.9	1.1	12.1	14.6

6.3.2 Accelerated weathering results:

Figure 6.1 illustrates the moisture content changes of treated and untreated uncoated wood samples during 12 weekly accelerated cycles. Although there was a significant difference among moisture contents of treated samples during wet periods, after each dry cycle (3 days UV) all samples reached similar moisture contents. Cu-amine treated wood samples (ACQ and CA) absorbed more water on average than untreated samples or samples treated with CCA (Figure 6.1). All coated samples showed similar trends as for the uncoated samples shown in Figure 6.1, but overall, coated samples had much lower moisture contents. CA-treated samples had on average 32% moisture content which was significantly higher than ACQ-treated wood (29%).

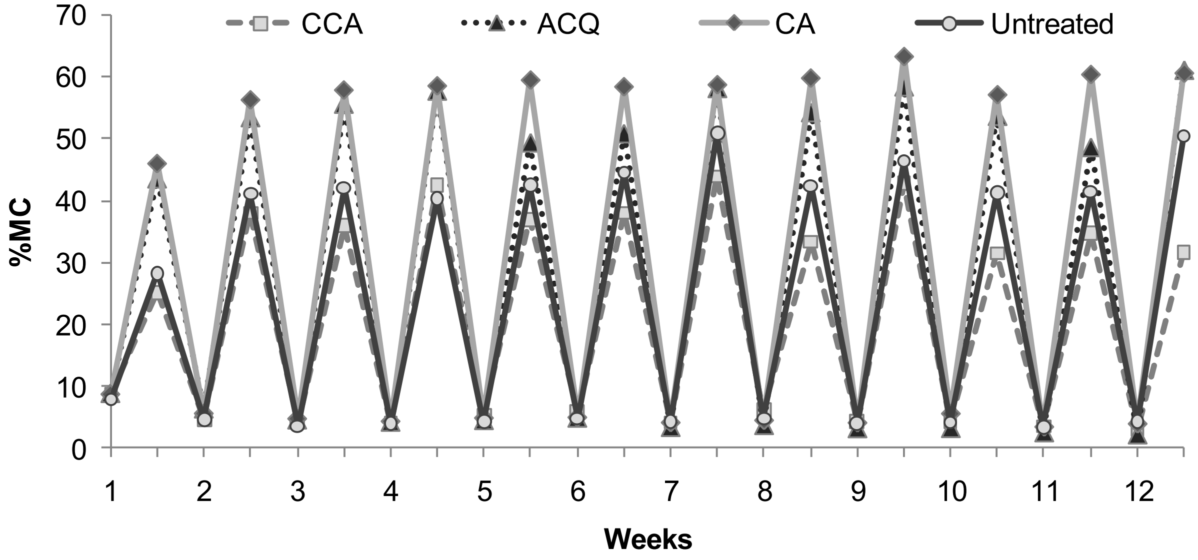

Figure 6.1: Average moisture contents of uncoated wood samples during 12 weeks of artificial weathering.

The average moisture contents of samples following the wetting cycles are presented in Fig. 6.2 and cumulative percentages leached for samples after 12 cycles of accelerated weathering are shown in Table 6.3. In addition to the significant effects of coatings and treatments on moisture absorption of wood samples, there was a significant interaction effect between coatings and treatments (α=0.05). Coating number 9 performed well on all treatments, but most other coatings had better performance on CCA and uncoated wood in comparison with Cu-amine treated woods. In general, among stains tested in artificial weathering, water-based stains had higher moisture contents than solvent-based stains.

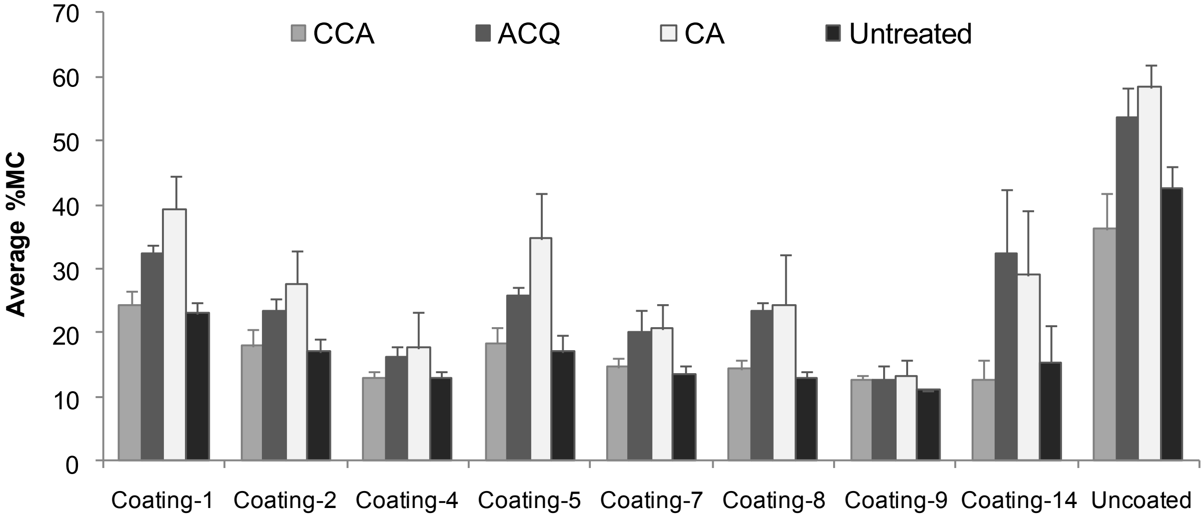

Figure 6.2: Average percent moisture content of samples during 12 weeks accelerated weathering.

All coated samples had lower water uptake and less preservative component leaching than uncoated ones. As with the screening results, coatings number 9, 14 and 4 performed better in terms of leaching reduction and coating-9 performed the best for water repellency.

Similar to the screening results, there were strong positive correlations between average wet period moisture contents of samples during 12 weeks and cumulative percentage leached in accelerated weathering tests. Based on the Pearson correlation analysis, the regression was the highest for As from CCA-treated wood (r=0.98) and the lowest for Cu from ACQ-treated wood (0.87), with all the correlations being highly significant at the 95% confidence interval.

Overall coatings number 5 and 1 were the worst and coating number 9 was the best in both leaching reduction and water repellency.

Table 6.3: Cumulative percent leached after three months of accelerated weathering.

Coating ID		Cumulative % leached					Two-way ANOVA Results
		CCA			ACQ	CA	
ID	Type	As	Cu	Cr	Cu	Cu	
1	Alkyd (W)	0.12	1.7	0.07	2.4	3.1	B*
2	Alkyd-Acrylic(W)	0.08	1.0	0.03	1.1	1.4	AB
4	Alkyd-Acrylic(W)	0.04	0.3	0.01	0.7	0.5	A
5	Alkyd(S)	0.06	0.6	0.04	3.6	3.6	B
7	Alkyd(S)	0.06	0.7	0.03	1.5	1.2	AB
8	Alkyd(S)	0.06	0.4	0.03	1.7	1.6	AB
9	Alkyd(S)	0.02	0.1	0.01	0.5	0.5	A
14	Polyurethane(W)	0.03	0.1	0.01	0.6	0.4	A
	Uncoated	0.25	1.8	0.2	8.9	9.9	

* Coating designated with the same later are not significantly different.

In addition to the significant treatment and coatings' effects, there was a significant interaction between coatings and preservative treatments. Coatings number 9, 14 and 4 were the best and coatings number 5 and 1 ranked statistically as the worst in comparison to the others in leaching reduction and water repellency.

6.3.3 Natural weathering results

Table 6.4 summarizes the average moisture contents of natural weathering samples during wet periods and cumulative amounts of preservative components leached after three years of exposure. There was a strong correlation between average moisture contents of ACQ- and CA-treated wood samples during wet periods and the cumulative amounts leached in three years, but no significant correlation between water uptake of CCA treatments and their leaching performance.

Table 6.4: Average % moisture content of samples in wet periods and cumulative percentage leached during three years of natural weathering (data from chapter 5).

Coating-ID	Ave. % Moisture Contents of wet periods in three years				Cumulative % leached				
					CCA			ACQ	CA
	CCA	ACQ	CA	Untreated	As	Cu	Cr	Cu	Cu
Coating-2	30 (11)	39 (18)	43 (19)	30 (15)	1.4 (0.1)	1.5 (0.2)	0.2 (0.02)	6.0 (1.4)	5.7 (1.2)
Coating-4	27 (11)	35 (16)	42 (20)	31 (17)	1.0 (0.1)	1.1 (0.2)	0.2 (0.01)	4.7 (1.0)	4.1 (0.1)
Coating-5	25 (10)	37 (17)	41 (16)	27 (13)	1.5 (0.2)	1.8 (0.2)	0.3 (0.02)	4.4 (0.6)	5.4 (1.2)
Coating-9	25 (10)	34 (16)	35 (17)	33 (17)	1.1 (0.2)	1.5 (0.2)	0.2 (0.02)	3.5 (0.1)	3.3 (0.6)
Coating-14	28 (10)	37 (17)	40 (18)	34 (18)	1.3 (0.2)	0.7 (0.2)	0.1 (0.01)	3.6 (0.4)	4.8 (0.7)
Uncoated	32 (10)	42 (17)	46 (17)	42 (18)	2.3 (0.2)	2.4 (0.1)	0.4 (0.03)	11.2 (2.4)	11.6 (3.1)

6.3.4 Protocol comparison

Leaching

Generally, the natural weathering performance of stains could be predicted by both short-term laboratory studies and by accelerated weathering exposures. The Pearson correlation analysis indicated a strong correlation between results of cumulative percentage leached from screening and accelerated weathering and cumulative amounts leached after three years of natural weathering [13] (Table 6.5).

Both techniques showed a good correlation to natural weathering leaching reduction performance, but the correlation between screening test and natural weathering was much better. Also, it is more convenient to perform a two-week lab tests for prediction of long-term natural exposure than the accelerated weathering test, we recommend this short term test (two-week) for predicting the ability of a new coating formulation to resist preservative component leaching [13].

Table 6.5: Correlation coefficient (r) of weathering tests comparison for cumulative percentage leached with 95% confidence intervals.

	Components	Natural weathering		
		Correlation Coefficient (r)	P_{Value}	Regression line
Screening	CCA-As	0.85	0.032	$y_{As\text{-}CCA} = 0.38x + 0.96$
	CCA-Cu	0.93	0.008	$y_{Cu\text{-}CCA} = 0.24x + 0.51$
	CCA-Cr	0.84	0.037	$y_{Cr\text{-}CCA} = 0.19x + 0.11$
	ACQ-Cu	0.96	0.004	$y_{Cu\text{-}ACQ} = 0.86x + 0.17$
	CA-Cu	0.95	0.001	$y_{Cu\text{-}CA} = 0.72x + 0.3$
Accelerated	CCA-As	0.96	0.002	$y_{As\text{-}CCA} = 4.96x + 1.02$
	CCA-Cu	0.84	0.035	$y_{Cu\text{-}CCA} = 0.73x + 1.04$
	CCA-Cr	0.97	0.001	$y_{Cr\text{-}CCA} = 1.22x + 0.16$
	ACQ-Cu	0.91	0.005	$y_{Cu\text{-}ACQ} = 0.79x + 3.51$
	CA-Cu	0.96	0.009	$y_{Cu\text{-}CA} = 0.76x + 3.73$

From the slopes of the regressions lines (Table 6.5), it can be seen that the amount leached in lab tests cannot be directly used for prediction. For example, the amount of Cr leached from screening samples sometimes was two or three time higher than the amount leached during three years of natural exposure, thus screening test results cannot be used directly for prediction purposes for CCA component leaching (Figure 6.3a). For Cu leaching from ACQ and

CA, the slopes are close to one, indicating that the two-week water immersion results (lab) corresponded much closer than CCA component to Cu leaching from Cu-amine preservatives after extended natural weathering (Figure 6.3b).

