PHOTOPROTECTION OF WOOD USING METAL ACETYLACetonates

by

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Abstract

Wood is a versatile material with a pleasant appearance that is widely used in architectural and interior applications. However, wood (including clear-coated wood) undergoes degradation when it is exposed outdoors. Wood can be protected from surface photodegradation (weathering) using reactive metal ions that are able to cross-link wood’s molecules and create complexes that are resistant to photodegradation. Metal acetylacetonates are coordination complexes of metal ions and the acetylacetonate anion. Metal acetylacetonates are used by industry to cross-link chemicals, and they have also been used as photostabilizers for polymers. One study has shown that titanium acetylacetonate can reduce the photodegradation of radiata pine veneers exposed to natural weathering. My general hypothesis is that metal acetylacetonates will be able to protect wood from photodegradation on their own or in combination with other protective systems, including clear finishes, oils and UV absorbers. I compared the photoprotective effects of six metal acetylacetonates on yellow cedar veneers and clear-coated yellow cedar and Scots pine panels. I found that the ability of metal acetylacetonates to photostabilize yellow cedar veneers varies depending on the metal in the coordination complex. Nickel, manganese, titanium and iron acetylacetonate were more effective than cobalt acetylacetonate at photostabilizing wood, based on the different measures I used to assess the degradation of weathered veneers. Iron acetylacetonate was more effective at photostabilizing lignin in weathered veneers than the other metal acetylacetonates. Manganese and titanium acetylacetonate had some positive effects on the performance of a clear polyurethane coating on Scots pine and particularly yellow cedar panels exposed to artificial accelerated weathering. Oils when combined with titanium acetylacetonate provided additional protection to wood surfaces, most notably water repellency, but the oils had negative effects (mould growth) on the appearance of panels exposed to natural weathering. I conclude that metal acetylacetonates can photostabilize wood surfaces and improve the performance of a
clear polyurethane coating on wood. However, the effectiveness of metal acetylacetonates depends on the metal in the coordination complex and the wood species that are treated with the acetylacetonate. Finally, I conclude that metal acetylacetonates have potential as protective treatments, particular photoprotective primers for coatings.
Lay Summary

Wood is damaged by the sun, rain and other elements of the weather, leaving grey and rough surfaces. Weathering of wood also affects the service life of coatings. The weathering of wood can be reduced significantly by certain transition metal compounds, and in this thesis I investigated the ability of metal acetylacetonates to prevent weathering to wood, and improve the performance of clear-coated wood exposed outdoors. My results show that metal acetylacetonates can reduce the weathering of wood and improve the performance of a polyurethane ‘varnish’ on wood, but the effectiveness of metal acetylacetonates varies depending on the metal in the complex. Oils combined with metal acetylacetonates had some protection on wood, but the oils encouraged the colonization of wood surfaces by mould fungi. Overall I conclude that some metal acetylacetonates show promise as treatments designed to restrict the weathering of wood, and improve the performance of clear coatings.
Preface

I was responsible for all the experiments data collection and thesis writing. My supervisor assisted me with experiment design, statistical analyses and editing of this thesis. My committee members, Dr. Scott Renneckar and Dr. Julie Cool gave me comments and feedback on parts of the thesis.
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1. Introduction

1.1 Weathering of wood

Wood is a versatile material with a pleasant appearance, low density and desirable mechanical properties, and, as a result, it is widely used in architectural and interior applications. Wood accounts for 19% of the Canadian construction market and specifically in British Columbia, wood has the largest share, 39% of total construction (CISC report 2012). However, as a biological material, wood undergoes degradation when it is exposed outdoors. Unprotected wood is sensitive to photo-induced weathering which adversely affects its appearance (Evans 2008). Coatings are able to provide some protection to wood surfaces, although photodegradation similar to that occurring on uncoated wood can be observed under clear coatings (Macleod et al 1995). As a result, wood is facing challenges from other ‘more durable’ materials such as concrete, metals and plastics. New approaches to improve the durability of wood products are necessary to prevent their substitution by other materials.

Weathering of wood is a degradation process involving a complicated series of reactions (Rowell 2005). There are many factors that contribute to the weathering of wood, such as solar radiation (ultraviolet and visible light), oxygen, water, heat, chemicals and abrasion (Feist and Hon 1984). Wood is an excellent light absorber and strongly absorbs UV light with wavelengths in the range 200 to 400 nm (Hon 1981). Photochemical reactions due to the absorption of light in the presence of oxygen initiate the oxidation of wood’s molecules, such as cellulose, hemicelluloses, extractives, and particularly lignin. Lignin is degraded rapidly and forms free radicals that can cause further degradation of wood (Feist and Hon 1984). Such chemical degradation causes intercellular and intracellular changes and deterioration such as discolouration, checking and erosion of wood surfaces (Feist 1990). Wood can also be hydrolyzed by water (Fang and Fang 2008), and moisture-induced dimensional changes cause wood to check.
1.2 Surface protection of wood

Considering the factors responsible for the photodegradation of wood, there are various methods either used by industry or studied in research institutions to photostabilize wood products. These methods are reviewed in Chapter 2.

Many of the approaches used to protect wood from weathering physically and chemically isolate wood surfaces from the environmental factors that cause weathering, such as light, moisture and oxygen etc. Inorganic transition metal compounds like chromium trioxide, ferric nitrate and various manganese compounds chemically modify and stabilize wood leading to more durable wood surfaces (Black and Mraz 1974; Chang et al. 1982; Feist 1979; Kubel and Pizzi 1981; Schmalzl and Evans 2003). Reactive metal ions are able to cross-link wood’s molecules and form complexes that are resistant to photodegradation (Schmalzl and Evans 2003; Hon and Chang 1985). Certain inorganic transition metal compounds can also improve the water repellency and mildew resistance of wood and retard the weathering of wood (Williams and Feist 1988; Schmalzl and Evans 2003). Thus, inorganic transition metal compounds have the potential to be an alternative to coatings, stains, and water repellents, or they can be used to enhance the performance of such finishes.

1.3 Metal acetylacetonates

Metal acetylacetonates are coordination complexes of metal ions and the acetylacetonate anion. Generally, all metals in the periodic table can be used to synthesize metal acetylacetonates, whereas here only reactive transition metals are studied. Transition metals have coordination numbers greater than two and can be used as ligands with acetylacetonate anions (Fig. 1.1). Metal acetylacetonates are reactive, thermally stable and soluble in organic solvents (Lamprey 1960).
Metal acetylacetonates are diversely used as catalysts, cross-linking and curing agents and adhesion promoters (Zhang and Wong 2002; Tanase et al. 2004; Guo 2011). They are used as catalysts in some important organic reactions like oligomerization and polymerization (Tanase et al. 2004; Shapkin et al. 2015). Metal acetylacetonates have found applications in a variety of industrial processes. They have been used to extract and separate metals and also find applications in semiconductors and as antioxidants (Chira and Mihir 1988). Metal acetylacetonates are incorporated in printing inks and coatings to improve the adhesion, water repellency and scratch resistance of these products (Guo 2011). These positive effects of metal acetylacetonates are due in part to their ability to cross-link with active functional groups such as –COOH, -OH, -NH₂ (Guo 2011). Hence, metal acetylacetonates help polymerization of paints and coatings and can shorten the curing times of inks and paints and improve their adhesion to different substrates. In addition, metal acetylacetonates have been examined for their ability to photostabilize PVC films, polypropylene and products such as PSA (pressure sensitive adhesive). Various metal acetylacetonates (Mg, Al, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Sn) have been shown to photostabilize the polyvinyl chloride (PVC) (Osawa and Aiba 1982). Copper and vanadium acetylacetonate accelerated the photodegradation of PVC while other metal acetylacetonates retarded photodegradation (Osawa and Aiba 1982). Ultra-violet spectra of PVC films containing metal acetylacetonates were examined after films were exposed to UV light (Osawa and Aiba 1982). PVC films containing copper or vanadium acetylacetonate had much higher UV absorption at 390 cm⁻¹ than films containing other metal acetylacetonates (Mg, Al, Ti, Cr, Fe, Co, Ni, Zn, Sn) (Osawa and Aiba 1982). Osawa and Aiba (1982)
concluded that some metal acetylacetonates (Mg, Al, Ti, Cr, Fe, Co, Ni, Zn, Sn) were capable of photostabilizing PVC whereas others (Cu and V) accelerated photodegradation.

There has only been one study that examined the ability of metal acetylacetonates to photostabilize wood. Schmalzl and Evans (2003) tested whether various titanium, zirconium and manganese compounds including titanium acetylacetonate could photostabilize radiata pine veneers (Pinus radiata (D. Don)) exposed to natural weathering. Titanium acetylacetonate significantly restricted the weight and tensile strength losses of veneers exposed to natural weathering for 35 days. However, FTIR spectra of veneers treated with titanium acetylacetonate and exposed outdoors suggested that it could not photostabilize lignin, but the authors suggested that it was able to complex cellulose, which reduced losses of tensile of veneers exposed to natural weathering (Schmalzl and Evans 2003).

1.4 Hypothesis and Outline of thesis

Modification of wood with transition metal compounds can photostabilize wood, and when used as a primer, enhance the performance of clear finishes and oils (Black and Mraz 1974). For example, chromium treatments improved the performance of oil-based stains on wood exposed to UV irradiation (Black and Mraz 1974), and significantly increased the service life of clear coatings on wood.

Metal acetylacetonates have been known and studied for over a century (Bhattacharjee and Chaudhuri 1989). Due to their cross-linking characteristics, metal acetylacetonates have the potential to cross-link wood’s molecular compounds and possibly protect wood against weathering. Evidence for this assertion is that metal acetylacetonates can photostabilize PVC, and titanium acetylacetonate has been shown to restrict the weight and tensile strength losses of radiata pine veneers exposed to natural weathering (Schmalzl and Evans 2003). Metal acetylacetonates might also enhance the effectiveness of other protective systems, for example oils and UV absorbers by cross-linking them. Therefore, my general hypothesis is that metal acetylacetonates will be able to protect wood from photodegradation on their own
or in combination with other protective systems, particularly clear finishes, oils and UV absorbers.

Following this introduction, Chapter 2 reviews the relevant literature on: (1) weathering of wood; (2) photoprotection of wood with inorganic compounds including reactive transition metal compounds, metal acetylacetonates, inorganic reflectors, inorganic metal nanoparticles and metal biocides and cross-linking agents; (3) protection of wood with oils; (4) photoprotection of wood with UV absorbers; (5) protection of wood with coatings, water repellents and stains.

Chapter 3 tests the hypothesis that the ability metal acetylacetonates to protect wood from weathering will vary depending on the metal in the coordination complex. Wood veneers were treated with metal acetylacetonates solutions (Mn, Fe, Ti, Cr, Co, Ni) exposed to natural weathering, and their chemical and physical properties were compared with those of similarly exposed untreated veneers.

Chapter 4 tests the hypothesis that metal acetylacetonates that can photostabilize wood (from Chapter 3) will be able to improve the performance of a clear polyurethane coating on wood exposed to artificial accelerated weathering. Wood panels were treated with selected metal acetylacetonates (Ti or Mn) finished with a clear polyurethane coating and exposed to artificial weathering. Properties of coatings (gloss, colour, adhesion etc.) were tested to assess the effects of the metal acetylacetonates on the performance of the clear coating.

Chapter 5 treated wood veneers and panels with combination of titanium acetylacetonate, oils and the reactive UV absorber, HEPBP (2-hydroxy-4(2,3-epoxypropoxy) -benzophenone). I hypothesized that the combination of titanium acetylacetonate and oils and HEPBP would provide enhanced protection to wood from the effects of weathering. The performance of the different treatments were compared.

Chapter 6 discusses the findings of the aforementioned experimental chapters, makes suggestions for future research and draws overall conclusions.
2. Literature review

2.1 Weathering of wood

Wood exposed outdoors soon loses its attractive natural appearance and becomes ‘weathered’ (Feist and Hon 1984). Weathered wood is grey and rough due to surface photodegradation, checking, preferential erosion of softer tissues, and colonization of the wood surface by melanized fungi (Feist and Hon 1984). Firstly, wood surfaces are photodegraded by light when they are exposed to the full solar spectrum (Williams 2005; Evans 2009). UV radiation has sufficient energy to cleave chemical bonds in lignin (Feist and Hon 1984). Ultraviolet light with wavelengths from 295 to 380 nm and visible light with wavelengths up to 504 nm are absorbed by lignin (Williams 2005; Derbyshire and Miller 1981). Light with wavelengths from 246 to 496 nm penetrated sugi (Cryptomeria japonica (L.f.)) earlywood and there was a positive correlation between wavelength and depth of penetration into wood (Kataoka et al. 2007). Kataoka et al. (2007) also found that violet light (403-434 nm) can degrade wood, and blue light (430–504 nm) causes bleaching of wood. In summary, UV and the more energetic components of visible light is absorbed by lignin and cause its degradation (Kalnins 1966; Derbyshire and Miller 1981; Kataoka et al. 2007). UV light can also break chemical bonds in carbohydrates, and the free radicals generated by photodegradation of lignin further accelerate photochemical degradation of wood’s molecular components (Hon and Chang 1985; Pandey 2006). As a result of such degradation, deterioration of middle lamella and other cell wall layers is commonly observed in various tissue at wood surfaces exposed to natural or artificial weathering (Borgin 1970). Decomposed lignin and carbohydrates are washed off weathered wood surfaces by water, thus creating a grey and rough surface (Feist and Hon 1984). Delignification caused by UV and visible light significantly increased the moisture-induced checking of wood surfaces exposed outdoors (Evans et al. 2008). Water influences the weathering of wood in other ways. When wood is exposed to water, its wettability increases because of leaching and hydrolysis of hydrophobic components (lignin and extractives) (Kalnins and Feist 1993). Leaching and
hydrolysis of extractives and lignin also lead to discolouration of wood surfaces exposed outdoors (Feist 1983). Finally, weathering of wood is associated with colonization of wood surfaces by melanized fungi (Duncan 1963). These fungi are responsible for the dark grey and blotchy colour of weathered wood surfaces.

2.2 Photostabilization and protection of wood with inorganic compounds

Weathered wood can have an attractive appearance, but in many situations it looks unattractive and hence there is strong interest in developing treatments to prevent the weathering of wood. For example, a large number of different inorganic compounds have been tested to determine their ability to photostabilize wood surfaces (Black and Mraz 1974; Chang et al. 1982; Feist 1979; Kubel and Pizzi 1981; Schmalzl and Evans 2003). In this section, the use of inorganic metal compounds to photostabilize wood will be reviewed, particularly chromium, iron, copper, other transition metal compounds, metal acetylacetonates, inorganic nanoparticles and metal biocides. My review focuses on their applications to protect wood against photodegradation, and to a lesser extent, surface fungi and dimensional changes.