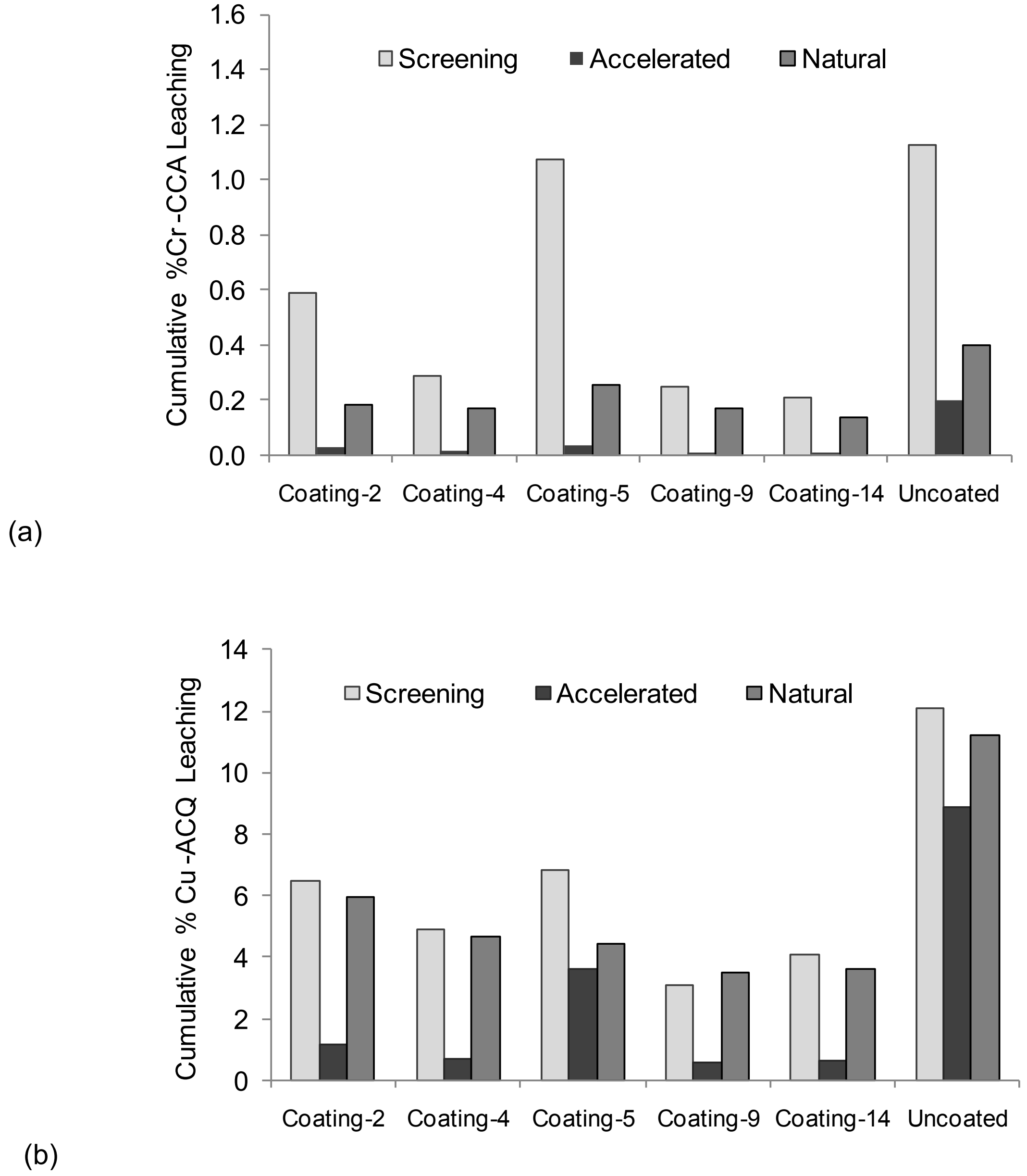

Figure 6.3: Cumulative percentage leached from three different weathering tests (a) Cr from CCA treated wood (b) Cu from ACQ treated wood samples.

Water Uptake

The relationship between water uptake by the screening (two-week) test and average water uptake during wet periods of natural exposure were only significant for ACQ-treated wood (r=0.83). The relationship between average water uptake in the accelerated (three Month) test and during natural weathering was only significant for ACQ (r= 0.93) and CA (r=0.83) treated wood. While the main focus of this accelerated weathering test was to obtain a detectable amount of leachate during water spray cycles, the water spray was not adequate to affect coated samples as much as it affected uncoated specimens. This could be the main reason why coated samples had much lower leaching compared to uncoated samples in accelerated tests (Fig. 6.3).

6.3.5 Modeling

Earlier evaluation of the properties of five coatings against their weathering performance for natural exposure (Chapters two and three) showed that coatings with higher viscosity and film thickness and low Tg had higher water repellency [12] and lower preservative leaching [13]. In this paper a PLS regression model was developed to correlate measured coatings properties of eight stains with their water repellencies and their abilities to reduce leaching after three months of accelerated weathering tests. The model had 78% fitting accuracy and 71% prediction ability after two PLS models. Figure 6.4 is the loadings plot of the PLS model which shows a strong positive correlation between the two response variables (leaching reduction and water repellency). In addition, similar to the modeling results for the natural weathering data, coatings with higher viscosity and film thickness and lower Tg had better water repellency and lower leaching. Also modeling of coating properties to performance of screening test samples (14 stains) confirm these results (not shown here). Therefore, it can be concluded that a flexible (low Tg), viscous coating which forms a thick film layer on the top of the wood surface is a better choice when leaching reduction and water repellency are required performance characteristics.

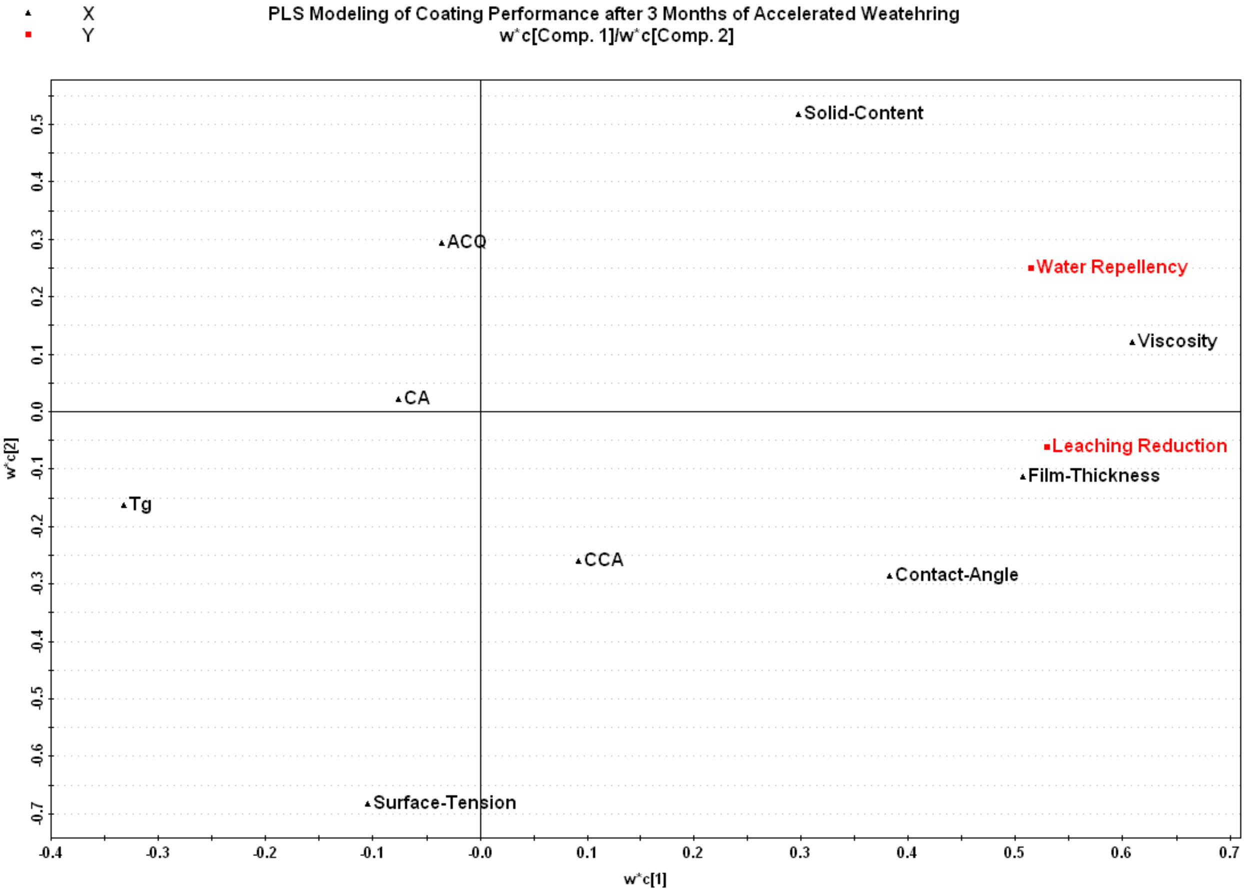

Figure 6.4: Loadings plot of PLS regression model of coating performances based on their properties after three months of accelerated weathering

Figure 6.5 shows the images of samples after 12 weeks of accelerated test cycles for coating #9 (left, one of the best stains) and uncoated samples (right). Developing of checks and mildew growth in uncoated samples were very evident while there was no sign of weathering degradation (checking of wood or mildew growth) or coatings failure (erosion) in the coated sample.

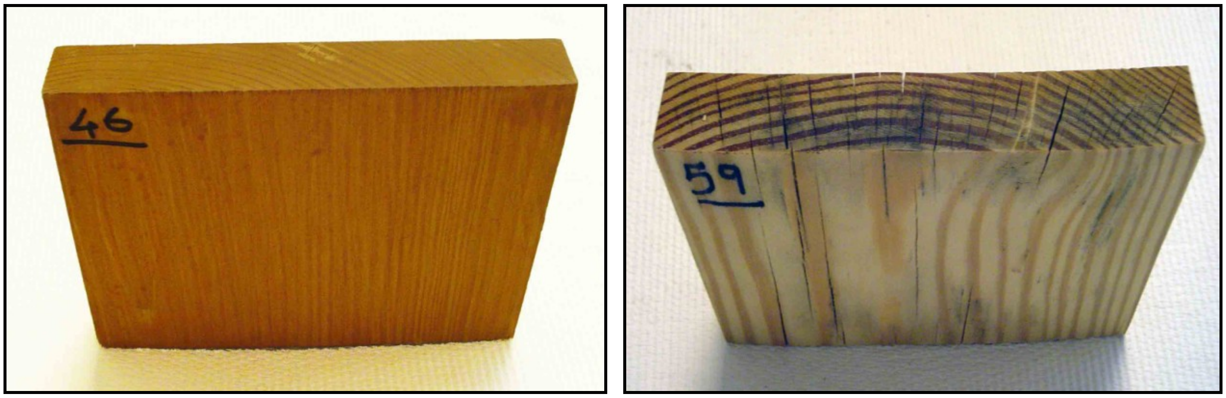

Figure 6.5: coated untreated sample number 9 (left) and uncoated untreated (right) after three months of accelerated weathering.