2.2.1 Chromium compounds

Chromium compounds in particular have been widely studied as treatments to protect wood from photodegradation. Chromic acid was able to effectively retard photodegradation of wood during weathering (Williams and Feist 1988). For example, SEM images of southern pine (*Pinus palustris* (Mill.)) treated with chromic acid and exposed to UV light for 500 h showed that chromic acid protected wood cell walls at exposed transverse surfaces. The protective effects were greater when wood was treated with higher concentrations of chromic acid (Chang et al. 1982). Chromic acid also protected the structure of simple and bordered pits at both radial and tangential surfaces compared with untreated controls (Chang et al. 1982). Insights into how chromium VI protects wood from photodegradation have been revealed by studies of the reaction of guaiacol and 2,6-dimethoxyphenol with chromic acid, chromium trioxide and ferric chloride (Schmalzl et al. 1995; 2003). These studies suggest
that lignin can be oxidized and complexed with chromium VI forming weathering-resistant chromium lignin quinone complexes (Schmalzl et al. 1995; 2003) (Fig. 2.1). Aqueous chromium trioxide solutions protected western red cedar (*Thuja plicata* Donn ex (D.Don)) and redwood (*Sequoia sempervirens* (D.Don) Endl) against UV degradation and reduced the erosion rate of western red cedar exposed to accelerated weathering (Feist 1979). Chromium trioxide was also able to restrict weight losses of radiata pine veneers exposed to natural weathering for 35 days, suggesting the photoprotection of lignin. However, chromium trioxide was ineffective at reducing the loss of tensile strength of veneers during weathering, suggesting that it was unable to photostabilize cellulose (Evans and Schmalzl 1989). The photoprotective effects of chromium trioxide have also been examined using Fourier transform infrared (FTIR) spectroscopy. FTIR of radiata pine veneers treated with chromium trioxide showed changes in bands at 1506 cm\(^{-1}\) and 1263 cm\(^{-1}\), suggesting modification of lignin. The reaction of chromium trioxide with the lignin model guaiacol suggested that chromium trioxide forms insoluble complexes with lignin, as mentioned above (Schmalzl et al. 1995). Weathering studies of veneers treated with Cr VI and untreated controls were carried out. FTIR spectroscopy of veneers showed reductions of lignin-related bands (1505 cm\(^{-1}\) and 1595 cm\(^{-1}\)) in spectra of all samples, but the reduction in treated samples was significantly less than that in the spectrum of untreated samples (Michell 1993). This observation provides strong evidence that chromium trioxide can photostabilize lignin in wood (Michell 1993; Evans et al. 1992). In subsequent work, Michell (1993) treated wood with chromic chloride, chromic nitrate, chromium trioxide, ferric chloride and ferric nitrate. FTIR spectra of treated samples showed that hydroxy and methoxy groups of phenylpropane (lignin units) were complexed by chromium compounds. Chromium trioxide also protected hemicellulose in wood from photodegradation (Schmalzl et al. 1995). Chromium trioxide is also able to reduce water uptake by wood surfaces and restrict swelling and shrinkage of wood according to Feist (1979). Williams and Feist (1985) reported that chromium nitrate (Cr III) could photostabilize wood, although the degree of protection was less than that of Cr.
VI. Chromium compounds can also protect wood from extractive staining and mildew, in addition to their positive effects on photostability and dimensional changes (Feist 1979; Williams and Feist 1985; Pizzi 1982).

Fig. 2.1: Phenolic oligomers extracted from the reaction mixture of chromium (VI) with guaiacol: dimer, trimer and an unstable diphenol quinone (Schmalzl et al. 1995)

2.2.2 Ferric compounds

Ferric compounds have also been tested for their ability to photostabilize wood surfaces (Chang et al. 1982). Aqueous ferric chloride at different concentrations was applied to radial, tangential and transverse surfaces of southern yellow pine and their photoprotective effects were examined (Chang et al. 1982). Ferric chloride protected bordered pits at radial and transverse surfaces exposed to UV radiation. This study suggested that ferric chloride photostabilized lignin in wood exposed to weathering. The effects of ferric salts on the photostability of lignin during weathering were also examined using FTIR spectroscopy by Evans et al. (1992) and Michell (1993). Wood veneers treated with ferric chloride or ferric nitrate and exposed to weathering retained lignin-related bands at 1,506, 1,263 and 870 cm\(^{-1}\) (Table 2.1) (Evans et al. 1992). The reactions of ferric chloride and ferric nitrate with lignin model compounds were also examined using FTIR spectroscopy (Michell 1993). Spectra of wood treated with ferric salts showed changes in the ‘lignin’ band at 1506 cm\(^{-1}\), suggesting that ferric salts modified lignin. Prior to the work by Evans et al. (1992) and Michell (1993), Hon and Chang (1985) showed that metal ions in ferric chloride or chromium trioxide solutions reacted with lignin model compounds to form insoluble complexes. They suggested
that the formation of ‘wood-ions complexes’ reduced photo-chemical energy and restricted photodegradation of wood during weathering. However, ferric compounds are less effective than chromium trioxide at protecting wood from weathering (Evans and Schmalzl 1989). For example, FTIR spectra revealed that lignin-related bands of ferric chloride and ferric nitrate treated samples exposed to weathering were diminished to a greater extent than those in similarly exposed chromium trioxide treated samples (Evans et al. 1992). Earlier work by Evans and Schmalzl (1989) showed ferric chloride treated veneers lost more weight during 35 days of natural weathering than untreated controls. Ferric chloride also increased the tensile strength losses of treated veneers exposed to natural weathering. Ferric nitrate slightly reduced weight losses during weathering, but increased losses of tensile strength (Evans and Schmalzl 1989). These results contrast with those of Chang et al. (1982). Schmalzl et al. (1995) reacted the lignin model guaiacol with ferric chloride solution and observed that a black precipitate was formed. However, unreacted guaiacol was also present whereas chromium trioxide fully reacted with guaiacol to form a highly insoluble complex as mentioned above, suggesting that ferric chloride was less effective than chromium trioxide at complexing lignin (Schmalzl et al. 1995; 2003).
Table 2.1: Assignments of bands in the infrared spectrum of radiata pine wood (Harrington et al. 1964 and Michell 1989)

<table>
<thead>
<tr>
<th>Freq. cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,728</td>
<td>C=O str. vibn. in acetyl and carboxyl in hemicell.</td>
</tr>
<tr>
<td>1,643</td>
<td>H—O—H deformation in absorbed water in carbohydrate</td>
</tr>
<tr>
<td>1,601</td>
<td>C=C str. vibn. in aromatic ring in lignin</td>
</tr>
<tr>
<td>1,506</td>
<td>C=C str. vibn. in aromatic ring in lignin</td>
</tr>
<tr>
<td>1,453</td>
<td>C=C str. vibn. in aromatic ring in lignin and CH₂ vibn. in cell.</td>
</tr>
<tr>
<td>1,425</td>
<td>CH₂ scissors vibn. in cell. and C=C str. in aromatic ring in lignin</td>
</tr>
<tr>
<td>1,369</td>
<td>CH bend. vibn. in cell. and hemicell.</td>
</tr>
<tr>
<td>1,330</td>
<td>OH in-plane deformation vibn. in cell. and hemicell.</td>
</tr>
<tr>
<td>1,315</td>
<td>CH₂ wagging vibn. in cell.</td>
</tr>
<tr>
<td>1,263</td>
<td>C=O str. vibn. in lignin and hemicell.</td>
</tr>
<tr>
<td>895</td>
<td>Anomeric carbon group frequency in cell. and hemicell.</td>
</tr>
<tr>
<td>870</td>
<td>CH out-of-plane bend. vibn. in lignin</td>
</tr>
<tr>
<td>809</td>
<td>mainly vibn. of mannan in hemicell. and CH out-of-plane bend. vibn. in lignin</td>
</tr>
<tr>
<td>775</td>
<td>Vibn. of galactan in hemicell.</td>
</tr>
</tbody>
</table>

2.2.3 Copper compounds

Copper compounds are well known for their ability to protect wood from fungal attack (Laks 1991), but they can also photostabilize wood (Lin et al. 2009). For example, copper azole decreased colour changes in wood exposed to weathering (Nejad and Cooper 2011). FTIR showed that copper azole was also able to reduce the delignification and degradation of middle lamellae in wood exposed to natural weathering (Cornfield et al. 1994). Copper ethanolamine (Cu-MEA) was used to treat southern pine sapwood exposed to artificial accelerated weathering (Zhang et al. 2009). Cu-MEA reduced colour changes of southern pine and restricted the loss of water repellency of wood surfaces. Copper/amine oxide was also investigated for its ability to protect wood from weathering. The treatment improved the water repellency of wood surfaces (Walker 2002). One set of wood samples was vacuum-pressure impregnated with alkaline (pH 9.8) copper (II) ethanolamine aqueous solution. Treated wood had less colour change when exposed to artificial UV light than similarly exposed untreated controls.
2.2.4 Titanium, zirconium, manganese, tin and zinc compounds

Transition metals are a unique class of metals and their compounds have diverse chemical and physical effects including oxidation and polymerization (Bury 1921). Transition metals can form coloured compounds because of their chemical properties and reactions with phenols. Some compounds have been tested for their ability to improve the weathering resistance of wood. A range of titanium, zirconium and manganese compounds were tested by Evans and Schmalzl (2003) for photoprotective effects on radiata pine veneers exposed to natural weathering. The photoprotective effects of the compounds were compared with those resulting from treatment of veneers with chromic acid. Chromic acid dramatically reduced weight loss of veneers as expected, and was the most effective treatment at protecting wood from weathering (Evans and Schmalzl 2003). Some of the titanium and zirconium compounds restricted weight and tensile strength losses of veneers during weathering. However, the oxidative manganese compounds (potassium permanganate and manganic acetate) were more effective than the titanium or zirconium compounds (Evans and Schmalzl 2003). Manganese compounds were more effective than chromic acid at restricting losses of tensile strength during weathering (Evans and Schmalzl 2003).

Tin (II) oxide and zinc oxide have been tested for their ability to complex the lignin model guaiacol, and also whether they increase the water repellency of wood surfaces (Kubel and Pizzi 1981). Zinc oxide was able to “waterproof” wood surfaces, but it was less effective than chromium trioxide. Kubel and Pizzi (1981) did not examine whether zinc oxide was able to photostabilize lignin in wood exposed to weathering.

2.2.5 Inorganic compounds and clear finishes

Inorganic compounds that are able to photostabilize wood have been tested to see if they can increase the service life of finishes on wood (Black and Mraz 1974). Chromate pre-treatments can photostabilize wood, reduce water absorption and dimensional changes of wood, and as a result they enhance the performance of coatings on wood exposed outdoors (Upreti and Pandey 2005). Chromic acid is the most effective treatment at
improving the performance of clear coatings on wood exposed outdoors (Black and Mraz 1974). It is noteworthy that pre-treatment of wood with chromic acid was able to extend service life of a clear silicone coating to over 15 years (Williams and Feist 1985) (Fig. 2.2).

![Image of wood panels after exposure](image)

**Fig. 2.2: Performance of a clear silicone finish on wood pre-treated with chromic acid after panels were exposed outdoors for 15 years in Madison, Wisconsin. The coatings adjacent to the silicone finish were degraded many years before the photograph was taken. (photo c/o Sam Williams US Forest Products Laboratory) (Williams and Feist 1985)**

Chromic acid also increases the adhesion of linseed oil based paint to wood (Black and Mraz 1974). Cr⁶⁺ compounds were able to restrict the loss of linseed oil-based stain and latex stain from wood exposed to weathering (Feist 1979). Acid-copper-chromate was also able to double the service life of the same stains (Black and Mraz 1974). Copper and various chromium salts were also able to stabilize extractives in redwood and western red cedar. As a result of the fixation of extractives, there was less discolouration of wood during weathering. Evans et al. (2015) observed that some titanium or zirconium compounds enhanced the performance of an alkyd clear coating on western red cedar panels exposed to 22 months natural exposure in Melbourne, Australia, even though they were unable to photostabilize lignin (Evans and Schmalzl 2003). Titanium or zirconium compounds were clearly able to restrict colour changes of the clear-coated western red cedar wood panels exposed to natural
weathering (Fig. 2.3).

Fig. 2.3: Performance of alkyd clear coating on wood panels pre-treated with reactive titanium or zirconium compounds after 22 months of natural weathering in Australia. Note the arrows on top pointing out the panels treated with one of the effective compounds. The arrows on bottom point out untreated controls (photo in Evans et al. (2015), provided by Karl Schmalzl, formerly of CSIRO Division Forestry and Forest Products, Melbourne, Australia)

2.2.6 Metal acetylacetonates

Metal acetylacetonates are coordination complexes derived from acetylacetonate anion and metal ions, as mentioned in the introduction (Fig. 2.4).

Fig. 2.4: Chirality structure of metal (acetylacetonate)$_3$

Metal acetylacetonates have been investigated as photoprotective treatments for polymers, and to a lesser extent wood (Osawa and Aiba 1982; Schmalzl and Evans 2003), as mentioned in the introduction. Table 2.2 shows some of the diverse uses of metal acetylacetonates as catalysts, cross-linking and curing agents and adhesion promoters.
Table 2.2: Applications of metal acetylacetonates and their market share in industry

<table>
<thead>
<tr>
<th>Applications</th>
<th>Proportion of use (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>34.4</td>
</tr>
<tr>
<td>Nano-materials</td>
<td>24.9</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>10.1</td>
</tr>
<tr>
<td>Oxides</td>
<td>7.9</td>
</tr>
<tr>
<td>Adhesive</td>
<td>7.6</td>
</tr>
<tr>
<td>Coating applications</td>
<td>7.6</td>
</tr>
<tr>
<td>Polymerization and curing</td>
<td>5.0</td>
</tr>
<tr>
<td>Oils</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Cobalt (II) acetylacetonate was used as a catalyst to increase the decomposition rate for deperoxidation of tert-butylhydroperoxide. Cobalt ions reacted with -ROOH groups and formed radical chains during the reaction. UV/VIS spectra (Fig. 2.5) showed that cobalt (II) acetylacetonate in solvent absorbed UV light in the region of 250 and 320 nm (Turrà et al. 2010).