6.4 Conclusions

A two-week water immersion screening test of coated CCA, ACQ and CA-treated and untreated wood samples proved to be a useful method for assessment of coating efficiency to reduce leaching under natural weathering exposure. Both results of three months accelerated weathering and screening tests showed strong positive correlations between average moisture contents of samples during wet periods and cumulative percentage of preservative components leached from treated woods. However, for natural exposure, only the cumulative amount leached from ACQ and CA–treated wood samples was related to the average moisture contents of samples during wet periods over the three-year exposure. Based on screening tests results which is also confirmed by natural weathering, water-based coating are more effective in CCA component leaching reduction than solvent-based coatings..

Partial least squares regression modeling of the coating properties with their performance in leaching reduction and water repellency during three months of accelerated weathering showed that coatings with higher viscosity, film thickness, and lower Tg have better water repellency and lower preservative leaching.

6.5 References

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Chapter 7

7 Effect of Coatings on ACQ Preservative Component Distribution and Availability after Natural Weathering Exposure

For submission to Journal of Wood Science and Technology

Authors: Mojgan Nejad, Tony Ung and Paul Cooper

Abstract

Copper and quaternary ammonium compound distributions across lumber and amounts of available or soluble components were measured in surface coated and uncoated alkaline copper quat (ACQ) treated southern pine lumber. Lumber that was not exposed to weathering had a slight copper gradient from the surface to the interior and a steeper quat gradient. After 3 years of natural weathering, different penetrating stains had effectively reduced copper and quat leaching compared to uncoated samples. The availability of copper was significantly reduced after weathering, even after accounting for the copper that had leached during the exposure. The relative amount of soluble monoethanolamine (Mea) remaining after weathering was low compared to copper. The resulting decrease in pH in the wood and reduction of soluble amine were most likely responsible for the reduced amounts of available copper. This effect was enhanced in coated samples since the coatings reduced copper leaching while the amount of soluble Mea decreased, resulting in the reduction in long-term potential for copper leaching. The reduced quat leaching from coated samples is attributed to the extended effectiveness of the coatings in the earlywood portions of the samples.

7.1 Introduction

Wood used out-of-doors is often protected against decay and insects by pressure impregnation with wood preservative chemicals. Increasingly, waterborne copper-monoethanolamine (Mea) based systems are used, especially for residential construction, as they elicit fewer health and environmental concerns at the treating plant, in-service and at the end of their life cycles than previously used chromated copper arsenate (CCA). These preservatives contain an organic co-biocide to improve efficacy, especially against copper tolerant decay fungi. The main copper amine based preservatives in use in various jurisdictions at this time are: alkaline copper quat (ACQ - copper amine with a quaternary ammonium compound); copper azole (CA - copper amine with tebuconazole); copper HDO (Bis-(N-cyclohexyl-diazeniumdioxy-copper amine) [1] and copper betaine (copper amine with didecyl polyoxyethyl ammonium borate [2]. ACQ and CA are the predominant copper amine preservatives used around the world at this time.

Although dissolved in water for treatment, ACQ preservative components (copper amine complexes, quat and Mea) interact with and bind to wood depending on pH and ambient conditions, rendering the copper and quat components resistant to water leaching. These reactions are thought to include ion exchange and other complexation reactions of cationic copper amine complexes [3, 4] and cationic quat [5, 6] with dissociated anionic groups in wood. Another possible mechanism for copper fixation is pH-dependent precipitation reactions within the wood structure [7]. Despite these reactions, relatively high copper leaching is observed when ACQ treated wood is exposed to laboratory leaching tests [8-11] or natural weathering exposure [12-16], particularly in high retention treatments.

The competition for and rapid binding of cationic quats and copper amine complexes to anionic binding sites in wood results in a gradient of components, even in a highly permeable wood like southern pine sapwood. For example, Cooper and Ung [11] noted shallow copper and steep quat gradients across 38mm thick ACQ treated southern pine lumber. After one year of natural weathering exposure, they observed some depletion of copper from the upper surface and extensive loss of quat.

Previous research notes that temporary protection of ACQ treated wood using finishes such as stains [17] or water repellents [16] appears to reduce the long-term leaching potential of the copper component. For example, Nejad and Cooper [17] noted that ACQ treated wood coated with penetrating stains and weathered for 36 months had significantly reduced copper leaching during the first year (while the coatings were still intact) and that this reduced leaching was maintained even after the coatings began to fail on the latewood tissue after approximately one year (Figure 7.1). These results suggest that temporary protection of wood from leaching during the initial exposure period may result in long term benefits in reduced leaching over the life of the product.

The objectives of this study were to determine whether the apparent reduction in copper availability for leaching could be confirmed and to explore potential causes of any effects. This was done through analysis of the copper and quat gradients in unexposed and weathered samples, and determination of the inherent availability of copper, quat and Mea under the different exposure conditions.

7.2 Methods and Materials

7.2.1 Specimen preparation

Southern pine (*Pinus* species group) lumber, 20mm X 140mm X 1.22 m was treated with 1.05 % ACQ-C solution (solids content 66.7 % copper expressed as CuO and 33.3 % quat as alkyl dimethyl benzyl ammonium chloride – ADBAC with monoethanolamine solvent at 2.75 X the CuO mass) to a retention of approximately 4.9 kg/m^3. The preservative was allowed to react with wood for 1 week at 50°C and 95% relative humidity. The lumber was then air-dried in the laboratory for several weeks. Short boards (20mm x 140mm x 280mm long), were brush coated on the top faces and edges with one of five commercial penetrating stains, representing a range of resin types, solvents and other coating properties [17] or left uncoated. These samples were retained in the laboratory for one additional week. Three replicate samples for each coating and for uncoated control samples were installed horizontally over water collection containers and exposed out-of-doors for three years in Toronto, Canada to monitor the preservative leaching losses. Additional coated and uncoated samples were retained in the laboratory during this 3-year period. Detailed information on the treatment, the coatings and the results of leaching are described in chapter-5 [17].

To investigate the apparent effect of coatings to reduce long-term leaching, preservative component distributions and availabilities were compared for weathered coated and uncoated samples and unweathered samples stored in the laboratory for three years.

7.2.2 Gradient analysis

Samples with three coatings, selected to represent high reduced leaching (coating 9), moderate performance (coating 5) and least efficient leaching reduction (coating 2) were evaluated for copper, quaternary ammonium compound (quat) and Mea concentration gradients in 5 equal thickness layers (approximately 4 mm thick) through the lumber depth. Samples were ground to pass a 1mm screen, digested based on AWPA A7-04 [18] and analyzed for copper retention by atomic absorption spectrometry (AAS, AAnalyst 100-Perkin Elmer). Total Mea contents in the ground wood of selected samples were estimated based on their nitrogen contents as measured by elemental combustion system (ECS 4010, Costech). The results were corrected for the natural N content of the wood, as measured in untreated wood and the quat content in the wood. A 1.0 g wood dust sample was extracted with 10 mL of denatured ethanol by ultrasonic extraction for 3 hours according to AWPA A16-93 [19]. Extracts were analyzed for quat retention by ion chromatography (Dionex DX 600) suppressed conductivity using an

IonPac®CS14 analytical column (4mm) equipped with cation suppressor (CSRS) and run isocratically at 1.0 mL/m flow rate. The eluents used for quat analysis were 20% 20 mM methanesulfonic acid and 80% acetonitrile.

7.2.3 Availability of components

The preservative component availabilities were estimated by vigorously extracting wood powder with water for an extended period to extract the readily soluble components [20]. Five gram samples of wood dust from different depths were extracted in 100 mL water without water exchange for 14 days. The pH of the water-wood-dust suspension was measured after 24 hours as a relative comparison of the wood pH. The leachate was analyzed for copper content by AA, as above. The Mea component in the leach water was determined by ion chromatography using 100% 20mM methanesulfonic acid as an eluent. The leached wood dust was extracted with ethanol as above and the extract analyzed for retained quat to determine the amount removed by the leaching process.

Full cross-sections of all coated and uncoated samples were ground and subjected to intensive leaching (2 grams of sawdust in 100 ml distilled water with water exchange after 1, 3, 10 and 30 days). Copper removed in the leachate was analyzed by an Optima 7300DV inductively coupled plasma optical emission spectrometer (ICP-OES).

7.3 Results and Discussion

7.3.1 Preservative component distribution (gradient) in wood

In uncoated samples retained inside for 3 years, copper concentration decreased slightly with depth while the quat gradient was more pronounced. Samples weathered for three years had copper selectively removed from near the top surface, while quat was lost from throughout the section and in proportionally higher amounts compared to copper (Fig. 7.2a). As a result, the copper: quat ratios increased with depth and were higher after weathering (Fig. 7.2b). Based on analysis of collected leach water over the three year exposure period, it was estimated that about 11 % of the total copper was leached during this period (Fig. 7.1).

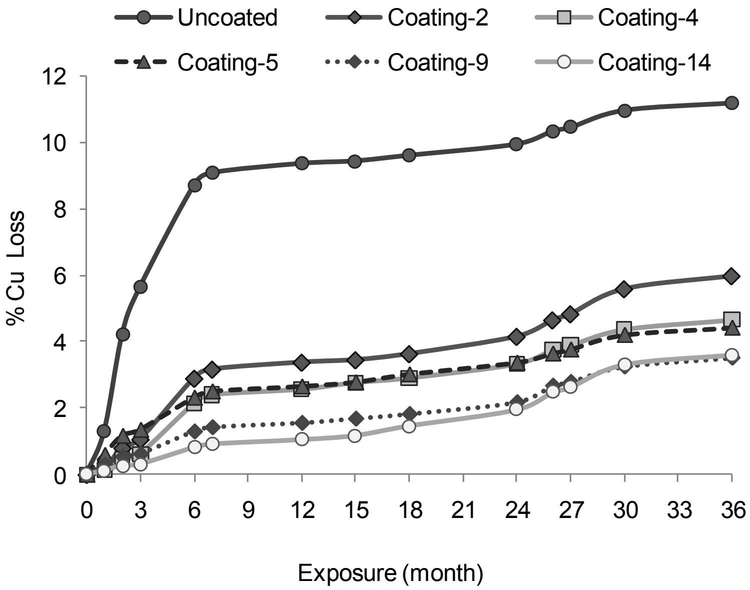
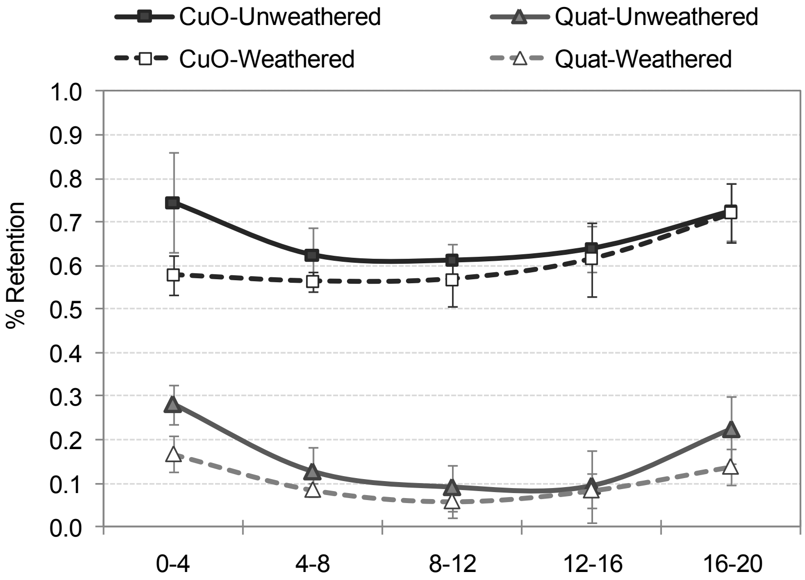
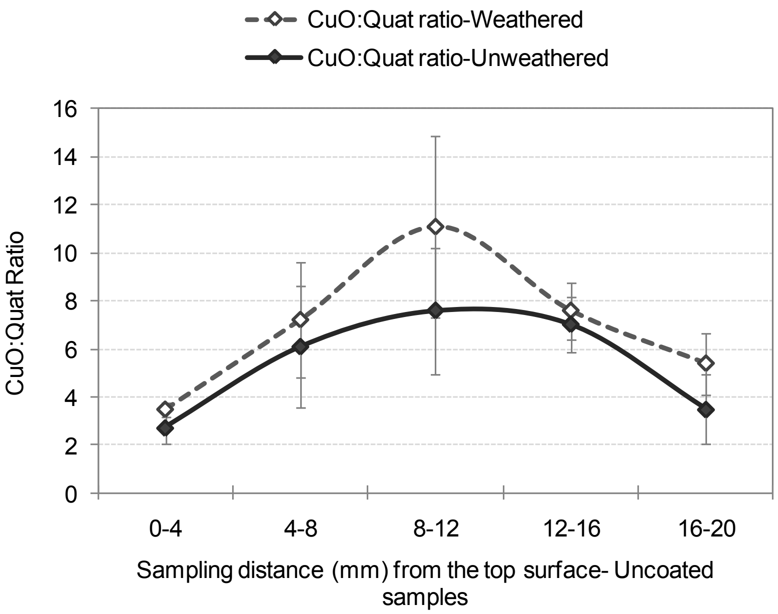


Figure 7.1: Effect of coatings on copper leaching from ACQ treated samples during 3 years of natural weathering exposure in Toronto, Canada



(a)



(b)

Figure 7.2: Average copper and quat retention gradients (a) and copper:quat ratios (b) for unweathered and 3 year naturally weathered southern pine boards (uncoated samples) – 3 replicate samples

The preservative component distribution in coated samples (Fig. 7.3a) confirmed the effectiveness of the penetrating stains to reduce leaching. Leachate analysis results (Figure 7.1) indicated that about 3-5 % of the total copper was leached during the three year exposure of coated samples. ADBAC concentrations were reduced at both surfaces, but the coatings were effective in minimizing these losses. As a result, the average copper to quat ratio was not greatly affected by the weathering period in coated samples (Fig. 7.3b).

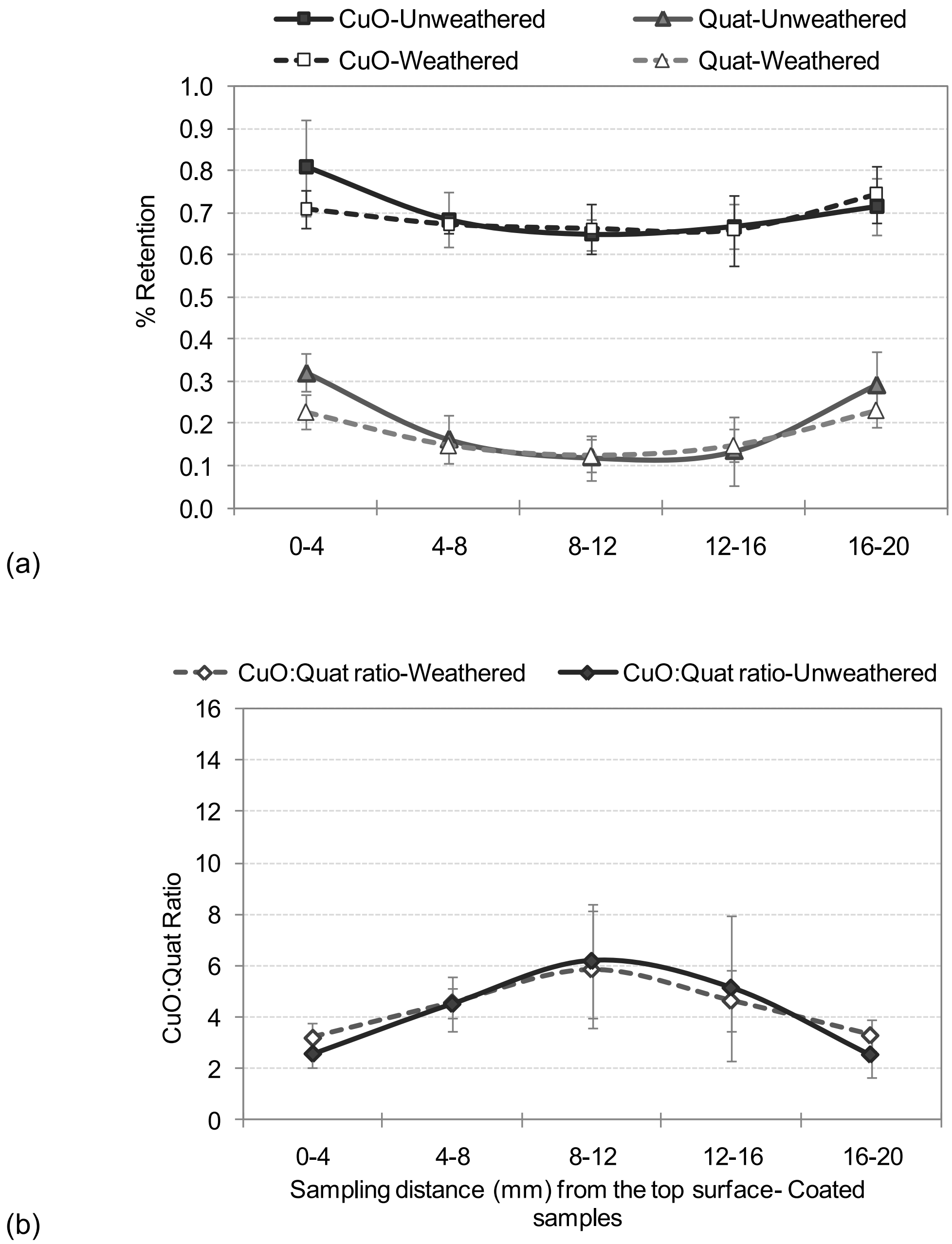


Figure 7.3: Average copper and quat retention gradients (a) and copper:quat ratios (b) for unweathered and three year naturally weathered 20 mm thick coated southern pine boards– Combined data for all coatings

7.3.2 Preservative component availability in wood

7.3.2.1 Copper availability or solubility

The readily available copper with a single extraction in aged coated or uncoated unweathered ACQ treated southern pine was similar at different depths in the wood, ranging between 15 and 20% (Fig. 7.4).

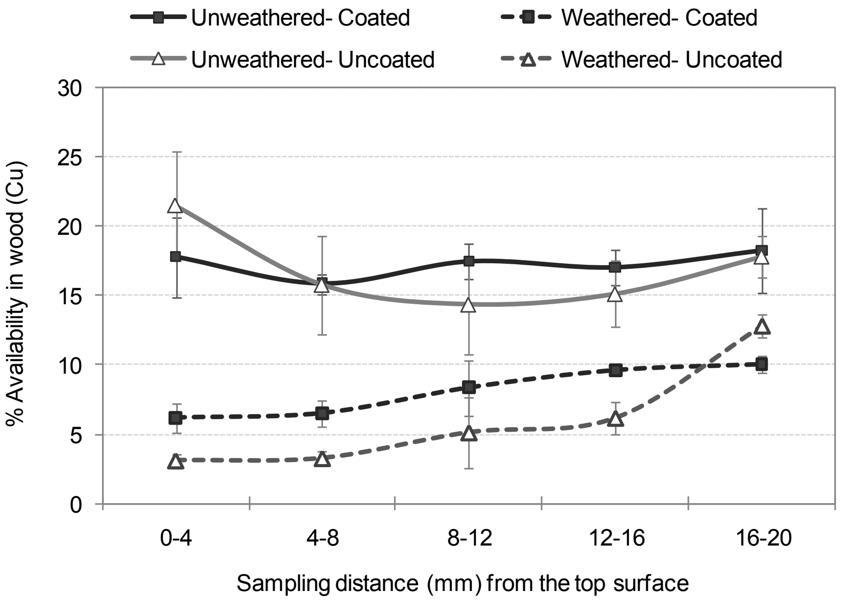


Figure 7.4: Availability of soluble copper as affected by exposure

The available soluble copper was much lower in the weathered samples, especially near the surface where there was relatively little soluble copper available for future leaching. For the uncoated sample, the discrepancy between the distributions of available copper in weathered and non weathered samples was about 9-10% of the total copper retention. This was slightly lower than the 11% loss of copper measured by leachate analysis during natural weathering. The coated weathered samples also had low copper availability, about 9% lower than that of the unweathered samples. Since only about 4% of the copper was leached from coated specimens during exposure, it is apparent that some of the originally available copper became unavailable over the exposure period, as suspected from the leaching rate data in Fig. 7.1. This effect was confirmed by a comparison of the amounts of available copper from full cross-sections taken from uncoated boards and boards coated with the five coatings. In this case, multiple water extractions were made and the amounts were higher than shown in Fig. 7.4. The extraction of copper from ground wood was rapid and approached an equilibrium amount after 30 days, which we assume to approach the total soluble amount available for leaching (Fig. 7.5).

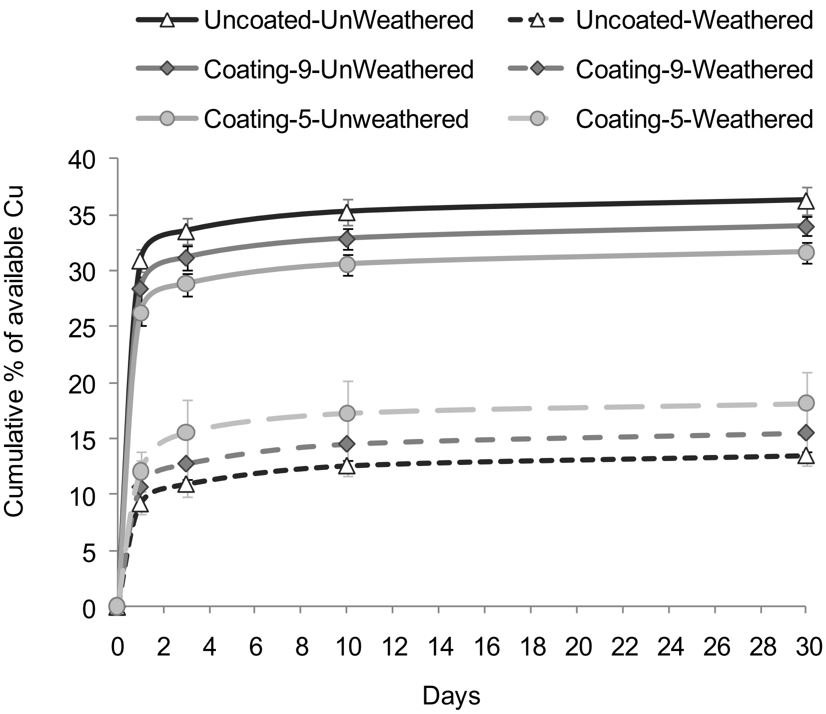


Figure 7.5: Examples of the copper availability or solubility over time from ground wood representing full cross-sections of different exposed boards

The amounts of copper available from full cross-sections of boards for different coatings and conditions are compared in Fig. 7.6. The solid bars represent soluble copper in the samples stored indoors for three years (no leaching exposure). The compound bars represent weathered samples; the hatched part of the bar is the average amount leached during exposure and the solid part is the available soluble copper after exposure.