Metal acetylacetonates also have other uses as catalysts in some important organic reactions like oligomerization and polymerization. Calcium acetylacetonate was used to polymerize glycolide and glycolide with lactide at 150 and 200°C (Dobrzynski and Bero...
Bis(acetylacetonato)cobalt(II) (Co(acac)\textsubscript{2}) has been used as a drier to promote curing of alkyd resins by interacting with pyrazole additives (Tanase et al. 2004). Co(acac)\textsubscript{2} increases the polymerization of ethyl linoleate, thus enhancing drying rate of alkyd resins. Metal acetylacetonates were used as catalysts for the hydrogenation of soybean oil to increase the stability of the oil (Koritala 1985). Dimethylgold(III) acetylacetonate was used as the principal component in a gold electrolyte used to coat gold on to nickel-plated surfaces (Gezerman and Çorbacıoğlu 2014). Metal acetylacetonates are also added to printing ink, paints and coatings to improve the adhesion, water repellency and scratch resistance of these products. There have been 728 patents for applications of metal acetylacetonates granted over the past five years. The distributions of these patents are shown in Fig. 2.6.

**Fig. 2.6: Patents distribution of metal acetylacetonates from 2012 to 2017**

A patent issued to Guo (2011) suggests that metal acetylacetonates can cross-link with functional groups such as –COOH, -OH, -NH\textsubscript{2}, which enables them to polymerize paints and other coatings. As a result, they can shorten the curing time of inks and paints and improve their adhesion to various substrates, as mentioned above. For example, zirconium acetylacetonate (ZrACAC) has been added to pressure sensitive acrylic adhesives (PSA) to cross-link and enhance the adhesion and shear strength of the adhesive (Czech and Wojciechowicz 2006). ZrACAC cross-linked with carboxylic and hydroxyl groups on the acrylic polymer chains. Aluminum acetylacetonate was used to cross-link a block copolymer
and develop an acid-functionalized, hydrogenated block copolymer. Solvent resistance and high temperature cohesive strength of the block copolymer were significantly improved at high temperatures after the copolymer was reacted with aluminum acetylacetonate (Clair 2003). Pereira et al. (2007; 2008) immobilised copper and vanadyl acetylacetonate onto a clay surface, thus creating clay-supported catalysts. Copper acetylacetonate can be immobilized on clay surfaces because the acetylacetonate ligand is able to react with hydroxyl groups on the clay surface. Clays functionalized with amine react strongly with copper acetylacetonate because the carbonyl groups of the acetylacetonate ligand react with amine-functional groups. The bonding between acetylacetonate and amine is stronger than that between acetylacetonate and hydroxyl groups (Pereira et al. 2008). Finally, metal acetylacetonates find applications in other diverse industrial processes. For example, they have been used to extract and separate metals (Hannaker and Hughes 1977), and the films of metal acetylacetonates complexes can be used as semiconductors (Chappe and Vargas 1972).

In summary, studies of the photoprotection of wood using reactive metal compounds including the one study that looked at titanium acetylacetonate, indicate that metal ions can chemically fix to wood by oxidation-reduction reactions. Some of the metal compounds are able to polymerize wood’s molecules, generating insoluble complexes, some of which are resistant to photodegradation. When lignin is stabilized, the formation of aromatic and other free radicals is reduced. This restricts further degradation of wood during weathering. In addition, some metal compounds (Cu, Zn) are able to protect wood from microbial attack of wood and increase its water repellency. Accordingly, when reactive metal compounds are used as primers for stains, clear coatings and paints, they can improve the performance of the finishes. Hence, metal compounds are promising chemical treatments for wood protection, although some (Cr, Sn, in particular) cannot be used for environmental reasons.

2.2.7 Inorganic nanoparticles

Nanoparticles are defined as particles having a dimension of 100 nanometers or less (Buzea et al. 2007). Nanoparticles are reactive because they have a greater surface area per
weight than other materials. Nanoparticles are increasingly being used to improve the properties of materials. For example, dispersions of inorganic nanoparticles can cross-link polymer matrices to improve the abrasion, scratch resistance, roughness and stiffness of polymers (Hong and Chen 2014). Wood surfaces coated with a layer of nano TiO$_2$ were very water repellent (Rassam et al. 2012). ZnO, TiO$_2$, CeO$_2$ and SiO$_2$ nanoparticles can reflect and absorb light (Vlad-Cristea et al. 2012). Nano-scale ZnO is added to sunscreens to provide protection against long-wave UV (Ghamsari et al. 2017). Nano-scale ZnO and CeO$_2$ have been tested in combination with UV absorbers for their ability to restrict the discolouration of wood (Blanchard and Blanchet 2011). UV/VIS absorption spectra of both metal oxides (Fig. 2.7) showed that they strongly absorb UV radiation especially at lower wavelengths. Weathering tests revealed that coatings containing inorganic nano particles (ZnO-40 nm) restricted the yellowing of sugar maple (*Acer saccharum* (Marshall)) especially when the coatings also contained organic UV absorbers. Inorganic nanoparticles are better than organic UV absorbers at providing long-term photoprotection to wood, but organic UV absorbers outperform nanoparticles in short-term weathering tests according to Blanchard and Blanchet (2011). In contrast, Liu et al. (2010) found that CeO$_2$ was unable to restrict weight losses of wood veneers exposed to natural weathering, indicating little or no photoprotection of wood.
Fig. 2.7: UV visible absorption spectra of a: ZnO with an average particle size of about 30 nm; b: CeO$_2$ with an average particle size of about 20-80 nm (Arefi and Rezaei-Zarchi 2012; Farahmandjou and Zarinkamar 2015)

A nano TiO$_2$ solution was combined with organic UV absorbers in a system designed to protect Jack pine (Pinus banksiana (Lamb.)) exposed to artificial UV radiation (Saha et al. 2011). UV/VIS spectroscopy of coatings containing TiO$_2$ indicated that the coating was able to absorb UV light from 285 to 320 nm (Fig. 2.8), depending on the concentration of TiO$_2$ and the thickness of the coating. When TiO$_2$ was combined with organic UV absorbers, UV transmission through the coatings was decreased (Saha et al. 2011). However, coatings containing TiO$_2$ and organic UV absorbers were not able to reduce colour changes of pine samples exposed to artificial weathering. Saha et al. (2011) suggested that this unexpected finding was due to the inability of the coatings to block UV radiation from reaching the underlying wood substrate. In contrast, Rassam et al. (2012) reported that the colour of wood surfaces coated with nano-sized TiO$_2$ was unchanged after the treated wood was exposed to 100 mW/cm$^2$ of UV for 200 hours. Godnjavec et al. (2012) modified nano-sized TiO$_2$ with 3-glycidyloxypropyltrimethoxysilane (GLYMO) to increase the ability of nano TiO$_2$ to absorb UV light. They concluded that GLYMO increased dispersion of nano TiO$_2$ in a clear coating, which enhanced the ability of the coating to protect wood from photodegradation. Tshabalala and Sung (2007) treated wood with nano-sized aluminum isopropoxide as precursor to form a hybrid inorganic-organic film at wood surfaces. The thin hybrid Al$_2$O$_3$-SiO$_2$ film was able to absorb and scatter light and prevent UV radiation from reaching
the wood substrate. The film also restricted water uptake by wood and reduced photo-discolouration.

Metal nanoparticles can also be added to coatings to improve their resistance to UV, mildew and fungal attack. For example, the addition of ZnO, TiO₂ or SiO₂ improved the durability and hardness of acrylic coatings during weathering (Vlad-Cristea et al. 2012). Zinc oxide was investigated as a UV stabilizer in coatings applied to rubber wood (Hevea brasiliensis (Müll. Arg.)) (Weichelt et al. 2010). Coatings containing nanoscale zinc oxide protected underlying wood from discolouration more effectively than traditional UV protection systems. Zinc oxide also reduced delamination of the coatings (Weichelt et al. 2010). Sun et al. (2012) examined UV resistance of poplar wood (Populus tremula (L.)) treated with ordered ZnO nanorod arrays. FTIR spectra indicated that films containing ZnO nanorods reacted with wood and formed stable chemical bonds. Wood coated with ‘ZnO films’ had higher UV resistance than unmodified wood. Sun et al. (2012) concluded that highly ordered ZnO protected wood from UV degradation due to absorption of UV radiation. Habibzade et al. (2014) incorporated nano-ZnO in wood polymer nanocomposites and compared the decay and weathering resistance of the wood composites with those of unmodified composites. They found that nano-ZnO treated wood composites had fewer

![Graph showing UV visible absorption of TiO₂ with an average particle size of 5-10 nm (Gouda and Aljaafari 2012)](image-url)
colour changes than the untreated controls during weathering. Nano-ZnO also increased fungal resistance of the composites. Auclair et al. (2011) investigated the photoprotective effects of ZnO and CuO in waterborne nano-composite urethane-acrylate coatings subjected to natural weathering. Coatings containing ZnO and CuO in water pre-dispersed and powder forms were tested. The pre-dispersed ZnO was the most effective at protecting coatings during weathering. ZnO was more effective than CuO at restricting colour changes of coated wood. The size of ZnO nanoparticles, and UV exposure conditions (wavelength) significantly affected the ability of ZnO to protect wood from weathering. In related work, Gu et al. (2010) investigated the effects of ZnO size and wavelength of UV on photodegradation of polyurethane coatings. They showed that ZnO acted as a photo-catalyst in coatings subjected to UV light in 290-400 nm range, but photostabilized coatings when they were exposed to more energetic UV radiation (185-254 nm). Anatase and rutile TiO₂ pigments were tested in acrylic and isocyanate acrylic coatings by Allen et al. (2002). Rutile TiO₂ was more effective at photostabilizing wood and coatings than anatase TiO₂. Rutile TiO₂ (70 nm in diameter) restricted photo-induced colour changes more effectively than larger sized (90 nm) rutile TiO₂. Coatings containing TiO₂ pigments were better at protecting wood than a coating containing a hindered amine light stabilizer (HALS) because the organic stabilizer in the coatings was degraded by UV radiation (Allen et al. 2002). Another study combined TiO₂ and clay nanoparticles and added them to a water-based acrylic coating (Fufa et al. 2013). This combination retarded photodegradation of Norway spruce (*Picea abies* (L. H. Karst.)) during weathering. However, higher concentrations of TiO₂ in coatings increased the degradation of wood (Fufa et al. 2013). Poor dispersion of TiO₂ in coatings accounted for the inability of higher concentrations of TiO₂ to protect Norway spruce from degradation. Iron oxides can also prevent photo-induced discolouration of wood (Liu et al. 2010), but they discolour wood surfaces and increase Tg (glass transition temperature) of coatings which increases the cracking of coatings during weathering according to Aloui et al. (2007).
2.2.8 Inorganic metal biocides

Biocides are commonly used to protect wood from microbial decay and insect attack (Table 2.3). Traditional biocides include metallic salts, oxides or organic compounds in water or oil, for example, creosote, pentachlorophenol or oilborne pentachlorophenol (penta). Chromated copper arsenate (CCA) was the most commonly used wood preservative (Chou et al. 1974; Bernard 1991), but its use has been restricted in Europe, Japan and to a lesser extent North America. The substitutes for CCA are copper-rich preservatives containing amine- or ammonia-complexed alkaline copper (II) and an organic co-biocide to control copper tolerant fungi (Freeman et al. 2008; Kamdem 2008). Copper compounds such as copper sulphate, copper acetate, copper hydroxide, copper oxide, copper borate, copper fluoride and basic copper carbonate have mainly been used for wood preservation due to their fungicidal activity and low cost (Goetsche and Borck 1997). Many new proprietary preservative systems have been developed to meet the needs of timber treaters, including alkaline copper quaternary (ACQ), copper azole, ammoniacal copper zinc arsenate (ACZA) and copper xyligen (CX) (Evans 2003; Freeman and McIntyre 2008; Baileys 2010).

Table 2.3: Types of wood preservatives and their uses (NPIC 2011)

<table>
<thead>
<tr>
<th>Types of wood preservatives</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Copper Chromate (ACC)</td>
<td>Industrial and commercial uses</td>
</tr>
<tr>
<td>Alkaline Copper Quaternary (ACQ)</td>
<td>Residential use (lumber, decking and fence posts)</td>
</tr>
<tr>
<td>Bis-(N-cyclohexyl)diazeneimdioxy)-copper (Cu-HDO)</td>
<td>Outdoor use (lumber, millwork and piles)</td>
</tr>
<tr>
<td>Borates</td>
<td>Interior construction (sheathing, joists and sill plates)</td>
</tr>
<tr>
<td>Chromated Copper Arsenate (CCA)</td>
<td>Industrial uses and residential uses in some countries</td>
</tr>
<tr>
<td>Chromium</td>
<td>Fixation agent in industrial use</td>
</tr>
<tr>
<td>Copper Azole (CA)</td>
<td>Above and below ground use, freshwater and marine decking</td>
</tr>
<tr>
<td>Creosote</td>
<td>Industrial uses</td>
</tr>
<tr>
<td>Cyproconazole</td>
<td>Siding, plywood, millwork, shingles and lumber</td>
</tr>
<tr>
<td>Micronized Copper</td>
<td>Decking, joists, beams and sills</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>Utility poles, railroad ties and wharf pilings</td>
</tr>
<tr>
<td>Propiconazole</td>
<td>Siding, plywood, millwork, shingles, shakes and above-ground structural lumber</td>
</tr>
</tbody>
</table>
More recently, micronized copper preservatives, which also contain an organic biocide, have taken a large share of the market for wood preservatives in North America (Schultz et al. 2007). Preservatives containing copper nano-particles of different sizes were developed as replacements for preservatives containing ionic copper (Leach and Zhang 2006). The efficacy of micronized copper preservatives is likely to be affected by the distribution of copper in wood and subsequent leaching of copper. Matsunaga et al. (2007) used field-emission scanning-electron-microscopy (SEM) and energy dispersive analyses of X-rays to examine the distribution of a micronized copper preservative and a conventional copper system in southern pine wood. Copper was present in cell walls of wood treated with both type of preservatives, and a higher concentration of copper was present in middle lamellae than in the secondary cell wall. Matsunaga et al. (2009) also found that copper particles were located in different areas of wood depending on their sizes. Clausen et al. (2011) investigated whether preservatives containing nano-zinc oxide (ZnO) particles (30nm and 70nm) were toxic to eastern subterranean termites (Reticulitermes flavipes (Kollar)). They found that nano-particles were able to effectively repel termites attack of wood and were more effective than soluble zinc sulphate (ZnSO₄) (Clausen et al. 2011).