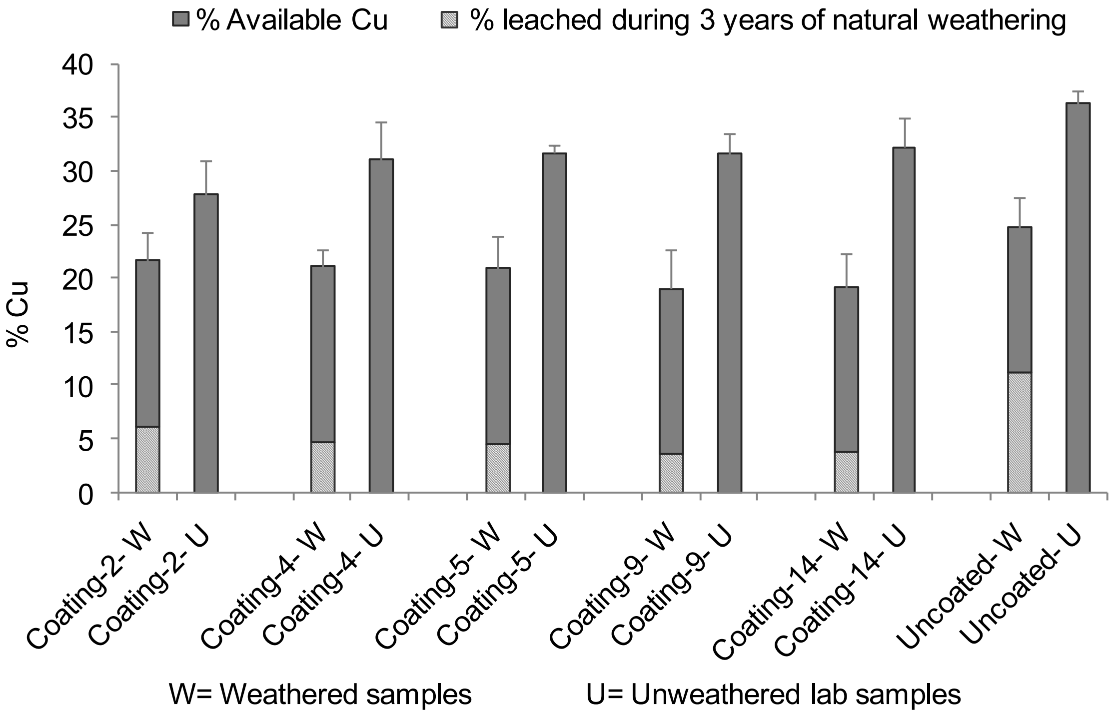


Figure 7.6: Total copper leached or available for leaching for coated and uncoated samples exposed to three year natural weathering (W) - "U" unweathered samples are those that were kept indoors for three years.

It is clear that the exposed boards, whether coated or not, still have significant potential to leach copper and re-finishing of the surfaces would be advised to control the rate of leaching of the still available copper. However, the sum of amounts leached and amounts available for leaching are significantly lower than the amounts available in unexposed samples; this effect is most evident for the coated samples but is also statistically significant for the uncoated samples. Furthermore, the coatings that were more effective at reducing leaching (coatings 9 and 14, Fig. 7.1) had the lowest total copper availability while the uncoated samples had the highest combined values. This suggests that changes occur to the treated wood system during exposure which reduce the availability of copper to leaching and that coatings help to protect the leachable copper from being removed until these changes have taken place. The average availabilities of copper in the coated unexposed samples appear to be lower than for the uncoated samples (comparing solid bars), although the difference is statistically significant only for coating 2 vs. uncoated. This could be an indication that the coatings themselves had an effect on inherent copper solubility by reaction of coating resins with free copper in the wood.

7.3.2.2 Quat availability

The soluble amount of quat varied greatly among the replicate samples but, on average, 40 – 50% was available for leaching in unexposed samples (coated or uncoated – Fig. 7.7). For coated samples, a similar amount remained soluble even after three years of weathering. This indicates that although there was moderate loss of quat during the weathering exposure (Fig. 7.3a), a substantial amount of quat was still available for leaching (Fig. 7.7). Uncoated samples had reduced amounts of soluble quat after exposure because of the greater loss of quat during weathering exposure. These results suggest that the inherent availability of quat was not affected in the same way as copper. Considering that the coatings remained intact on the earlywood portions of annual rings after three years of weathering, effective sealing of the earlywood was most likely responsible for the reduced quat leaching in coated samples. During treatment, the earlywood absorbs more treating solution and because of the rapid and efficient reaction of quat in the wood cell walls [4], the quat concentration is higher in the earlywood [21], allowing the coating to be very effective. The distribution of available quat in uncoated samples after leaching was much higher near the surface than in the interior, indicating that quat was mobilized during weathering exposure to migrate towards the surfaces.

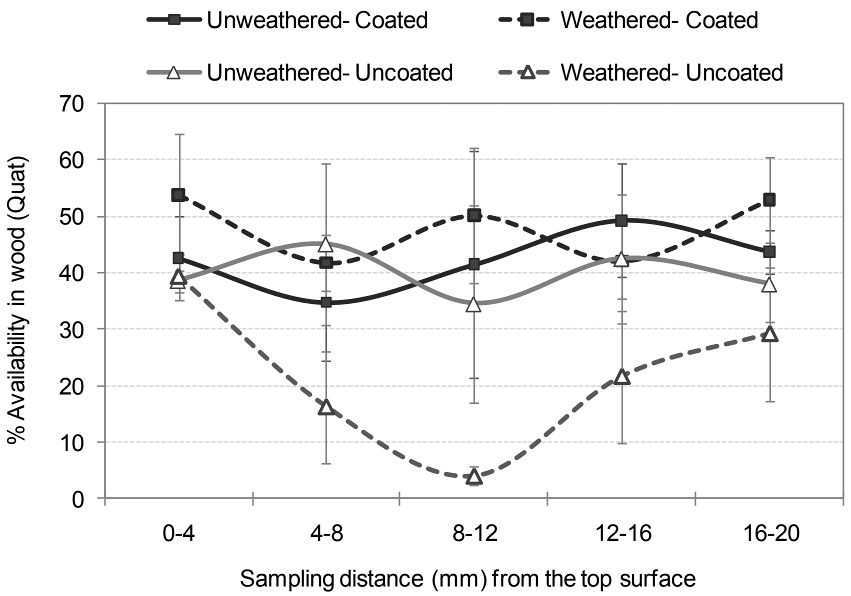


Figure 7.7: Availability of quat in wood for different exposure conditions

7.3.2.3 Mea availability

The distribution of total Mea in the unexposed lumber (coated and uncoated), as estimated from the N content, showed a steep gradient from the surface to the interior (Fig. 7.8). This is very different from the initial copper gradient in wood and suggests that in addition to the ion exchange of cationic copper-Mea complexes to wood, there is also adsorption of Mea, possibly in the protonated form, although this species is most abundant at lower pHs. After three years of weathering (coated and uncoated samples showed similar distributions so they are averaged together), there was a significant reduction in Mea content, especially near the top surface.

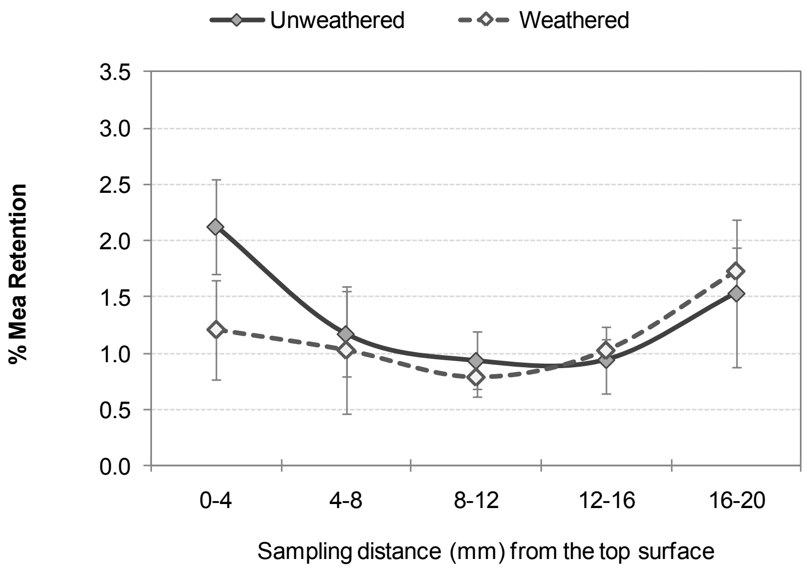


Figure 7.8: Distribution of Mea across unweathered and weathered boards

Intensive leaching of sawdust of both coated and uncoated samples that were not exposed to weathering removed 30% to 50% of the Mea from the samples depending on the depth (Figure 7.9). There was relatively more Mea lost from the surface indicating that the higher amounts present near the surfaces of the samples initially were more available to leaching. The remaining unextracted Mea component is presumably complexed with copper and bound to the wood. On average, about 0.8 % of the Mea could not be extracted, which is similar to the amount of copper fixed in the wood. The availability of Mea in the samples after three years weathering was greatly reduced in both coated and uncoated samples (Figure 7.9). It is not clear whether this is attributed to the leaching observed (Figure 7.8) only, or whether additional stabilization of Mea occurred within the wood. However, it is apparent that Mea became considerably less available during the three years of natural weathering.

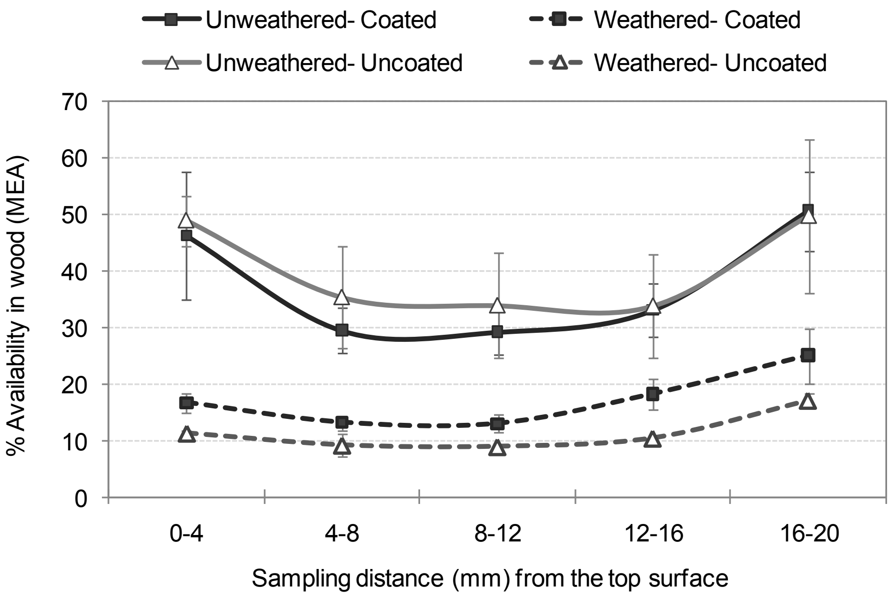


Figure 7.9: Effect of natural weathering on availability of Mea remaining in the wood

7.3.2.4 Relative pH of the wood

The pH values for the wood in water suspension (5 g wood dust in 100 ml water) after 24 hours are shown in Table 7.1. The wood pH was highest in the lumber stored inside for three years. It appears that the preferential leaching of Mea from the weathered (both coated and uncoated) wood resulted in lower pH in the wood. This lower pH could promote precipitation of copper compounds such as basic copper carbonate, to enhance the leach resistance of residual copper in the wood, or make it more favorable for copper to react in the cell walls than to remain in solution.

Table 7.1: pH of wood dust - water suspension – means (s.d.)