Boric acid and borax were first used as wood preservatives and patented in 1933 (Brooke 1951). Borate treatments were first used industrially in 1949 as rapidly diffusing borate mixtures (Cockroft and Levy 1973; Freeman et al. 2009). Boron (Borax-Boric Acid) and its derivatives are also effective at preventing fungal decay and insect attack of wood used above ground (Lebow 2010). Borates combined with azole and thujaplicin were used to prevent fungal and termite attack of southern pine in a study carried out by Clausen and Yang (2007). They found that different borate-based formulations were able to protect southern pine wood from fungal and termite attack during a four week bioassay (Clausen and Yang 2007). Borates were tested on solid wood, wood composites and gypsum wallboard by Fogel and Lloyd (2002). Borates significantly decreased the colonization of mould on wood surfaces exposed to natural weathering.
2.3 Photostabilization and protection of wood with organic compounds

Oils are viscous liquid derived from natural resources or the breakdown of fats (Piskur 1946), and are commonly used to improve weather and water resistance of wood surfaces. Oils are classified as drying, semi-drying oils and non-drying oils (Bradley and Johnston 1940) (Table 2.4).

<table>
<thead>
<tr>
<th>Oils</th>
<th>Drying or non-drying oils</th>
<th>Main compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Danish</td>
<td>Drying faster than linseed oil</td>
<td>Polymerized linseed oil</td>
</tr>
<tr>
<td>Linseed</td>
<td>Drying</td>
<td>Linolenic acid</td>
</tr>
<tr>
<td>Mineral</td>
<td>Non-drying</td>
<td>Isoparaffinic, naphthenics, alkylated aromatics</td>
</tr>
<tr>
<td>Olive</td>
<td>Non-drying</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>Tung (Chinese wood oil)</td>
<td>Drying oil</td>
<td>Linolenic acid</td>
</tr>
<tr>
<td>Tall</td>
<td>Drying oil</td>
<td>Oleic acid</td>
</tr>
</tbody>
</table>

Oils have a long tradition of use as wood treatments. Oil was first used in Buddhist painting by Chinese and Indian painters (Barry 2013). Creosote oil was being used to protect wooden ships in 1796 according to Koski (2008). Oils penetrate into wood in addition to forming a thin film on wood surfaces. Oil treatment increases the water repellency of wood and restricts dimensional changes (Dubey et al. 2010; Hyvonen et al. 2006). However, most oils do not provide long-term protection to wood, and they can encourage the colonization of wood surfaces by mould fungi (Feist 1977). Oils or modified oils are added to water repellents and wood preservatives designed to treat wood for exterior applications. The use of oils for wood protection will be reviewed in this section.

There are a range of different oils that are used for wood surface protection (Table 2.4). Linseed oil, also called flaxseed oil, is extracted from flax seed (Linum usitatissimum (L.)). It has been widely used for wood preservation, and in paints, stains and finishes. Linseed oil has been used since 15th century in varnishes and oil-based house paints in Europe (Lazzari 1999). Van Eckeveld et al. (2001) examined the effects of linseed oil and other drying oils (cocos oil and wood oil) on the water repellency of Scots pine (Pinus sylvestris (L.))
sapwood exposed to wet-dry cycles. Linseed oil and wood oil significantly reduced water uptake of the Scots pine samples. Linseed oil and tung oil have also been used as water repellents for wood. For example, Humar and Lesar (2013) examined both long-term and short-term effects of linseed oil and tung oil on the water repellency of wood. The oils effectively reduced water uptake in laboratory tests and also in samples exposed outdoors. Linseed oil restricted colour changes of wood exposed to artificial weathering according to Ozgenc et al. (2013). Dubey et al. (2010) tested the weather resistance of radiata pine that was treated with oil. The wood was first soaked in linseed oil at temperatures of 160°C, 180°C and 210°C for 1, 3 and 6 hours, and then exposed to accelerated weathering for 2100 hours. The oil treatment increased dimensional and colour stability of the wood and the wood was less susceptible to surface checking during weathering. Linseed oil and tung oil are also able to protect wood from degradation by brown- and white-rot fungi according to Humar and Lesar (2013).

One of drawbacks of using oils for wood protection is the slow drying rate of many oils. Therefore, metallic salts of manganese, cobalt and zirconium are used as driers to accelerate the curing of oils (Lazzari and Chiantore 1999; Mallégol et al. 2016). Oils can also be chemically modified to increase their curing rate. For example, the natural curing rate of linseed oil is low, although it is categorized as a drying oil (Lidefelt 2007). To overcome this limitation, linseed oil was modified to produce an acrylated epoxidized linseed oil (AELO) (Fig. 2.9). AELO was synthesized by reacting acrylic acid with an epoxidized linseed oil (Mahendran et al. 2012). Photoinitiators were also added to create a coating that could be cured by UV light. Photoinitiators significantly increased the curing rate of the coatings, although only one of them created a coating that performed well (Mahendran et al. 2012). Olsson (2012) synthesized epoxy functionalized soybean oil, which when combined with UV absorbers, protected wood veneers from photodegradation during weathering.
Castor oil is extracted from the seed of the plant (*Ricinus communis* (L.)) which belongs to the family Eurphorbiaceae (Naughton 1979). The oxidation of castor oil occurs in the absence of oxygen or air at temperatures of 80-130°C (Ogunniyi 2006). Transition metals like iron, manganese and copper can be used as catalysts for oxidizing and polymerising castor oil. Oxidized or polymerized castor oil has high viscosity. Therefore it is non-migrating and non-volatile. Castor oil is used for the manufacture of cellulosic resins, poly(vinyl butyral), polyamides, shellac finishes, and natural and synthetic rubber. Oxidized castor oil with high viscosity is useful in urethane coatings. Castor oil is the only common vegetable oil which has active hydroxyl groups (Naughton 1974) enhancing its reactivity with other chemicals and aiding polymerization.

There are other oils that have been used for wood protection. For example, crude tall oil was able to reduce water uptake of pine sapwood (Van Eckeveld et al. 2001; Hyvönen et al.)
Cocos oil also reduced water uptake by wood because it is a solid at room temperature and can block capillary openings (Van Eckeveld et al. 2001). Oils are also used as a medium to thermally modify wood, as mentioned above (Dubey et al. 2010). In addition, oils such as universal oil, thermowood oil and teak oil have been used to protect thermally modified wood during accelerated weathering (Miklečić et al. 2010). (Miklečić et al. 2010) found that oils restricted colour changes at wood surfaces during weathering and reduced the permeability and checking of wood surfaces. However, the oils had little effect on water absorption of wood when the wood was exposed to water for long periods of time. Vegetable oils are increasingly used as substitutes for petroleum based products for wood surface protection. For example, Ozgenc et al. (2013) examined the ability of parsley seed oil, pomegranate seed oil, linseed oil, nigella seed oil, canola oil, sesame seed oil, and soybean oil to protect wood surfaces from degradation during artificial weathering. All of the vegetable oils restricted colour changes at wood surface after 600 hours of artificial weathering. Pomegranate seed oil was the most effective treatment at restricting colour changes. Wood treated with the vegetable oils had higher strength after weathering compared to untreated controls. Tomak et al. (2011) confirmed that vegetable oils increased the mechanical stability of wood. However, the enhancement of mechanical properties of wood by oils was closely related to the entire treatment process from pre-treatment to post-treatment including the temperature of oil and chemicals used to cure the oils. Pánek and Reinprecht (2016) treated four tropical woods with commercially available vegetable oils and examined the performance of the treated woods during natural and also artificial weathering. Pigmented oils increased the colour stability of treated wood exposed to six months of natural weathering whereas treatment with transparent oils had little effect.

Some oils have been tested to see if they can prevent organisms from attacking wood. Lemon grass, rosemary, tea tree, thyme (Clausen and Yang 2007), anise, lime tangerine (Matan and Matan 2008) cinnamon and clove oils (Mattan and Matan 2011) were tested to
see if they could restrict mould growing on wood. All of the oils prevented colonization of wood by mould. However, other oils increase the colonization of wood surfaces by mould (Feist 1990). Cassia, cinnamon, wood tar and sandal wood oil and also some oils derivatives were tested to determine if they could protect wood from fungal and termite attack (Kartal et al. 2006). Cinnamic acid, ferulic acid, tall oil and cinnamaldehyde prevented fungal decay. All of the treatments protected wood from termite attack (Kartal et al. 2006). Tall oil derivatives were also able to prevent decay by brown rot fungi, but they were prone to leaching when treated wood was exposed to wet conditions (Temiz et al. 2008).

2.4 UV stabilizers

Organic UV absorbers in wood or in coatings act as light stabilizers by filtering (absorbing) UV light (Rogeza 2001). Ultra-violet (UV) stabilizers are a range of organic compounds that protect materials from UV light. They are often used in finishes designed to protect wood from photodegradation. UV absorbers absorb UV radiation up to 400 nm and harmlessly dissipate radiation as heat (McCusker 1999). They reduce the amount of radiation from reaching wood surfaces. Some inorganic metal nano-compounds are also able to reflect light (UV/Vis) depending on their sizes and chemical composition, as reviewed above. However, inorganic UV absorbers can lower the transparency of clear coatings and for this reason, organic UV absorbers are more widely used in clear coatings. Organic UV absorbers include compounds such as benzophenones and benzotriazoles (Fig. 2.10) that absorb UV light in the region of 325-345 nm (Hayoz et al. 2003).

Fig. 2.10: Energy transition of a benzophenone UV absorbers under UV light (Huang et al. 2016)

In order to obtain broader absorption, benzophenones and benzotriazoles can be combined with derivatives of tris-resorcinol-1,3,5-triazine (TRT), which have strong absorption in the 300-400 nm region. The resulting mixtures were more effective at
protecting wood than benzophenones and benzotriazoles on their own (Hayoz et al. 2003). Ravichandran et al. (2007) adopted a different approach to Hayoz and Rogez (2003). They developed novel ultraviolet light absorbers from benoxazinone, oxanilide, benzylidene malonate, quinazoline and benzotriazole compounds. These UV absorbers were able to reduce the light-induced degradation of polymethyl(methacrylate) films. Aloui et al. (2007) compared the ability of a range of UV absorbers including TiO$_2$ (15 nm) and TiO$_2$ (10 nm); transparent yellow and red iron oxides; the organic UV absorbers Tinuvin 1130 (2-hydroxy phenyl triazole) and Tinuvin 5151 (2-(2-hydroxyphenyl)-benzotriazole UVA and a basic HALS) to photostabilize wood. As expected the UV absorbers reduced colour change at wood surfaces exposed to artificial weathering. UV/VIS spectra indicated that when both organic and inorganic UV absorbers were used in clear coatings, they reduced the transmission of light to the underlying wood substrate. Inorganic UV absorbers were more effective at absorbing visible light than organic UV absorbers, as expected. However, inorganic UV absorbers increased the susceptibility of coatings to cracking because they increased the Tg of the coatings leading to low elasticity and flexibility (Aloui et al. 2007). Alternatively, benzotriazole and phenylacrylate UV absorbers can be combined with nano-sized titania and silica gel in coatings to significantly increase UV absorption over a broad range of wavelengths, thereby reducing the transmission of visible light through coatings (Mahltig et al. 2005). Thus, coating performance can be enhanced using both organic and inorganic UV absorbers to absorb a broader range of photoenergies. For example, Ozgenc et al. (2012) investigated the photo-discolouration of Scots pine and European beech (*Fagus sylvatica* (L.)) treated with HPT (hydroxyphenyl-s-triazine) micronized TiO$_2$. The most effective system for enhancing the performance of clear coatings on Scots pine was HPT with TiO$_2$, whereas in the case of European beech, HPT without TiO$_2$ was more effective. Forsthuber et al. (2013) compared discolouration of Norway spruce treated with TiO$_2$ or a HPT UV absorber during irradiation of treated wood in a xenon-arc weatherometer. TiO$_2$ was less effective at protecting wood surfaces from discolouration than HPT.
Forsthuber et al. (2013) also used artificial and outdoor weathering tests to compare the ability of 2-(2-hydroxyphenyl)-benzotriazole (BTZ) and HPT to reduce discolouration of wood. HPT was more effective than BTZ at stabilizing wood surfaces exposed to natural weathering or artificial weathering (Forsthuber et al. 2013). Some UV absorbers have been modified with epoxy or isocyanate groups to protect wood surfaces more effectively against light radiation. In theory, the epoxy or isocyanate modified UV absorbers are able to react with hydroxyl groups on wood’s molecules and form a strong bond (Williams 1983; Kiguchi et al. 2001). Such grafted UVAs should be less susceptible to leaching from wood surfaces exposed to weathering. One UV absorber, 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) (Fig. 2.11) that can be grafted to wood has been tested for its ability to enhance the performance of uncoated and coated wood exposed to weathering. HEPBP is synthesized using DHBP and epichlorohydrin (Manasek et al. 1976).

![Schematic description of the synthesis of HEPBP](image)

**Fig. 2.11: Schematic description of the synthesis of HEPBP (Manasek et al. 1976) and its reaction with wood**

HEPBP reduced the erosion of western red cedar exposed to artificial weathering (Williams 1983). HEPBP restricts the weight losses of veneers exposed to natural weathering (Kiguchi and Evans 1998). An alternative to grafting HEPBP to wood was investigated by Evans and Chowdhury (2010). They reacted HEPBP with dicarboxylic acid anhydrides to create high molecular weight UV absorbers (Evans and Chowdhury 2010). HEPBP reacted with phthalic anhydride (PA) significantly restricted weight and tensile strength losses of wood veneers exposed to weathering. This combination strongly absorbed UV light and created weathering-resistant films at wood surfaces. As a result, the HEPBP-PA combination
was more effective at photo-stabilizing wood surfaces than HEPBP on its own or HEPBP in combination with maleic or succinic anhydride (Evans and Chowdhury 2010). Other modified UV absorbers have been tested for their ability to photostabilize wood. Chang and Chou (2016) tested Tinuvin 1130, Tinuvin 292 and the modified UV absorber BPMA (2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)-benzophenone) in urethane-modified acrylic coatings applied to red oak (Quercus rubra (L.)). Results suggested that BPMA was more effective at restricting photo-discolouration of wood than the commercial (Tinuvin series) UV absorbers. Evans et al. (2002) investigated whether the aromatic compound benzoyl chloride could protect Scots pine from photodegradation. Benzoyl chloride was reacted with hydroxyl groups in wood to create a system containing large numbers of UV absorbing moieties. In theory, benzoyl groups acted as UVA to effectively prevent UV light from degrading wood during weathering. Chemical modification with benzoyl chloride significantly decreased weight losses of wood veneers during weathering. FTIR spectroscopy and SEM confirmed that benzoyl chloride effectively retarded photodegradation of lignin during weathering. This study suggested it is possible to create UV absorbers in wood using low cost chemicals, however, substantial weight gains were required to photostabilize lignin. Many UV absorbers are able to inhibit the photodegradation of wood, but some are unstable and do not provide long-term protection. UV absorbers are more effective when they are used in combination with another type of organic photostabilizer, hindered amine light stabilizer (HALS) (Fig. 12). The use of HALS can increase the performance of both UV absorbers and coating films (Avar and Bechtold 1999). HALS are able to scavenge free radicals generated from photodegradation (Fig. 13) and reduce the rate of degradation of wood. The combination of UVA and HALS in coating systems can provide much better photoprotection to wood and coatings than UV absorbers on their own according to Avar and Bechtold (1999).
HALS are often used as additives for the photoprotection of polymers, wood and coatings. HALS restrict the photodegradation of wood by scavenging free radicals generated by the degradation of wood’s molecules (Sedlar et al. 1982). Low concentrations of HALS can be used to stabilize polymers, since HALS react with free radicals in a cyclic process, regenerating, rather than being consumed (McCusker 1999). When HALS and UV absorbers (UVA) are used together in coatings, UVA reduces the amount of light reaching the wood substrate, while HALS trap free radicals. Hence, blends of UV absorbers and HALS give better stabilization of wood and coatings than either of the additives on their own (Ávár and Bechtold 1999).

Antioxidants are another class of organic photostabilizer that can be used to prevent oxidation of lignin and other components that are degraded during weathering. Antioxidants can be synthetized artificially or extracted from wood itself. Some wood species have
naturally-durable extractives that have protective effects at wood surfaces (Scheffer 1966). Natural preservatives can be extracted from the bark of poplar (*Populus ussuriensis* (Kom.)) which has antioxidant activities (Si et al. 2011). In addition, extracts from *Acacia* (*Acacia confusa* (Merr.)) bark and heartwood can act as free radical scavengers and have strong antioxidant effects (Chang et al. 2001). Thus, natural antioxidants can be applied to wood surfaces as coatings or as protective primers.

### 2.5 Surface finishes

Surface coatings, water repellents and stains are widely used to protect wood from weathering and will be briefly reviewed in this section.

#### 2.5.1 Coatings

Coatings are the most common way of protecting wood surfaces from the deleterious effects of water, light and oxygen (Rowell and Bongers 2015). Coatings are categorized as film-forming or penetrating coatings (Williams and Feist 1993; Bulian and Graystone 2009). Film-forming coatings contain pigments that conceal wood’s grain and act as a barrier to light and moisture, effectively protecting wood from weathering. Semi-transparent and transparent coatings are becoming more popular because they can protect wood without completely obscuring wood’s grain. However, their ability to protect wood from weathering is less than that of opaque coatings because some UV/Vis light is transmitted through the coatings and degrades both the coating and wood substrate (Bulian and Graystone 2009). Coatings can also be degraded by water and other environmental factors leading to blistering and delamination of coating layers (Feist 1990; de Meijer 2001; MacLeod et al. 1995). Checking of coatings can also occur because coatings may not accommodate wood’s dimensional movement when it absorbs water and then dries out (Koski 2008). Checks facilitate water penetration, which accelerates degradation of both wood and coating layers. Photodegraded coatings lose their elasticity and adhesion to wood during weathering (Macleod et al. 1995). Finally, paints are not able to preserve wood from attack by fungi.
which degrade wood in an entirely different way to the factors responsible for the weathering of wood (Feist 1990).

2.5.2 Water repellents

Moisture contributes to the degradation of wood surfaces as described in Section 2.1 (Siau 1995). Maintaining wood at a moisture content in equilibrium with its environment reduces dimensional change and the susceptibility of wood to fungal decay and checking (Feist and Mraz 1978). Thus, water repellents, which minimize the absorption of water, are commonly used to protect woodwork used outdoors. Water repellents can also be applied as a pre-treatment beneath coating systems to reduce the water uptake of coated wood, thereby increasing coating longevity (Williams and Feist 1993; Williams et al. 2016). Water repellents create a hydrophobic layer at wood surfaces and can be used on their own as a protective treatment as well as a pre-treatment beneath coatings (Williams and Feist 1999). Water repellents used on wood are mostly a mixture of oils, waxes and natural or artificial resins. They can also contain pigments and biocides (fungicides and insecticides). Water repellents can be applied to wood in a variety of ways including brushing, spraying, immersion or vacuum impregnation (Rowell and Banks 1985). Deep penetration enhances and prolongs the protective effects of water repellents and enables them to remain effective despite degradation of the upper-most layer of water-repellent treated wood. Water repellents are effective because water is not able to spontaneously penetrate into the microstructure of treated wood (Banks and Voulgaridis 1980). However, water repellents cannot penetrate wood cell walls because the wax or resin molecules are too large. Instead, they are bonded to wood by weak Van der Waals forces. Hence, during prolonged exposure of water repellent treated wood to water, the bonding of hydrophobes to wood is weakened as wood-water hydrogen bonding preferentially replaces weak Van der Waal’s forces between water repellents and wood (Banks 1973). Therefore, water repellents do not stop water absorption completely, rather they restrict the rate of water uptake and dimensional changes.
2.5.3 Stains

Stains are a mixture of a colourant (pigment), resin and a carrier (solvent or water). They can also protect wood from weathering (Trauth and Vamvakaris 1992). Colourants such as pigments or dyes are usually added into solutes such as water, alcohol or acetone. Stains act rather like pigmented coatings because they can block light from reaching the wood surface, thereby restricting photodegradation of wood (Feist and Mraz 1980; Feist 1983). However, wood that is stained will degrade once the colourant is degraded and eroded from finished surfaces.

In the market place, there are penetrating and non-penetrating stains. Non-penetrating stains are commonly referred to as solid-colour stains or hiding stains. Such stains are available in a wide range of colours and contain high concentrations of pigments (Sabnis 2010). Oils or latex based polymers are used as the binder and form thin films on finished wood surfaces. Oil or latex-based stains perform in much the same way as thinner paints because they mask the colour and grain of wood, and block light and water from reaching wood surfaces (Feist and Mraz 1980). On the other hand, penetrating stains are similar to water repellents, but in addition they contain additives such as pigments, UV absorbers and biocide to retard the degradation of wood (Egan 2012). Such stains can penetrate into wood without having the problems of film-forming stains such as blistering and delamination (Feist 1983).

2.6 Summary

Weathering of wood results from the effects of light, water, heat and organisms at wood surfaces (Feist and Hon 1984). Weathering often makes wood visually unappealing. The effects of weathering on the appearance of wood can be restricted using coatings including paints, pigmented stains and water repellent preservatives (Feist 1990). Paints are effective at restricting the weathering of wood, but they completely mask wood’s attractive features, for example its colour and grain (Feist and Hon 1984). Clear finishes preserve the characteristics of wood, but they do not last long because light passes through the coating degrading the
underlying wood leading to coating failure (Miniutti 1964). Therefore, pre-treatments that photostabilize wood are required to prolong the lifetime of clear coatings. For example, as this review has shown, brush-on coatings of certain inorganic compounds are highly effective at enhancing the performance of clear coatings on wood exposed to natural or artificial weathering (Black and Mraz 1974).

Various inorganic compounds have been studied to determine their ability to photostabilize wood exposed to weathering, although metal acetylacetonates have received little attention. Studies described in Section 2.2 have shown that metal ions can bond to woods molecular compounds and interfere with photo-oxidation process when wood is exposed to weathering. Inorganic metal compounds are able to protect wood surfaces through oxidation-reduction reactions creating stable metal-centered polymers, as described in Section 2.2.1. Various studies have shown that oils and UV absorbers restrict photodegradation of wood, but they are unable to protect wood surfaces in the long-term (Feist 1990; Blanchard and Blanchet 2011). Studies reviewed in Sections 2.3 and 2.4 indicate that oils and UV absorbers can be modified to provide more efficient protection for wood. Therefore, it is possible that combinations of inorganic metal compounds with oils and UV absorbers may be able to provide better protection to wood exposed outdoors than the compounds used on their own.
3. Surface protection of yellow cedar with metal acetylacetonates

3.1 Introduction

A large number of different inorganic compounds have been investigated for their ability to photostabilize wood, as described in Chapter 2 (Black and Mraz 1974, Preston and Chittenden 1978, Chang et al. 1982, Williams and Feist 1988, Schmalzl and Evans 2003). Chromic acid is the most effective treatment and it can also significantly enhance the performance of coatings (Williams and Feist 1988). However, its use has been limited by its toxicity and the fact it discolours wood. Other metal compounds have been tested, but one group of compounds that have received little attention are acetylacetonates of transition metals. One study showed that titanium acetylacetonate could photostabilize radiata pine (Schmalzl and Evans 2003). Other studies have shown that the effectiveness of metal acetylacetonates as photostabilizers for polymers varies with the metal in the coordination complex (Osawa and Aiba 1982). There are similarities between the radical-induced photodegradation of polymers and wood (Evans 2009). Therefore, I hypothesize that the ability of acetylacetonates to photostabilize wood will vary depending on the metal in the coordination complex. I test this hypothesis here by treating yellow cedar (Cupressus nootkatensis (D. Don) Spach) veneers with different acetylacetonates (Co, Cr, Fe, Mn, Ni, and Ti), exposing them to natural weathering, and measuring changes in physical and chemical properties of treated veneers and untreated controls.

3.2 Materials and methods

My experiment examined the effects of seven chemical treatments replicated six times (six blocks) on the following response variables: (1) Weight losses of veneers; (2) Erosion of veneers; (3) Tensile strength of veneers; (4) Contact angles of veneers; (5) Colour changes of veneers (ΔL*, Δa*, Δb*, ΔE).

Analysis of variance (ANOVA) for a randomised block design was used to analyse data. Statistical computation was performed using Genstat (v. 18.2). The controls were untreated.
or treated with the parent solvent dimethylformamide. A sub-routine (convstrt) within Genstat was used to produce contrasts between the ‘weathering’ of these controls and the other treated samples, and also between all of the treated samples (Buysse et al. 2004).

Weight gain of treated veneers was used as a covariate in the analysis of weight loss data. Results are presented in graphs and error bars (2 x standard error of difference) or a least significant (p<0.05) difference bar on each graph can be used to estimate whether differences between individual means are statistically significant (Abdi and Williams 2010). These error bars are derived from analyses of variance and are not measures of within treatment variability (±standard deviation).

3.2.1 Metal acetylacetonates

Metal acetylacetonates were purchased from Sigma-Aldrich. Their concentrations (w/w) in dimethylformamide (DMF) are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Colour</th>
<th>Solvent</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron acetylacetonate</td>
<td>Red</td>
<td>DMF</td>
<td>3</td>
</tr>
<tr>
<td>Nickel acetylacetonate</td>
<td>Dark green</td>
<td>DMF</td>
<td>3</td>
</tr>
<tr>
<td>Cobalt acetylacetonate</td>
<td>Green</td>
<td>DMF</td>
<td>1</td>
</tr>
<tr>
<td>Manganese acetylacetonate</td>
<td>Purple</td>
<td>DMF</td>
<td>3</td>
</tr>
<tr>
<td>Titanium acetylacetonate</td>
<td>Pale yellow</td>
<td>DMF</td>
<td>1</td>
</tr>
<tr>
<td>Chromium acetylacetonate</td>
<td>Deep maroon</td>
<td>DMF</td>
<td>3</td>
</tr>
</tbody>
</table>

3.2.2 Preparation and treatment of veneers with metal acetylacetonates

Eighty wood veneers, 100 mm long, 19 mm wide and 95-115 μm thick were cut from the radial faces of each of six water-saturated yellow cedar heartwood blocks using a microtome (Fig 3.1), as described previously (Evans et al. 2013). Yellow cedar veneers were air-dried under ambient laboratory conditions for 12 h and then equilibrated at 20 ± 1°C and 65 ± 5% r.h. for 1 week. Ten veneers from each of the six parent blocks of wood were selected at random and allocated to each of the six different acetylacetonates treatments and untreated and solvent-based DMF controls (60 veneers for each of the eight treatments, 480
Veneers were oven-dried to a constant weight at 105 ± 5°C for 2 h and the weights of individual veneers were measured using an analytical balance (± 4 mg). Veneers were then reconditioned, as above for 1 week.

![Microtome used to cut veneers: (a) Wood block; (b) Clamping of wood block in brass chuck; (c) Blade holder and blade; (d) Black arrow indicates direction of sectioning](image)

Fig. 3.1: Microtome used to cut veneers: (a) Wood block; (b) Clamping of wood block in brass chuck; (c) Blade holder and blade; (d) Black arrow indicates direction of sectioning

Batches of veneers allocated to different treatments were fixed to separate glass plates measuring 39.5 x 9 cm using opaque Perspex strips and butterfly clips. Veneers were sprayed using an air brush (Paasche H & HS model) (Fig. 3.2) with the appropriate metal acetylacetonates dissolved in DMF (3% w/w for Cr, Fe, Mn and Ni or 1% w/w for Co and Ti) or DMF. The volumes of the cobalt and titanium acetylacetonate solutions sprayed on to veneers were increased to ensure the mass of chemical applied to batches of veneers was the same as those applied to veneers treated with the other metal acetylacetonates. All batches of treated veneers and untreated controls were air-dried for 1 h, oven-dried at 105 ± 5°C for 2 h and the weights of individual veneers obtained, as described above. Treated veneers were then reconditioned, as above for 7 days and their thicknesses were measured using a digital micrometer (Lorentzen and Wettre HWS 5781, Sweden).
Fig. 3.2: Air-brush (a) and compressor (b) used to deliver metal acetylacetonates solutions on veneers

3.2.3 Weathering trial

Forty treated veneers and untreated controls from each parent block of yellow cedar were secured (as above) on wooden backing boards using wooden clamps. An equal number of veneers for each treatment, including untreated controls were stored in a conditioning room. These veneers acted as treated, unweathered, controls. Wooden backing boards containing the veneers were exposed outdoors, above ground, oriented at 25 degrees to the horizontal in Harden, New South Wales, Australia (34°33’8” S, 148°21’51” E, 422 m elevation) from 8th to 28th December, 2014 (Fig. 3.3). After weathering, veneers were carefully removed from wooden backing boards and conditioned, as above, for one week. The oven dry mass of individual weathered veneers was then re-measured. Mass losses of treated and untreated veneers during weathering are expressed as the difference in oven dry masses of veneers before and after weathering.
Fig. 3.3: Natural weathering of veneers treated with metal acetylacetonates and controls (untreated and treated with DMF) in Harden, New South Wales, Australia for 20 days: (a) Veneers on backing boards before exposure to the weather; (b) Veneers being exposed to natural weathering

3.2.4 Characterization of veneers exposed to weathering

3.2.4.1 Measurement of colour

A Minolta CM-2600D spectrophotometer was used to measure the colour of treated and untreated veneers (both weathered and unweathered). This device measures lightness (L*), redness (a*) and yellowness (b*) values of materials according to the CIE three dimensional space system (CIE 1976). Conditioned, weathered and unweathered veneers were placed on a sheet of white matt paper. Measurements were made at two points on each conditioned veneer and were the average of three readings for each point (10°/D65). CIE colour parameters (L*, a* and b*) were recorded after white and zero background data was collected and the spectrophotometer was calibrated (CIE 1976). The difference in colour (ΔE) was calculated using the following formula (CIE 1976):

$$\Delta E_{ab}^* = \sqrt{\left((L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2\right)}$$

All measurements were conducted in a conditioning room with controlled temperature and humidity (20 ± 1°C and 65 ± 5% r.h.).
3.2.4.2 Measurement of contact angle

The sessile drop method with a goniometer (KSV CAM 101) was used to measure the hydrophobicity of veneer surfaces before and after veneers were weathered (Fig 3.4). The method employed a digital camera to capture images of distilled water droplets on veneers surfaces. The contact angle of droplets was calculated using Young-Laplace algorithm (CAM 200 software, KSV Instruments, 2007. CAM 200, 3rd edition, Espoo, Finland) (Fig 3.5). Conditioned, weathered and unweathered veneers were secured to the platform with butterfly clips. Three measurements were made on each veneer and were averaged to get the final contact angles. 5μL of distilled water was placed on each sample and images were recorded every 16 ms for 70 frames and then, one frame every 5s for 9 frames. The distilled water droplets on each veneer formed an angle between the droplet interface and the stage, as shown in Fig. 3.6. All measurements were conducted in a conditioning room with controlled temperature and humidity (20 ± 1°C and 65 ± 5% r.h.).
3.2.4.3 Measurement of weight losses and tensile strength of veneers

Conditioned, weathered and unweathered veneers were oven dried at 105 ± 5°C for 2 h, and then placed in a desiccator over silica gel for five minutes. The weights of veneers were measured using a digital scale (A&D GR-200). Weight losses were calculated as the difference between the oven-dried weights of treated weathered veneers and their treated oven-dry weights prior to weathering.