Wood sample	pH
Coated samples-Unweathered (stored inside for 3 years)	6.5 (0.4)
Coated samples-Weathered (for 3 years)	5.8 (0.05)
Uncoated samples- Unweathered (stored inside for 3 years)	6.3 (0.5)
Uncoated samples- Weathered (for 3 years)	5.9 (0.05)

7.3.2.5 Discussion of potential mechanisms for effects of coatings on long term leaching performance

Coatings reduced the quat leaching, but a significant amount of quat remained available for leaching after 3 years of exposure. Thus, the effectiveness of the coatings to reduce leaching of ADBAC may be attributed to the fact that coatings effectively sealed the earlywood tissue over the three year exposure period. Since earlywood absorbs more solution than latewood during treatment and the quat reacts rapidly with the wood cell walls, the quat concentration will be higher and more susceptible to leaching in earlywood. The coatings remained intact in the earlywood, effectively reducing leaching. However, with longer weathering exposure, the coatings will deteriorate further to expose the earlywood tissue and quat leaching will increase if coatings are not renewed on a regular basis.

The reduction in copper's potential to leach was enhanced by the coatings and appears to be associated with the reduction in available soluble Mea as a result of natural weathering exposure. This reduced the pH in the wood tissue, which could promote some precipitation of low solubility copper compounds. Also, reduced amounts of free Mea in the solution as a result of preferential leaching or further reaction could result in less competition to keep the copper-Mea complexes in solution, allowing them to react in the wood cell walls. The decrease in pH leads to higher protonization of the free Mea in the wood (pK~9.4). In this form, Mea does not complex with copper, reducing the tendency of Mea to keep the copper in solution, and allowing more copper complexation with the wood cell walls.

An alternative, or possibly complementary process is related to the observation [22] that unfixed copper diffuses from earlywood to the latewood during post treatment conditioning of ACQ treated southern pine. Earlywood absorbs more solution and cannot fix all of the copper, while latewood accepts less treating solution during treatment but has higher capacity to fix copper. If this redistribution is not complete when samples are exposed to the weather, charged unfixed copper-Mea complexes could continue to diffuse from earlywood to latewood during the alternate wetting and drying that occurs during weathering, The more available complexes in the earlywood would be protected by the effective sealing of this tissue by the coatings until they had time to diffuse into and react with the latewood.

7.4 Conclusions

It was confirmed that application of a penetrating stain to ACQ treated wood resulted in both short-term and long-term reduction in copper and quat leaching during weathering.

1. Copper leaching characteristics appear to be fundamentally changed over long term weathering exposure, so the potential for leaching is permanently reduced during weathering exposure; this reduction is enhanced by the penetrating stains.

2. The most likely cause of this effect is the preferential leaching or further reaction of Mea in both coated and uncoated samples, resulting in reduced pH in the system, reduced free soluble amine content, and in particularly neutral or unprotonated Mea reduced copper solubility within the wood.

3. Quat (ADBAC) leaching was also reduced by the use of coatings, but apparently by a different mechanism. The quat remained available after three years of exposure and could leach if the coating is not maintained. This may be attributed to the good sealing of the earlywood by the coatings and the fact that the earlywood is expected to contain most of the quat in the wood. Thus this effect is less permanent and repeated of application of sealants is recommended.

7.5 References

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Chapter 8

8 Conclusions and Recommendations

This study initially focused on investigating the efficiency of semitransparent stains in enhancing exterior wood performance, factors include their ability to reduce preservative component leaching, reduce checking and water uptake, and improve the colour stability of the wood. To explain the observed performance, for first time the relationship between coating properties and their performances were considered. Generally, penetrating stains are recommended for exterior applications because they penetrate deep into the wood and do not form a film layer on the top as paint does. However, monitoring and comparing coating performance during three years of natural weathering showed that coatings which penetrated deep into the wood without forming a film layer on the surface had poorer performance overall than those which formed a film layer. To protect the wood from weathering, a coating should at least form a thin layer of protective film on the surface of the wood. Film formation depends mainly on coating viscosity: higher viscosity coatings form thicker film layers regardless of whether they are water-based or solvent-based.

Coatings which formed a thick flexible layer of film (low Tg) on top of the wood surface had higher water repellency overall, better leaching reduction, and better appearance ratings, but less color retention. The poor colour retention of these coatings can be explained as follows: during natural weathering, coatings are eroded from the latewood areas, exposing bare wood. Comparing the colour of the wood samples with the initial colour of the coated samples in fact meant comparing weathered wood with that of the unexposed coated wood samples. In long term natural weathering, comparing the colour of coated samples after the coating has eroded from the surface with the colour immediately after the initial coating application is not a fair evaluation of the colour change of the coating, because there is no coating left on the surface. Thus, colour change comparisons either should be conducted under laboratory conditions, or in the case of natural weathering should be performed while the coating is still intact.

Water repellency is one of the main criteria for evaluating coating performance. However, after one year of natural weathering we observed that all the coatings lost most of their ability to reduce water uptake effectively. This was approximately at the same time as the coatings started eroding from latewood sections of the pine samples. Since there is a significant density difference between latewood and earlywood areas of southern pine and coatings were exposed to severe stresses caused by 50 degrees temperature differences from winter to summer in Toronto, Canada, this was a very harsh condition for evaluating coating performance.

The ability of CCA-treatments to enhance coating performance due to the presence of chromium in the CCA formulation was demonstrated by other studies, and our results confirmed this. Our study was the first, to monitor coating performance on Cu-amine-based wood preservative in long-term natural weathering. Even though, ACQ and CA treatments do not contain Cr, they significantly improved colour retention and the general appearance ratings of coated wood samples. This may be attributed to lignin modification by Cu, as with Cr, resulting in less colour change in the wood samples and better adhesion of coating to treated wood. The main performance difference observed was the water uptake of CCA compared with that of Cu-amine treated wood. The improved water repellency and better performance of solvent-based coatings versus water-based coatings found by previous studies was observed only for CCA; ACQ and CA-treated wood, either coated or uncoated under all weathering conditions had significantly higher water absorption than CCA. The high water uptake of wood treated with ACQ and CA formulations masked any effect of the coating base on the reduction in water uptake. This indicates, it is not preferable to use a solvent-based coating over a water-based coating when the wood underneath is treated with Cu-amine-based preservatives.

Differences in the chemistry of the preservative formulations were considered likely to affect the surface properties of the treated wood. However, the negligible differences in the coating contact angles on different preservative treated woods indicated that treatment does not change the surface characteristics (wettability) appreciably. Therefore, there is no need for coating formulators to focus on reducing the surface tension of coatings. The coating contact angles on latewood were significantly higher than those on earlywood in southern pine. The higher contact angles of coatings on latewood could help to explain the poor adhesion and early failure of coatings on latewood of southern pine.

The image analysis method developed for this study proved to be a valuable technique for quantifying surface checking of wood in comparison studies. Coatings reduced surface checking of wood on average 30 to 40% compared with uncoated wood samples after 3-year natural weathering. Coatings which had higher film thickness on the surface were more effective on checking reduction. Checking of wood is one the main reasons that people replace their sound decks; this result indicates that coatings can increase the service life of wooden decks especially with proper maintenance and timely reapplication.

Measuring film thickness of penetrating stains on wood is not as easy task, but studying the cross-section of osmium treated coated wood samples in back-scatter mode of SEM was found to be a very useful method for accurately determining average coating film thickness. Analysis of samples after short-term weathering showed that checking of wood was initiated through the rays. To reduce wood checking, a coating should have initially low viscosity to penetrate deep and fill the rays and should stay flexible during weathering (low Tg) with good cohesion, and adhesion to the wood.

Investigating the relationship between coating performance characteristics and various coating properties yielded information helpful for the development of new coating formulations. Partial least squares regression (PLS-R) modeling proved to be an excellent tool for modeling highly correlated X variables such as the coating properties, allowing us to consider a number of coating performance characteristics simultaneously. The model developed which had a 77% fitting accuracy, and a 69% predictive ability, showed that the coating base (water or solvent) or type of resin (alkyd, acrylic or PU) were not important factors in the prediction of coating service life.

Although CCA-treated wood has been phased out for residential construction, CCA decks made before January 2004 are still in service, and they can last for a long time. Health Canada recommends the application of penetrating stains every year to reduce CCA component leaching; however, the stains evaluated in this study reduced arsenic leaching by 50% on average and chromium by 57%, even after three years of natural weathering. This will hopefully be a good solution for concerned CCA deck owners discouraging them from replacing their sound decks and adding to the problem of CCA disposal in landfills. Based on our results, the application of stains every year is not necessary and is required only when most of the coating film is eroded from the surface of wood. Depending on the quality of the stain and the exposure conditions, reapplication may be needed just every two to three years.

Leaching reduction was mainly related to coating film thickness, viscosity and Tg (based on modeling results). Higher viscosity coatings which formed thicker film layers and had higher flexibility (lower Tg) provided a better barrier for preservative components. In addition, water-based coatings, which are low in VOC and more environmentally friendly also proved to be more effective for CCA component leaching reduction than solvent-based coatings.

Currently the most common decking treatments in Canada are based on copper amine which they leach Cu in a greater amount than CCA. Application of semitransparent stains reduced Cu leaching from these treatments by about 70%, after three years, resulting in reduced risk of toxicity in aquatic environments. The Cu amount in leachate of coated wood samples never reached that of uncoated ones even after coating failure.

Gradient and component solubility analysis of ACQ-treated wood samples compared with unweathered samples after three years of natural weathering, showed that application of a coating before or soon after construction and weathering exposure would result in both short term and long term reduction in Cu leaching. A permanent reduction of available Cu could be explained either by preferential leaching or further reaction of Mea, resulting in reduced free soluble amine content and reduced copper solubility within the wood.

Since erosion of coatings was mainly on latewood, and earlywood was sealed by coatings for a longer period of time, the reduced quat (quaternary ammonium) leaching could be explained by this effect. Therefore repeated maintenance of the coating at the time of significant erosion of the coating from the wood surface will be needed to ensure reduced quat leaching over the treated-wood service life.

Natural weathering exposure is a costly and time-consuming approach for evaluation of new coating formulations and effective short-term lab tests are needed. The two-week water immersion (screening) test reliably predicted efficacy of coatings to reduce preservative leaching. The three month accelerated weathering test was promising too, but since it is more convenient to conduct the two-week lab test and obtain good results, it is preferable compared to the accelerated weathering test for leaching prediction.

8.1 Recommendations

8.1.1 Coatings formulator

Formulating coatings for ACQ and CA-treated wood should be more focused on improving water repellency of the coating, since ACQ and CA absorb more water than CCA and untreated wood.

To reduce checking of wood, instead of focusing on formulating a coating that penetrates deep into the cell wall of wood to achieve wood stabilization, coatings that are able to fill the rays initially (low viscosity), have good adhesion with wood, cohesion and flexibility (low Tg) and that build a layer of film on the top of the wood surface should be considered.

Since the contact angle of coatings is higher on latewood than on earlywood of southern pine wood samples, it is better to conduct wettability tests during development of new coatings on the latewood rather than on earlywood area to achieve better adhesion.

8.1.2 Deck owners

CCA deck owners can reduce risk of As and Cr exposure by applying even one coat of a water-based semitransparent stain which is viscous enough to build a barrier film layer on the wood surface. Reapplication is only needed when the coating erodes from the wood surface and the area of the bare wood is exposed (maybe every two to three years depending on the quality of stain).

In addition, to reducing risk of Cu-leaching from ACQ and CA-treated decks, in areas close to aquatic environments, application of a high quality stain during the first six months of weathering exposure can permanently reduce Cu-leaching. This coating can be applied by owners or as a pre-finished product by the industry to reduce soil and water contamination, increase efficacy and extend the life (aesthetics) of the structure.