The tensile strengths of veneers before and after weathering were measured using a Pulmac paper tester (Boucai 1971). Both weathered and unweathered veneers were tested and ratios of tensile strength (after/before weathering) were calculated. Veneers were conditioned for one week prior to tensile strength tests. Tensile strength tests were carried...
out at zero-span using a clamping pressure of 60 psi (413.7 KPa). The thickness of veneers was measured using a digital micrometer (Lorentzen and Wettre HWS 5781, Sweden). Tensile strength was calculated by dividing the maximum load (Kg) at failure by the cross sectional dimensions (mm$^2$) of each veneer (Evans and Schmalzl 1989).

### 3.2.4.4 Measurement of erosion

The erosion of veneers as a result of natural weathering was measured using a surface confocal profilometer (Fig. 3.6) with a 3 mm (3024 μm to 92 nm) probe (Altisurf 504®, ALTIMET, France). A linear line profile scan was carried out on earlywood of each veneer. This scan traversed 13 mm across the weathered section of each veneer and also 4 mm across wood that had been shielded from weathering by the opaque wooden clamps used to fix veneers to wooden backing boards (Fig. 3.3). The line scans were analysed using the software PaperMap (v. 3.2.0, Digital Surf 2004) to obtain height differences between the weathered and unweathered sections of each veneer, as shown in Fig. 3.7.

![Confocal profilometer used to measure the erosion of wood veneers (left). Veneer was fixed onto a microscope slide (right) using double-sided tape (Scotch® 665 Permanent Double-Sided Tape)](image)

**Fig. 3.6**: Confocal profilometer used to measure the erosion of wood veneers (left). Veneer was fixed onto a microscope slide (right) using double-sided tape (Scotch® 665 Permanent Double-Sided Tape)
3.2.4.5 Scanning electron microscopy

Sections 3 mm² in size were cut from treated and untreated veneers (weathered and unweathered) and attached to aluminium stubs using double-sided tape. Veneer sections were coated with a thin layer of gold or carbon and viewed using a Zeiss UltraPlus field emission scanning electron microscope equipped with an INCA Energy 450 EDX system. An accelerating voltage of 5 kV was used for gold-coated sections, and 15 kV was used for sections coated with carbon. An in-lens secondary electron detector was used to create images of gold-coated sections whereas an angular sensitive backscatter detector (AsB) was used for sections coated with carbon. The EDX probe was used to detect metals at veneer surfaces. EDX spectra and secondary electron and back-scattered electron images of the surface of treated and untreated veneers (weathered and unweathered) were saved as TIFF files.

3.2.4.6 Fourier transform infra-red (FTIR) spectroscopy

Fourier transform infra-red (FTIR) spectroscopy was used to probe the chemical composition of treated and untreated cedar veneers before and after natural weathering. Veneers were dried for 24 h over silica gel and FTIR spectra of veneer surfaces were obtained using a single bounce attenuated total reflectance accessory (PikeMIRacle, PIKE Technologies, Madison, USA) attached to a spectrometer (Spectrum One, PerkinElmer). Each spectrum represents 32 accumulations at 4 cm⁻¹ resolution. The spectra were processed...
using software (v.5.3, PerkinElmer 2005), which performed smoothing, baseline correction and normalisation at 1708 cm$^{-1}$. The heights for the peak at 1508 cm$^{-1}$ (C=C in benzene rings) in weathered veneers are expressed as a ratio of the peak at 1160 cm$^{-1}$ (C-O-C in polysaccharides) to compare the ability of the different metal acetylacetonates to photostabilize lignin (Rodrigues et al. 1998).

3.3 Results

The significance of experimental factors on the weathering of treated and untreated wood veneers exposed outdoors in Australia for 20 days is summarised in Table 3.2. There were significant effects of the metal acetylacetonates treatments on weight losses (p<0.001), tensile strength (p<0.001), contact angle (p<0.05) and colour changes (p<0.001) of veneers exposed to natural weathering (DMF excluded). There was also a significant (p<0.05) effect of treatment on the erosion of veneers exposed to the weather when results are averaged across all treatments and compared to those of similarly exposed untreated veneers (DMF excluded). Acetylacetonate treatments had significant effects on weight losses (p<0.001), tensile strength (p<0.001), contact angle (p<0.05), erosion (p<0.05) and colour changes (p<0.001) of veneers exposed to natural weathering when results are compared with veneers treated with DMF. The covariate used in the analyses of variance (weight gain due to treatment) had significant (p<0.05) effects on weight losses of veneers during weathering (Table 3.2).
Table 3.2: Summary of the statistical analyses of the effects of metal acetylacetonate treatments on different measures of the weathering of wood veneers exposed outdoors in Australia for 20 days

<table>
<thead>
<tr>
<th>Response Variables</th>
<th>Statistical significance (p-values)</th>
<th>Covariate</th>
<th>UNT vs TRs</th>
<th>TRs+</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
<td>(a) Weight losses</td>
<td></td>
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<td>**</td>
<td>***</td>
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<tr>
<td>Excluding Erosion</td>
<td></td>
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<tr>
<td>DMF control</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colour changes</td>
<td>L*</td>
<td>*</td>
<td></td>
<td>***</td>
</tr>
<tr>
<td></td>
<td>a*</td>
<td>***</td>
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<tr>
<td></td>
<td>b*</td>
<td>***</td>
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<tr>
<td></td>
<td>∆E</td>
<td>*</td>
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<tr>
<td>Tensile strength</td>
<td>Unweathered</td>
<td>*</td>
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<tr>
<td></td>
<td>Weathered</td>
<td>**</td>
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<tr>
<td></td>
<td>Ratios</td>
<td>*</td>
<td>***</td>
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<tr>
<td>Contact angle</td>
<td>Unweathered</td>
<td>*</td>
<td>***</td>
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<tr>
<td></td>
<td>Weathered</td>
<td>*</td>
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<td>Ratios</td>
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<tr>
<td>(b) Weight losses</td>
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<td>***</td>
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<tr>
<td>Excluding Erosion (Ln)</td>
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<td>*</td>
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<tr>
<td>untreated control</td>
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</tr>
<tr>
<td>Colour changes</td>
<td>L*</td>
<td>*</td>
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<td>***</td>
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<tr>
<td></td>
<td>a*</td>
<td>***</td>
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<td>b*</td>
<td>***</td>
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<tr>
<td></td>
<td>∆E</td>
<td>*</td>
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<td></td>
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<tr>
<td>Tensile strength</td>
<td>Unweathered</td>
<td>*</td>
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<tr>
<td></td>
<td>Weathered</td>
<td>*</td>
<td>***</td>
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<tr>
<td></td>
<td>Ratios</td>
<td>*</td>
<td>***</td>
<td></td>
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<tr>
<td>Contact angle</td>
<td>Unweathered</td>
<td>*</td>
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<tr>
<td></td>
<td>Weathered</td>
<td>*</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Ratios</td>
<td>*</td>
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</tbody>
</table>

* = p<0.05; ** = p<0.01; *** = p<0.001; +: TRs = treated; UNT = control

3.3.1 Effect of metal acetylacetonates on weight losses of veneers

Fig 3.8 compares weight losses of treated veneers with those of untreated veneers or veneers treated with DMF. Veneers treated with titanium, nickel, manganese or iron acetylacetonates lost significantly (p<0.05) less weight than the controls (untreated veneers or veneers treated with DMF) during natural weathering. Chromium and cobalt acetylacetonates were ineffective (p>0.05) at restricting weight losses of veneers during
weathering. Veneers treated with cobalt acetylacetonate lost significantly more weight than veneers treated with DMF (Fig. 3.8b).

![Graphs showing weight losses of yellow cedar veneers treated with different metal acetylacetonates and exposed to the weather in Australia for 20 days. The photoprotective effects of the acetylacetonates can be assessed by comparing weight losses of treated veneers with those of similarly exposed a. untreated controls (UNT) or b. veneers treated with dimethylformamide, (DMF)](image)

**Fig. 3.8:** Weight losses of yellow cedar veneers treated with different metal acetylacetonates and exposed to the weather in Australia for 20 days. The photoprotective effects of the acetylacetonates can be assessed by comparing weight losses of treated veneers with those of similarly exposed a. untreated controls (UNT) or b. veneers treated with dimethylformamide, (DMF)

### 3.3.2 Effect of metal acetylacetonates on erosion of veneers

The acetylacetonates significantly (p<0.05) reduced the erosion of veneers during weathering when results are averaged across all treatments (excluding DMF) and compared to the erosion of untreated veneers. The average weathering-induced erosion of veneers treated with metal acetylacetonates was 16.2 m compared to a figure of 22.7 m for erosion of untreated veneers. The most effective acetylacetonates at reducing erosion of veneers during weathering were manganese (13.0 m), iron (15.4 m) and titanium (15.5 m). On the other hand, there was no significant (p>0.05) difference in the average erosion of all treated veneers and erosion of veneers treated with DMF when untreated control were excluded from the analyses. However, manganese, iron and titanium acetylacetonate restricted erosion of veneers during weathering in comparison with nickel, cobalt acetylacetonate and DMF treatments (Fig. 3.9).
Fig. 3.9: Surface erosion of yellow cedar veneers treated with different metal acetylacetonates and dimethylformamide (DMF) after veneers were exposed to the weather in Australia for 20 days

3.3.3 Effect of metal acetylacetonates on tensile strength

The acetylacetonates increased the initial (unweathered) tensile strength of veneers, and their effect on tensile strength is significant when results are averaged across all treatments (excluding DMF) and compared to the tensile strength of untreated veneers (10.19 [treated] v 9.23 [untreated], kg/mm²). The acetylacetonates had a significant (p<0.05) effect on tensile strength of veneers after natural weathering (Fig. 3.10).

Veneers treated with nickel, manganese, titanium or chromium acetylacetonate were significantly (p<0.05) stronger after 20 days of natural weathering than the controls (untreated or treated with DMF, Fig. 3.10). Veneers treated with cobalt acetylacetonate were significantly (p<0.05) stronger after weathering than untreated controls, but not veneers treated with DMF (Fig. 3.10). Treatment of veneers with iron acetylacetonate had no significant (p<0.05) effect on losses of tensile strength of veneers during weathering (Fig. 3.10a).
Fig. 3.10: Tensile strength of yellow cedar veneers treated with different metal acetylacetonates and exposed to the weather in Australia for 20 days. The photoprotective effects of the metal acetylacetonates can be assessed by comparing tensile strengths of treated veneers with those of similarly exposed (a) untreated controls (UNT) or (b) veneers treated with dimethylformamide, (DMF)

3.3.4 Effect of metal acetylacetonates on water repellency of veneers

The metal acetylacetonates increased the initial (unweathered) contact angle of veneers when average contact angles for all treated veneers are compared with those of untreated controls (excluding DMF). Veneers treated with acetylacetonates had an average contact angle of 102.4° (degree), which was significantly (p<0.05) higher than contact angles on untreated veneers, 89.7°. The acetylacetonates had a significant (p<0.05) effect on contact angles on veneers after natural weathering. Veneers treated with cobalt acetylacetonate had significantly lower contact angles than the untreated control, and also veneers treated with chromium or nickel acetylacetonate (p<0.05) (Fig. 3.11). When contact angles of untreated veneers and veneers treated with chromium and nickel acetylacetonate are compared (Fig. 3.12), results show that contact angles on the untreated control decreased faster than those on wood treated with chromium or nickel acetylacetonate (Fig. 3.12). In addition, veneers treated with chromium or nickel acetylacetonate had significantly (p<0.05) higher contact angles than veneers treated with DMF and also veneers treated with manganese or cobalt acetylacetonate (Fig. 3.11).
Fig. 3.11: Contact angles on yellow cedar veneers treated with different metal acetylacetonates and exposed to the weather in Australia for 20 days. The hydrophobic effects of the acetylacetonates can be assessed by comparing initial contact angles on treated veneers with those of similarly exposed a. untreated controls (UNT) or b. veneers treated with dimethylformamide, (DMF).

Fig. 3.12: Changes in contact angles over 0.384 s on wood veneers treated with chromium or nickel acetylacetonate and untreated control after they were exposed to natural weathering.

3.3.5 Effect of metal acetylacetonates on colour and colour changes of veneers

The acetylacetonates discoloured veneers before weathering (Fig. 3.13). Veneers treated with iron or manganese acetylacetonate became brown whereas veneers treated with nickel or titanium acetylacetonate became yellower (Fig. 3.13). Veneers treated with chromium or cobalt acetylacetonate became pink and green, respectively as a result of treatment (Fig.
L*, a* and b* of treated and untreated control are shown in Fig. 3.14. The results accord with colour changes that can be observed visually in Fig. 3.13. Iron and manganese acetylacetonate significantly (p<0.05) darkened and reddened veneers (p<0.001). Veneers treated with nickel and titanium acetylacetonate are significantly (p<0.05) yellower compared with untreated control and samples treated with DMF (Fig. 3.15).