8.2 Future Work

More detailed research is needed to understand the mechanisms of liquid water absorption in Cu-amine based preservatives and to find ways to improve their water repellency.

Future studies are recommended to measure performance criteria of a wide range of coating formulations on species with uniform texture and on a single preservative treatment. This will result in building a prediction model that is less influenced by preservative treatments and magnifies the effects of coating properties on their performance.

Also, measuring water vapour permeability of coated wood samples would be a great addition to measured properties in similar future studies.

With care in sample preparation, application of TOF-SIMS in both high spatial and high mass resolution mode has potential for the study of penetration of different coatings' components like resin and pigment into the wood structure. Investigation of penetration of resin into the wood cell wall may help explain coatings' weathering performance clearly. This is especially useful when a coating e.g. alkyd coating, cures inside the wood and reduces water uptake and swelling.

Appendices

A-1: Average moisture contents of CCA-treated screening coated and uncoated wood samples after 1, 3 and 14 days of water immersion test.

Treatment	Coating	MC-1	MC-3	MC-14
CCA	1	46.1	61.7	77.1
CCA	2	43.5	53.1	68.8
CCA	3	37.2	49.0	64.8
CCA	4	26.8	42.1	62.3
CCA	5	41.5	54.4	76.9
CCA	6	40.2	53.3	75.7
CCA	7	38.7	51.3	70.2
CCA	8	39.8	51.1	68.6
CCA	9	27.4	39.5	56.4
CCA	10	39.7	51.4	65.5
CCA	11	43.4	55.6	77.4
CCA	12	55.1	61.3	76.1
CCA	13	27.6	42.7	56.1
CCA	14	36.2	45.2	57.5
CCA	Uncoated	53.5	58.6	76.3

A-2: Average moisture contents of ACQ-treated screening coated and uncoated wood samples after 1, 3 and 14 days of water immersion test.

Treatment	Coating	MC-1	MC-3	MC-14
ACQ	1	49.1	57.4	72.0
ACQ	2	47.8	57.2	75.4
ACQ	3	43.0	51.0	69.0
ACQ	4	35.7	50.1	67.9
ACQ	5	47.5	56.5	75.2
ACQ	6	44.8	54.3	71.5
ACQ	7	44.2	52.6	69.0
ACQ	8	41.0	50.5	65.9
ACQ	9	32.2	43.7	60.3
ACQ	10	42.5	52.1	69.0
ACQ	11	45.2	54.6	73.2
ACQ	12	48.1	55.7	70.4
ACQ	13	38.3	51.4	67.9
ACQ	14	30.0	44.0	62.6
ACQ	Uncoated	56.6	62.6	77.8

A-3: Average moisture contents of CA-treated screening coated and uncoated wood samples after 1, 3 and 14 days of water immersion test.

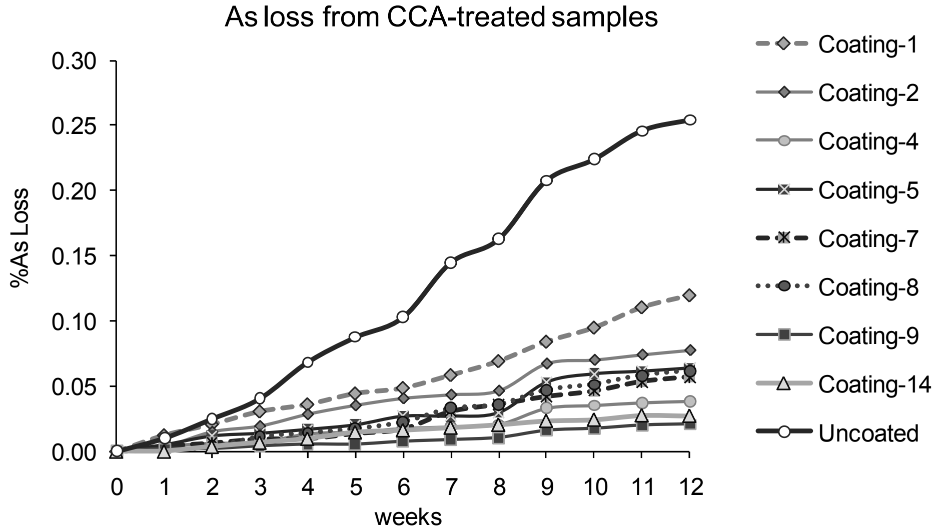
Treatment	Coating	MC-1	MC-3	MC-14
CA	1	46.2	54.9	70.4
CA	2	46.2	52.9	71.6
CA	3	43.6	51.6	70.0
CA	4	33.3	47.0	66.3
CA	5	48.4	57.6	78.0
CA	6	48.2	56.7	75.6
CA	7	43.3	52.0	71.5
CA	8	46.2	55.0	73.5
CA	9	35.8	45.6	64.1
CA	10	40.3	48.2	66.9
CA	11	46.1	55.8	77.0
CA	12	53.2	59.3	79.5
CA	13	34.8	45.0	64.6
CA	14	29.3	42.1	62.0
CA	Uncoated	56.7	62.0	83.6

A-4: Average moisture contents of untreated screening coated and uncoated wood samples after 1, 3 and 14 days of water immersion test (3 replicates).

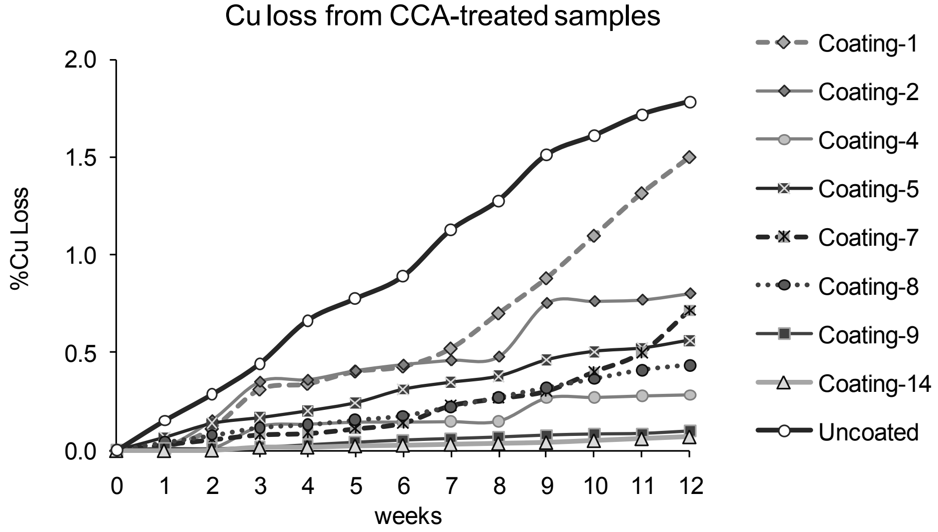
Treatment	Coating	MC-1	MC-3	MC-14
Untreated	1	42.8	54.7	76.9
Untreated	2	42.8	47.4	73.8
Untreated	3	38.7	44.1	62.1
Untreated	4	44.4	49.2	77.4
Untreated	5	39.1	44.8	68.5
Untreated	6	32.8	39.3	62.7
Untreated	7	38.9	43.6	64.0
Untreated	8	37.8	43.9	64.3
Untreated	9	28.7	40.6	61.7
Untreated	10	43.0	47.9	78.6
Untreated	11	35.7	41.5	64.8
Untreated	12	50.1	54.2	80.6
Untreated	13	32.5	39.9	65.8
Untreated	14	26.0	37.1	64.4
Untreated	Uncoated	50.8	55.4	81.8

A-5: Average moisture contents of accelerated weathering samples during wet periods of 12 weeks terms (3 replicates).

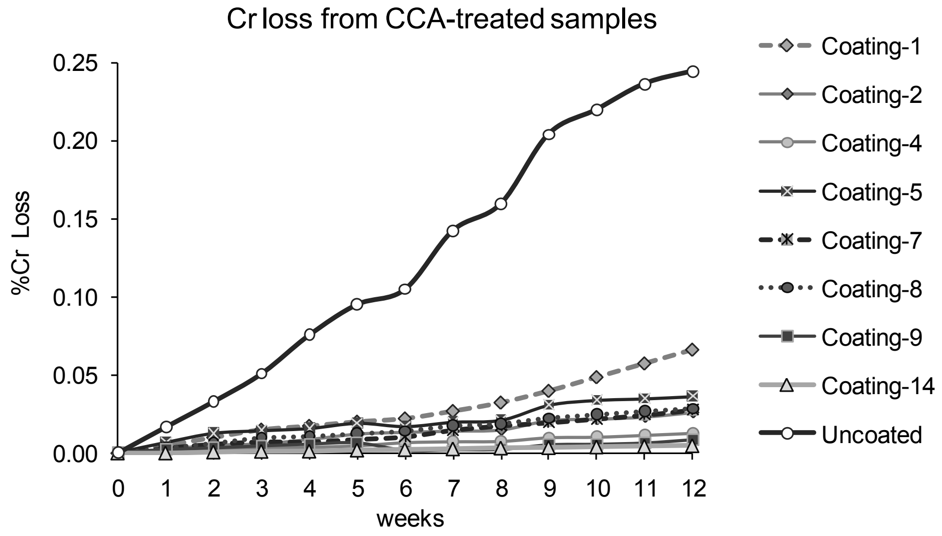
Treatment	*Coating*	*Average % Moisture Contents of Accelerated Weathering Samples (weeks)*											
		1	2	3	4	5	6	7	8	9	10	11	12
CCA	*1*	20	22	22	19	19	20	20	33	27	27	29	30
CCA	*2*	14	17	17	19	20	20	16	16	24	16	19	17
CCA	*4*	14	14	13	13	14	14	13	12	15	11	12	12
CCA	*5*	14	16	12	19	17	21	18	12	41	19	17	14
CCA	*7*	13	13	12	13	12	13	15	17	16	15	17	18
CCA	*8*	14	13	14	12	14	13	15	14	18	13	15	17
CCA	*9*	13	13	12	12	13	15	13	10	15	11	11	10
CCA	*14*	10	12	11	13	12	11	15	14	11	12	13	15
CCA	*Uncoated*	14	14	15	18	16	16	18	20	22	19	22	21
ACQ	*1*	19	22	29	25	33	20	33	38	37	43	49	43
ACQ	*2*	14	16	15	26	24	28	18	20	38	19	30	30
ACQ	*4*	16	16	15	16	15	20	14	13	21	14	18	13
ACQ	*5*	12	13	19	30	22	33	28	23	54	21	29	21
ACQ	*7*	13	13	12	13	14	15	21	27	30	27	28	30
ACQ	*8*	16	15	18	21	19	17	24	30	28	29	33	34
ACQ	*9*	12	12	11	15	13	15	13	10	17	10	12	9
ACQ	*14*	18	22	29	30	27	38	41	39	37	38	34	34
ACQ	*Uncoated*	15	19	25	27	29	30	27	21	41	38	30	30
CA	*1*	24	34	28	35	40	23	44	41	49	47	55	51
CA	*2*	17	19	16	23	24	34	25	28	49	28	35	33
CA	*4*	16	16	15	21	18	21	18	13	23	15	18	19
CA	*5*	15	22	32	37	43	42	31	19	62	50	34	30
CA	*7*	15	16	18	18	15	19	23	22	20	26	26	30
CA	*8*	11	19	15	18	20	22	31	32	28	22	40	32
CA	*9*	12	14	13	14	15	16	13	11	19	12	12	12
CA	*14*	23	21	22	28	25	27	37	25	36	39	36	31
CA	*Uncoated*	11	12	12	11	13	13	13	14	14	14	16	15
Untreated	*1*	24	19	20	17	23	20	22	22	26	24	29	32
Untreated	*2*	13	18	16	18	17	21	16	15	25	16	16	18
Untreated	*4*	13	14	13	15	14	15	12	11	13	12	12	11
Untreated	*5*	12	17	16	17	21	19	16	12	24	19	18	13
Untreated	*7*	13	13	12	11	13	12	13	14	15	16	18	15
Untreated	*8*	10	11	11	12	12	13	13	14	14	13	15	15
Untreated	*9*	11	12	11	12	11	13	11	9	13	11	10	9
Untreated	*14*	12	13	12	13	14	16	17	14	18	18	21	17
Untreated	*Uncoated*	25	38	36	42	37	38	44	33	43	31	35	32



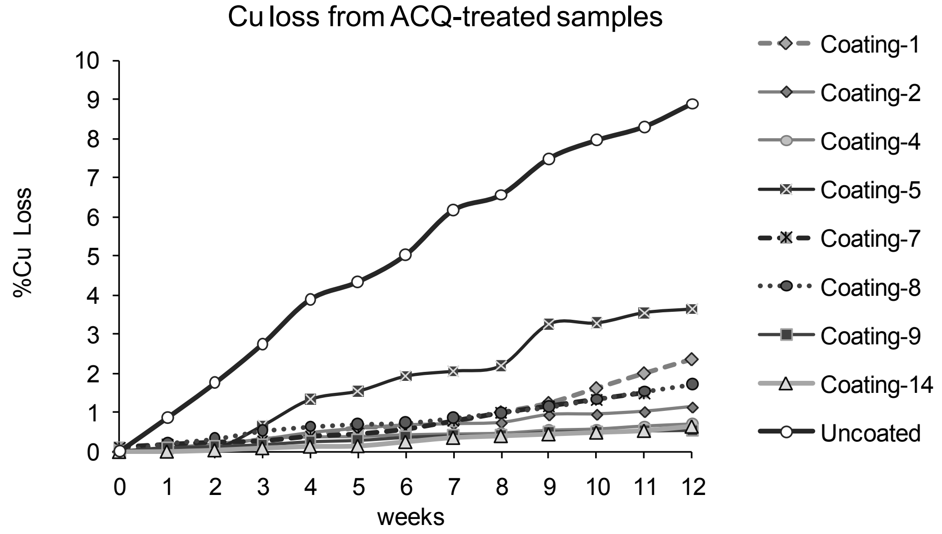
A-6: Cumulative % of As leached from CCA-treated samples during 12 weeks of accelerated weathering.



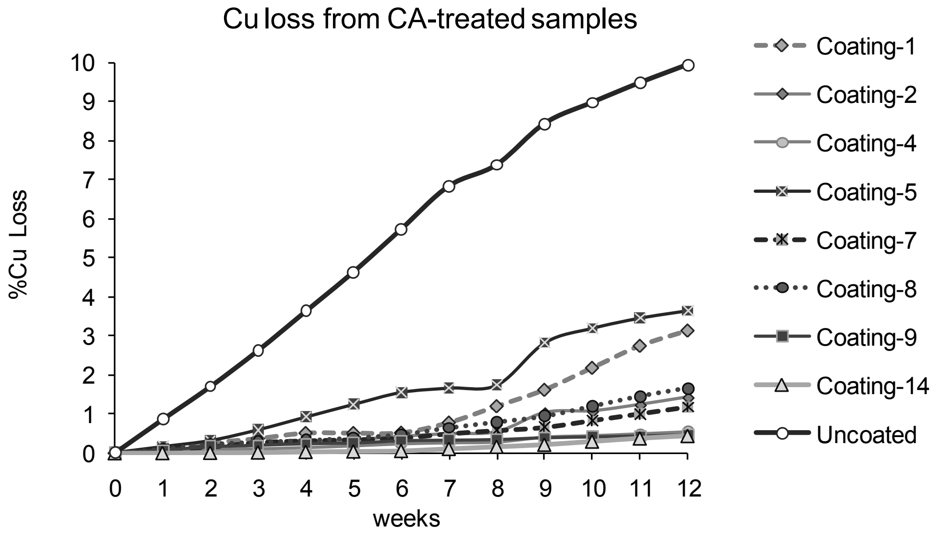
A-7: Cumulative % of Cu leached from CCA-treated samples during 12 weeks of accelerated weathering.



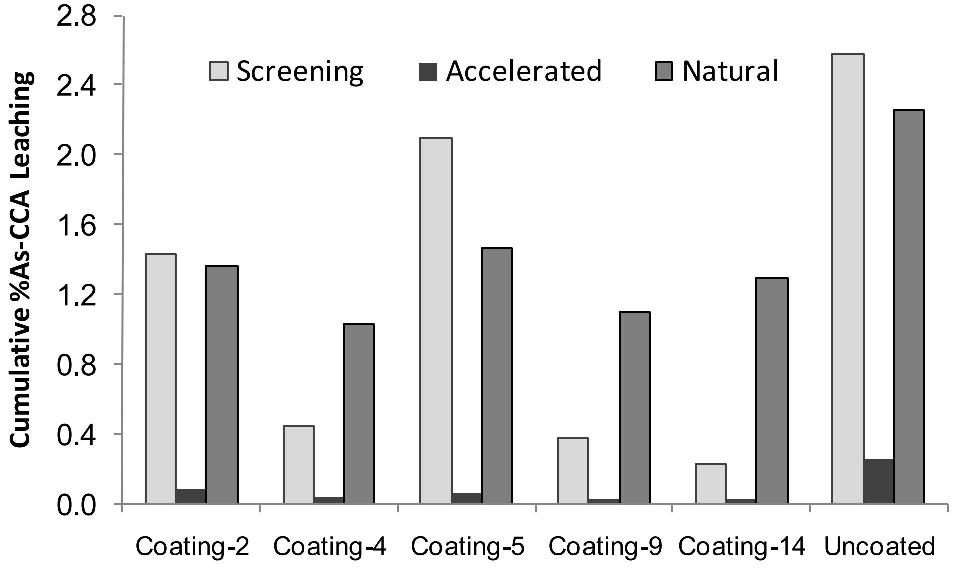
A-8: Cumulative % of Cr leached from CCA-treated samples during 12 weeks of accelerated weathering.



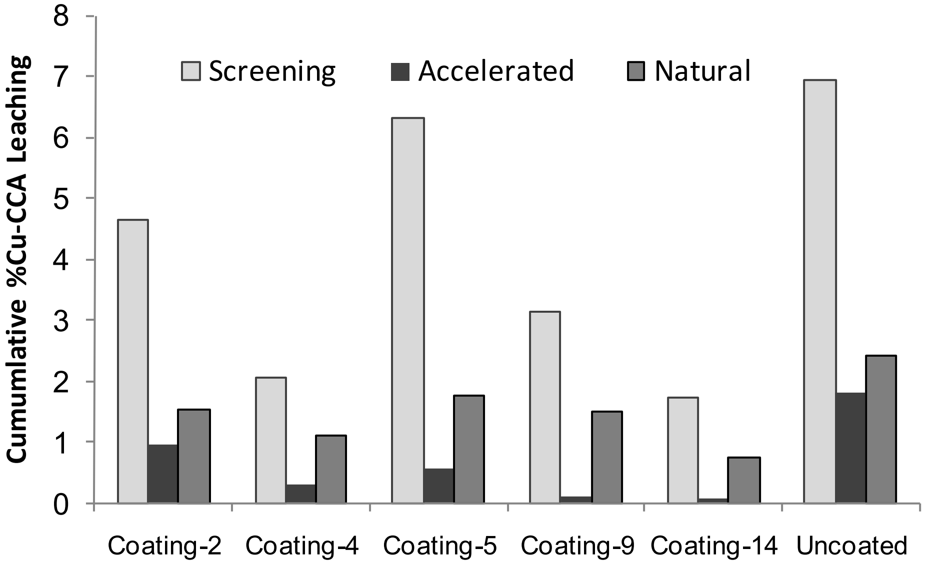
A-9: Cumulative % of Cu leached from ACQ-treated samples during 12 weeks of accelerated weathering.



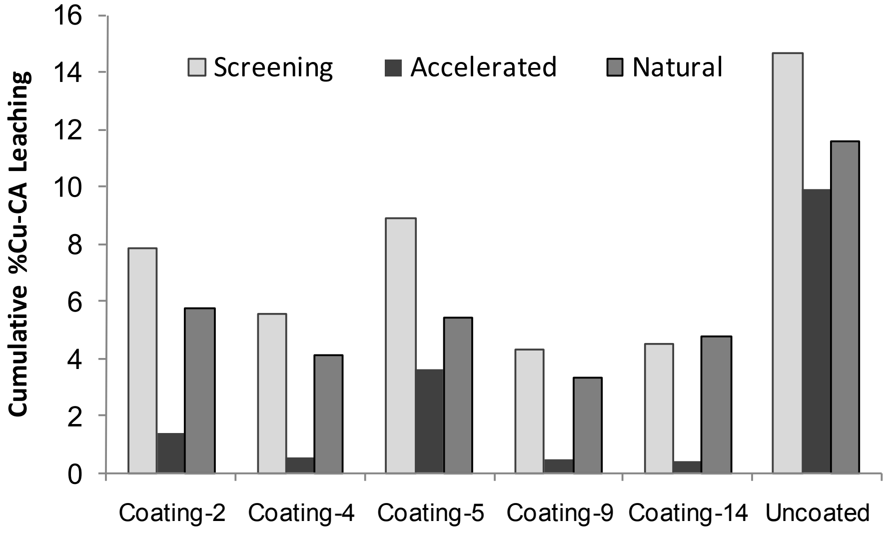
A-10: Cumulative % of Cu leached from CA-treated samples during 12 weeks of accelerated weathering.



A-11: Cumulative percentage of As leached from CCA-treated wood comparison of three different weathering tests



A-12: Cumulative percentage of Cu leached from CCA-treated wood comparison of three different weathering tests



A-13: Cumulative percentage of Cu leached from CA-treated wood comparison of three different weathering tests

A-14: Correlation coefficient (r) of weathering tests comparison for cumulative percentage leached with P_{value} calculated at 95% confidence intervals.

Pearson correlation coefficients and P_{value} for each data at 95% confidence interval		Cumulative % leached in Natural weathering (3-year)				
		As	Cu-CCA	Cr	Cu-ACQ	Cu-CA
Screening (two-week)	As	0.85	0.90	0.89	0.77	0.81
	*	0.03	0.02	0.02	0.07	0.05
	Cu-CCA	0.79	0.93	0.85	0.70	0.74
		0.06	0.01	0.03	0.12	0.09
	Cr	0.78	0.83	0.84	0.67	0.73
		0.07	0.04	0.04	0.15	0.10
	Cu-ACQ	0.95	0.83	0.95	0.96	0.97
		0.004	0.04	0.004	0.003	0.001
	Cu-CA	0.95	0.88	0.96	0.94	0.95
		0.004	0.02	0.002	0.01	0.003
Accelerated (3-Month)	As	0.96	0.82	0.94	0.99	0.99
		0.002	0.05	0.005	<.0001	0.001
	Cu-CCA	0.91	0.84	0.89	0.97	0.94
		0.01	0.03	0.02	0.002	0.005
	Cr	0.96	0.85	0.97	0.97	0.98
		0.002	0.03	0.001	0.002	0.001
	Cu-ACQ	0.96	0.87	0.99	0.91	0.95
		0.002	0.03	<.0001	0.01	0.003
	Cu-CA	0.97	0.87	0.99	0.93	0.96
		0.001	0.02	<.0001	0.01	0.002

* These are P_{values} at 95% confidence intervals numbers less than 0.05 are significant.