![Fig. 3.13: Colour of yellow cedar veneers treated with different metal acetylacetonates before (top row) and after (bottom row) exposure to the weather in Australia for 20 days](image-url)
(a) Colour parameters for treated vs. untreated (UNT), before weathering

(b) Colour parameters for treated vs. DMF, before weathering

**Fig. 3.14:** CIE colour parameters of yellow cedar veneers treated with different metal acetylacetonates before weathering (L* = lightness; a* = redness; b* = yellowness). The colour parameters of veneers treated with the acetylacetonates are compared separately with a. Untreated controls (UNT) or b. Veneers treated with dimethylformamide, (DMF)
Fig. 3.15: CIE colour parameters of yellow cedar veneers treated with different metal acetylacetonates after weathering (L* = lightness; a* = redness; b* = yellowness). The colour parameters of veneers treated with the acetylacetonates are compared separately with a. Untreated controls (UNT) or b. Veneers treated with dimethylformamide, (DMF)

The colour of veneers changed after they were exposed to the weather (Fig 3.13 bottom). Veneers treated with chromium and cobalt acetylacetonate lost their pink and green colouration, respectively, and became yellow-brown after weathering (Fig. 3.13). Similarly, the dark brown colour of manganese acetylacetonate treated veneers was lost during weathering, and they also became yellow-brown in colour (Fig 3.13). In contrast, veneers treated with iron acetylacetonate changed from a dark brown to a blue-black colour as a result of weathering (Fig. 3.13). Veneers treated with titanium acetylacetonate changed from
a yellow to a brown colour (Fig. 3.13). Untreated veneers became darker as a result of weathering (Fig. 3.13). These visual observations are supported in part by $L^*$ (lightness), $a^*$ (redness) and $b^*$ (yellowness) parameters of weathered veneers. The $L^*$, $a^*$ and $b^*$ values of veneers treated with iron acetylacetonate are significantly smaller than veneers treated with other acetylacetonates and the controls (untreated and veneers treated with DMF) (Fig. 3.15).

The changes in the colour of treated veneers during weathering are also apparent in the $L^*$ (lightness), $a^*$ (redness) and $b^*$ (yellowness) colour space values in Fig. 3.16, which expresses CIE colour space values ($L^*, a^*$ and $b^*$) as the ratio of colour parameters after weathering to those of initial parameters (unweathered). These ratios confirm the statistical significance of some of the changes in colour described above, particularly changes in the colour of veneers treated with the iron, manganese and titanium acetylacetonates. Veneers treated with manganese acetylacetonate brightened during weathering (Fig. 3.16). Veneers treated with iron acetylacetonate became darker during weathering, and they had the lowest $L^*$, $a^*$ and $b^*$ ratios. Ratios of $a^*$ and $b^*$ of veneers treated with iron acetylacetonate were significantly higher than those of other treated veneers and controls. The yellowing of wood that usually occurs when it is exposed to the weather is not apparent in Fig. 3.16, possibly because yellow cedar is yellow in its native (unweathered) state. Overall colour changes are expressed using the Delta E parameter (Fig. 3.17). Veneers treated with nickel and manganese discoloured significantly ($p<0.05$) less than untreated controls.
Fig. 3.16: Ratios of colour parameters (after/before weathering) of yellow cedar veneers treated with different metal acetylacetonates ($L^*$ = lightness; $a^*$ = redness; $b^*$ = yellowness). The colour parameters of veneers treated with the acetylacetonates are compared separately for a. untreated controls (UNT) or b. veneers treated with dimethylformamide, (DMF)
Fig. 3.17: Delta E of yellow cedar veneers treated with different metal acetylacetonates compared separately with a. untreated controls (UNT) or b. veneers treated with dimethylformamide (DMF)

3.3.6 Scanning electron spectroscopy

Weathering caused extensive micro-checking of bordered pits at the surface of untreated veneers, as expected (Fig. 3.18 a, b). Micro-checking of bordered pits also occurred at the surface of veneers treated with nickel, or manganese acetylacetonate, but was less pronounced than that at the surface of untreated controls (Fig. 3.18 c,d,e,f). In comparison, it was less easy to discern any protective effects of the other metal acetylacetonates on the microstructure of veneers exposed to weathering (3.19, and Appendix 1 which contains all of the SEM photographs of weathered veneers and controls).
Fig. 3.18: Scanning electron microscope photographs of the surface of veneers before and after exposure to the weather for 20 days in Australia; (a), Untreated, unexposed; (b) Untreated, weathered; (c) Treated with nickel acetylacetonate, unexposed; (d) Treated with nickel acetylacetonate, exposed; (e) Treated with manganese acetylacetonate, unexposed; (f) Treated with manganese acetylacetonate, exposed
Fig. 3.19: Scanning electron microscope photographs of the surface of veneers before and after exposure to the weather for 20 days in Australia; (a), Treated with iron acetylacetonate, unexposed; (b) Treated with iron acetylacetonate, exposed; (c) Treated with chromium acetylacetonate, unexposed; (d) Treated with chromium acetylacetonate, exposed; (e) Treated with titanium acetylacetonate, unexposed; (f) Treated with titanium acetylacetonate, exposed

Micro-checking at the surface of veneers treated with cobalt acetylacetonate, which was ineffective at reducing weight and tensile strength losses of veneers (Figs. 3.8 and 3.10), was
also more pronounced than that at the surface of veneers treated with nickel and manganese acetylacetonate (Fig. 3.20). The surface of veneers treated with cobalt acetylacetonate contained numerous square and rhomboid-shaped deposits (Fig. 3.20a). These deposits can be easily seen as bright spots in back-scattered electron images (Fig. 3.20c). The deposits were absent from the surface of weathered veneers (Fig. 3.20b), but weathered veneers contained smaller and more numerous small bright deposits (Fig. 3.20d). EDX examination confirmed the presence of cobalt in the square/rhomboid-shaped deposits at the surface of unweathered veneers treated with cobalt acetylacetonate (Fig. 3.21a). Deposits containing the parent metals were also present at the surface of veneers treated with the different metal acetylacetonates such as manganese acetylacetonate (Fig. 3.22a). Manganese was also present in cell walls of wood surfaces treated with manganese acetylacetonate before exposure (Fig. 3.22b). However, metals crystals were far more numerous at the surface of veneers treated with cobalt acetylacetonate. The deposits at the surface of weathered veneers treated with cobalt acetylacetonate contained magnesium and silicon (Fig. 3.21b) or aluminium, iron, potassium, silicon and sodium (Fig. 3.21c). Similar deposits were observed at wood surfaces treated with manganese acetylacetonate after weathering (Fig. 3.22c) (see Appendix 2.1 for back-scattered electron images of all treated and untreated veneers). Deposits with similar chemical composition were also present at the surface of all weathered veneers (treated and untreated), irrespective of chemical treatment.
Fig. 3.20: Scanning electron microscope photographs of the surface of veneers treated with cobalt acetylacetonate before and after exposure to the weather for 20 days in Australia; (a) Treated, unexposed, note square and rhomboid-shaped deposits (arrowed); (b) Treated, exposed; (c) Treated, unexposed; (d) Treated exposed. Note pit micro-checking in the exposed veneer (arrowed) (b) and the presence of deposits at the surface of veneers before (a, c) and after weathering (d)
3.3.7 Fourier Transform Infra-red (FTIR) Spectroscopy

FTIR internal reflectance spectroscopy was used to detect chemical changes at the surface of treated and untreated veneers exposed to natural weathering. The intensity of the
peak 1508 cm\(^{-1}\) \((C=C\) in benzene rings in lignin\) at the surface of untreated veneers decreased when they were exposed to natural weathering, as expected (Evans et al. 1992). The heights of the peak at 1508 cm\(^{-1}\) in weathered veneers are expressed as a ratio of the polysaccharide peak at 1160 cm\(^{-1}\) \((C-O-C)\) in Table 3.3 to compare the ability of the different metal acetylacetonates to photostabilize lignin (Harrington et al. 1964; Michell 1989).

Table 3.3: Effects of different metal acetylacetonates on the delignification of yellow cedar veneers exposed to natural weathering in Australia for 20 days

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ratio of height of aromatic skeletal peak at 1508 cm(^{-1}) ((C=C)) to that of the polysaccharide peak at 1160 cm(^{-1}) ((C-O-C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron acetylacetonate</td>
<td>4.36</td>
</tr>
<tr>
<td>Nickel acetylacetonate</td>
<td>3.73</td>
</tr>
<tr>
<td>Chromium acetylacetonate</td>
<td>3.46</td>
</tr>
<tr>
<td>Manganese acetylacetonate</td>
<td>3.42</td>
</tr>
<tr>
<td>Titanium acetylacetonate</td>
<td>3.39</td>
</tr>
<tr>
<td>Cobalt acetylacetonate</td>
<td>2.92</td>
</tr>
<tr>
<td>Untreated</td>
<td>2.69</td>
</tr>
</tbody>
</table>

The most effective treatment at photostabilizing lignin was iron whereas cobalt acetylacetonate was the least effective (Table 3.3 and Fig. 3.23). The photostabilization of lignin by chromium, manganese, nickel and titanium acetylacetonate was similar (Table 3.3).
Fig. 3.23: FTIR internal reflectance spectra of untreated yellow cedar veneers (before and after natural weathering) compared to spectra of veneers treated with iron or cobalt acetylacetonate and then weathered

The intensity of the peak at 1265 cm\(^{-1}\) (C-O in lignin and hemicellulose) and the peak at 1452 cm\(^{-1}\) (C=O in aromatic rings in lignin and CH\(_2\) in cellulose) decreased at the surface of untreated veneers when veneers were exposed to natural weathering. Compared to veneers treated with iron acetylacetoante, the intensity of the peak at 1265 cm\(^{-1}\) and 1452 cm\(^{-1}\) at the surface of untreated veneers and veneers treated with cobalt acetylacetonate decreased to a greater extent during weathering (Fig. 3.23). Full spectra of all treatments and controls (before and after weathering) can be found in Appendix 1.

3.4 Discussion

There were significant differences in the capacity of the different metal acetylacetonates to protect wood exposed to the weather, with the exception of erosion of veneers (excluding untreated control). Therefore my results partially support my hypothesis that the ability of metal acetylacetonates to photostabilize wood will vary depending on the metal in the coordination complex. Nickel, manganese, titanium and iron acetylacetonate were more effective than cobalt acetylacetonate at photostabilizing wood, based on the different measures I used to assess the effectiveness of metal acetylacetonates at restricting
photodegradation of veneers. My findings for titanium acetylacetonate accord with a previous study by Schmalzl and Evans (2003) that found that titanium acetylacetonate could restrict weight and tensile strength losses of radiata pine veneers exposed to natural weathering. Iron acetylacetonate was the most effective compound at photostabilizing lignin, but it was unable to restrict tensile strength losses of veneers, in accord with a previous study that showed that iron compounds increase tensile strength losses of wood veneers exposed to the weather (Evans and Schmalzl 1989). Iron compounds can photostabilize lignin according to Chang et al. (1982) and my findings accord with those of Chang et al. (1982). However, weathered veneers treated with iron acetylacetonate were a blue-black colour, which is not desirable for a pre-treatment designed to improve the performance of clear coatings. For the same reason, cobalt acetylacetonate is unsuitable as a wood pre-treatment because it imparted a green colour to veneers, and it was also the least effective compound at preventing the degradation of veneers exposed to the weather. Cobalt acetylacetonate tended to crystallize at wood surfaces after treatment. Crystals were absent from the surface of weathered veneers, suggesting that loss of chemical accounted for the relatively high weight losses of veneers treated with cobalt acetylacetonate. Losses of chemical from the surface of treated veneers during natural weathering may explain why weight gain due to treatment when used as a covariate in the analyses of variance had a significant (p<0.05) effect on weight losses of veneers during weathering. Weathered veneers also contained particles composed of a range of metals and also silicon. The chemical composition of these particles suggests that they were mineral particles, and not ones deposited at the surface of the veneers as a result of treatment with metal acetylacetonates (Škrbić et al 2012). The metal acetylacetonates increased the hydrophobicity of wood surfaces before exposure, possibly because they reacted with hydroxyl groups (Czech and Wojciechowicz 2006). But, the acetylacetonates were unable to restrict the loss of hydrophobicity of wood during weathering, suggesting that the complexes formed between the metal acetylacetonates and wood were not highly resistant to weathering.
Metal acetylacetonates, with the exception of titanium acetylacetonate, have not been used as photoprotective treatments for wood, but they have been used to photostabilize polyvinyl chloride (PVC) (Osawa and Aiba 1982). Osawa and Aiba (1982) tested all of the metal acetylacetonates used here, with the exception of iron acetylacetonate, and found they could photostabilize PVC. My findings are different because Mn, Ni and Ti acetylacetonate were able to restrict degradation of wood veneers whereas cobalt acetylacetonate was ineffective, possibly because it was leached from wood surfaces during weathering. Furthermore, manganese and chromium acetylacetonate, which protected wood veneers from degradation here, accelerated the photodegradation of high-density polyethylene films (Kiryakova et al. 2016). Metal acetylacetonates are intimately mixed with polymers whereas they were applied to the surface of wood veneers here. This difference in the chemical and physical characteristics of wood and polymers treated with metal acetylacetonates may account, in part, for the discrepancies between our findings and those of previous studies that have tested the photostability of polymers containing metal acetylacetonates.

A previous study of the effects of manganese, titanium and zirconium compounds on the photostability of wood veneers, tested titanium acetylacetonate, as mentioned above (Schmalzl and Evans 2003). They found that titanium acetylacetonate restricted weight and tensile strength losses of radiata pine veneers exposed to the weather for 35 days, however they found ‘no partial retention or protection of lignin’ in weathered veneers, in contrast to my results, which showed modest retention of lignin in veneers treated with titanium acetylacetonate and exposed to the weather for 20 days. The difference in the lengths of time that veneers were exposed to the weather in the two studies may explain the discrepancy between our findings and those of Schmalzl and Evans (2003). In comparison to titanium acetylacetonate, iron and to a lesser extent nickel acetylacetonate were more effective at photostabilizing lignin. Iron, manganese and chromium (VI) compounds have been shown to provide partial protection to lignin in wood veneers exposed to natural weathering (Evans et al. 1992, Schmalzl and Evans 2003), but I am not aware of any reports on the
photostabilization of lignin in wood with nickel compounds. Aromatic nickel chelates are used as photostabilizers for polymers (Briggs and McKellar 1968, Briggs and Hurlock 1971), and it’s possible that the photostabilization of wood by nickel acetylacetonate occurs as a result of the formation of aromatic complexes with lignin, as occurs when wood is treated with iron or chromium compounds (Schmalzl et al. 2003). Further research is needed to test this hypothesis.

3.5 Conclusions

I conclude that the ability of metal acetylacetonates to photostabilize yellow cedar veneers varies depending on the metal in the coordination complex. Nickel, manganese, titanium and iron acetylacetonate were more effective than cobalt acetylacetonate at photostabilizing wood, based on the different measures I used to assess the degradation of weathered veneers. Iron acetylacetonate was more effective at photostabilizing lignin in weathered veneers than the other metal acetylacetonates. I suggest why cobalt acetylacetonate was ineffective at photostabilizing wood veneers, and suggest that the ability of iron and nickel acetylacetonate to photostabilize lignin is due to their capacity to complex lignin. Further research is needed to test this hypothesis and also to examine whether the more effective metal acetylacetonates tested here can improve the performance of coatings applied to wood. The ability of some of the metal acetylacetonates to improve the performance of clear coatings on wood will be examined in the next chapter.
4. Performance of a clear polyurethane coating on yellow cedar and Scots pine panels pre-treated with manganese or titanium acetylacetonate

4.1 Introduction

Clear coatings are attracting increasing attention from architects and consumers because they are transparent and do not mask wood’s attractive colour and grain. However, clear coatings have the major limitation that their service life is much shorter than that of opaque or even semi-transparent wood finishes. The major reason why clear coatings have a shorter service life than opaque coatings is that they are unable to block light (UV and visible light) from reaching the underlying wood. Light that is transmitted through the coatings causes significant degradation of wood substrate and loss of coating adhesion, which is the primary cause of clear coating failure (Miniutti 1964; Singh and Dawson 2003). Thus, it is necessary to photostabilize wood to improve the performance of clear coating (Derbyshire and Miller 1981). Several studies have demonstrated that the longevity of clear coatings on wood is improved if the photostability of the wood is increased prior to application of clear coatings. For example, Black and Mraz (1974) investigated the performance of latex stains, linseed oil-based paint, clear latex coatings, and oil-base varnishes on wood pre-treated with reactive metal compounds including chromium, copper and iron compounds. Their results showed that compounds with the ability to photostabilize wood, were able to significantly improve the performance of the clear coats on wood exposed to natural weathering.

I tested the photoprotective effects of metal acetylacetonates on wood surfaces in Chapter 3 and my results showed that nickel, iron manganese, and titanium acetylacetonate were able to photostabilize wood. Titanium and manganese acetylacetonate did not reduce the strength properties of wood (unlike iron) and titanium and manganese are less toxic than nickel (Bhattacharjee and Chaudhuri 1989). Therefore I selected them as photoprotective pre-treatments for clear coatings. In this chapter I hypothesize that manganese and titanium acetylacetonate applied as photostabilizing pre-treatments will enhance the performance of a
clear polyurethane coating on yellow cedar and Scots pine panels. I applied manganese and titanium acetylacetonate and other photostabilizing pre-treatments to wood panels and then coated treated panels with a clear exterior polyurethane clear coating. The performance of the coating on treated wood panels was tested after samples were exposed to artificial accelerated weathering. My results partially support my hypothesis and suggest that titanium and manganese acetylacetonate has potential as a photostabilizing pre-treatment to enhance the performance of clear finishes.

4.2 Materials and methods

The experiment described in this chapter examined the effects of two experimental factors (wood species and chemical pre-treatments) on the performance of a clear coating on yellow cedar and Scots pine panels exposed to artificial weathering. The following response variables were measured: (1) Colour changes of wood panels ($\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta E$); (2) Gloss of wood panels; (3) Adhesion of the clear coating. Analyses of variance (ANOVA) for a randomized block design were used to analyse data. Statistical computation was performed using Genstat (v. 18). Error bars or a least significant different bar ($p<0.05$) on each graph can be used to estimate whether differences between individual means are statistically significant. These error bars are derived from analyses of variance and, as mentioned in Chapter 3, are not measures of within treatment variability ($\pm$standard deviation) (Abdi and Williams 2010).

4.2.1 Preparation and treatment of wood panels with titanium and manganese acetylacetonate and between individual matt polyurethane coating

The preparation of yellow cedar and Scots pine panels followed European Standard EN 927-6 (2006). Six wood panels measuring 75 mm (width) x 150 mm (length) x 13 mm (thickness) were cut from each of four parent yellow cedar boards and also from each of four Scots pine boards (48 specimens in total). The longitudinal sides of panels were rounded using a small hand-held router (Speed Palm Router, Bosch ColtTM). Panels were planned
using a Martin thicknesser (Martin T44) and then hand-sanded with 220 grit sandpaper (1948 Siaflex aluminum oxide, Sia abrasives). Panels were conditioned at 20 ± 1°C and 65 ± 5% r.h. for seven days before chemical treatment. The density of the yellow cedar and Scots pine specimens was measured using the water displacement and oven drying method as follows (Olesen 1971). Wood specimens measuring 10 mm (width) x 10 mm (length) x 10 mm (thickness) cut from each parent board were soaked in distilled water for three days until they were saturated with water. Then their green volume (cm³) was measured by water displacement. Specimens were oven dried at 105°C until they reached constant weights. The basic density of specimens was calculated (Table 4.1). Growth rates of specimens were recorded by counting the growth ring number every centimetre (Table 4.1).

Table 4.1: Growth ring number and density of yellow cedar and Scots pine samples

<table>
<thead>
<tr>
<th>Board No.</th>
<th>Yellow cedar</th>
<th>Scots pine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of growth rings/cm</td>
<td>Density (g/ cm³)</td>
</tr>
<tr>
<td>1</td>
<td>22-37</td>
<td>0.402</td>
</tr>
<tr>
<td>2</td>
<td>35-44</td>
<td>0.503</td>
</tr>
<tr>
<td>3</td>
<td>10-18</td>
<td>0.376</td>
</tr>
<tr>
<td>4</td>
<td>35-45</td>
<td>0.480</td>
</tr>
</tbody>
</table>

Panels in each experimental block (Table 4.2) were randomly allocated to different treatments. Manganese and titanium acetylacetonate were dissolved in DMF and applied to panels using the same method that as described in Chapter 3. Since concentrations of all treatments were lower (1%) than the concentration of manganese acetylacetonate (3%), more spraying passes were required to deliver the same amount of chemicals onto each wood panel. Each panel was placed onto a glass plate and held in place using bespoke clip (DTM 1300, stainless steel bulldog clips). Panels were sprayed with their allocated chemical using the same method and amounts as those described in Chapter 3. All treated specimens and untreated controls were air-dried for one hour in the laboratory and then conditioned at 20 ± 1°C and 65 ± 5% r.h. for seven days. A clear polyurethane coat (Clear matt polyurethane...
self-sealer for exterior used 6OPU901SO1G30.04, Innovative Manufacturing) (Table 4.3) was sprayed onto conditioned wood panels using a HVLP (High Volume Low Pressure) spray gun at 20 psi pressure (137.9 KPa). Two coats were applied to achieve a wet thickness of 101.6-152.4 µm. The remaining faces of each panel, except the backside, were brush-coated with epoxy sealer (Part A: epoxy resin; Part B: hardener, System Three, Auburn, Washington). Coated samples were reconditioned as above for seven days.

Table 4.2: Chemical treatments with their solvents and concentrations

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Symbol</th>
<th>Solvent</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti acetylacetonate</td>
<td>Ti</td>
<td>DMF</td>
<td>1</td>
</tr>
<tr>
<td>Ti acetylacetonate+HEPBP</td>
<td>TiHEPBP</td>
<td>DMF</td>
<td>1</td>
</tr>
<tr>
<td>HEPBP</td>
<td>HEPBP</td>
<td>DMF</td>
<td>1</td>
</tr>
<tr>
<td>Manganese acetylacetonate</td>
<td>Mn</td>
<td>DMF</td>
<td>3</td>
</tr>
<tr>
<td>DMF</td>
<td>DMF</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Untreated</td>
<td>UNT</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

Table 4.3: General information on the commercial clear coating applied to yellow cedar and Scots pine panels

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (DIN 6 at 68°F)</td>
<td>95”±’’</td>
</tr>
<tr>
<td>Weight solids</td>
<td>45±1%</td>
</tr>
<tr>
<td>Volume solids</td>
<td>40±1%</td>
</tr>
<tr>
<td>Coverage</td>
<td>378 sqft/gal</td>
</tr>
<tr>
<td>Application amounts</td>
<td>4-6 (wet mils)</td>
</tr>
<tr>
<td>Number of coats</td>
<td>1-2</td>
</tr>
<tr>
<td>Dry time (sandable)</td>
<td>6 hours</td>
</tr>
</tbody>
</table>

4.2.2 Artificial accelerated weathering

Artificial accelerated weathering of clear coated panels followed European Standard: prENV927-6 (British Standard 2008). The artificial weathering cycle consisted of separate condensation, UV irradiation and water spraying steps together with sub-cycling steps as described in Table 4.4. This cycle was programmed into a QUV/SPRAY weatherometer.
(Q-Panel Lab Products, 0.68W/m² at 340 nm) (Fig. 4.1). Coated specimens were exposed to artificial accelerated weathering for a total of 3024 hours.

**Table 4.4: Artificial accelerated weathering cycle used to test the performance of a polyurethane clear coating on treated yellow cedar and Scots pine panels and untreated controls. The cycle is the same as that described in the European Standard: prENV927-6 (British Standard, 2008)**

<table>
<thead>
<tr>
<th>Step</th>
<th>Function</th>
<th>Temperature (°C)</th>
<th>Duration (h)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Condensation</td>
<td>45</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Subcycle step 3+4</td>
<td></td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>UV</td>
<td>60</td>
<td>2.5</td>
<td>UVA-340 nm</td>
</tr>
<tr>
<td>4</td>
<td>Spray 6-7 Liters/min</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Go to step 1</td>
<td></td>
<td></td>
<td>UV light off</td>
</tr>
</tbody>
</table>

Total (1 cycle) = 168 h
Repetition of cycle = 3 x (i.e. 3 weeks)
Total exposure = 504 h

**Fig. 4.1: QUV artificial weatherometer containing clear coated panels (left) and without clear coated panels (right), showing fluorescent UV tubes**

**4.2.3 Characterization of wood panels exposed to artificial accelerated weathering**

**4.2.3.1 Measurement of colour and gloss of wood panels**

Measurements of colour and gloss of clear-coated panels were made on reconditioned panels before and after each 504 h exposure period (up to 3024 h). Changes in colour are expressed as the ratios of each parameter after each 504 h exposure period to the initial
unexposed parameter. Changes in colour are used in preference to absolute colour value because some of the treatments on their own altered the colour of the wood panels. Colour (L*, a*, b*) was measured using a spectrophotometer as described in Chapter 3. Ruled paper templates with punched holes were placed on panels to make sure that colour was measured at precisely the same place on each specimen before and after each weathering period. Three measurements were performed on each panel after each exposure period and the three readings were averaged to obtain L*, a* and b* values. Gloss is the sheen of coatings and indicates the light reflected from the coating surface (ASTM 2014). Gloss was measured at a reflective angle of 60° (medium gloss) using a Micro-TRI-Gloss Meter (BYK Gardner Model 4551/HWS 5820). Paper templates as above were used to ensure that gloss was measured at the same places on clear coated panels before and after each weathering period.

### 4.2.3.2 Measurement of adhesion

A cross-cut tape test was carried out to measure the adhesion of the polyurethane coatings to wood panels after they were exposed to accelerated weathering for 3024 h. A similar test was carried out on unexposed controls. The testing procedure followed the ASTM D3359-17 standard test methods for rating adhesion by tape test (ASTM 1974). A disposable razor blade (HS120259, Heathrow Scientific) was used to cut through the film to reach the underlying wood substrate. Six cuts were made in both horizontal and vertical directions and each cut was spaced 2 mm apart (Fig. 4.2). A length of tape (double sided tape 665, 3M Scotch) measuring 12 mm (wide) x 33 m (long) was applied over the grid with some degree of pressure and left on for 60s-120s. The tape was removed from the panels. Tape containing degraded coating and wood was placed on white paper and scanned using a desktop scanner (ScanMaker i800, Microtek). The program ImageJ (v 1.48) (Rasband 2016) was used to measure the area of coating and wood removed from each panel.
Fig. 4.2: Diagram of cross-cuts used as part of a test to measure the adhesion of a clear polyurethane coating on unweathered Scots pine and yellow cedar panels, and panels weathered in a QUV weatherometer for 3024 h.

4.3 Results

Table 4.5 below summarizes the statistical significance of experimental factors on the response variables for clear-coated panels exposed to artificial accelerated weathering. There were significant (p<0.05) effects of chemical treatments and wood species on colour changes and gloss of clear coated panels and also the adhesion of the coating to panels. There were also significant (p<0.05) interactions of treatments and species on lightness (L*) and yellowness (b*). Only those results that are statistically significant (p<0.05) are described in this ‘results’ section.

4.3.1 Effects of chemical treatments on response variables of Scots pine and yellow cedar coated with a polyurethane clear coating

4.3.1.1 Colour changes of clear coated panels

Chemical treatments had significant effects on L* (lightness) and b* (yellowness) of clear coated panels (Table 4.5), which are expressed as the ratios of these colour parameters after weathering to their initial values (0 h) as mentioned in Section 4.2.3.1. Statistical analyses showed significant (p<0.05) effects of ‘wood species’ on L*, a* and b* ratios of clear coated panels after artificial weathering (Table 4.5). Moreover, the analyses revealed significant interactions of chemical treatment x species on lightness and yellowness (Table 4.5).
Table 4.5: P values of species (S), metal acetylacetonates treatment effects (TR) and species x treatments interactions (S x TR) on L*, a* and b* measured on clear-coated panels exposed to 3024 hours of accelerated weathering. Measurements were made every 504 hours.

<table>
<thead>
<tr>
<th>Experimental factors</th>
<th>P values for lightness ratio (L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a* 504 h</td>
<td>a* 1008 h</td>
<td>a* 1512 h</td>
<td>a* 2016 h</td>
<td>a* 2520h</td>
</tr>
<tr>
<td>Species (S)</td>
<td>0.347</td>
<td>0.624</td>
<td>0.234</td>
<td>0.765</td>
<td>0.158</td>
</tr>
<tr>
<td>Treatments (TR)</td>
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<td>0.493</td>
<td>0.031</td>
<td>0.013</td>
<td>0.051</td>
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<td>S x TR</td>
<td>0.032</td>
<td>0.003</td>
<td>0.044</td>
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<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
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<tr>
<td></td>
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<td>a* 1008 h</td>
<td>a* 1512 h</td>
<td>a* 2016 h</td>
<td>a* 2520h</td>
</tr>
<tr>
<td>Species (S)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Treatments (TR)</td>
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<td>0.436</td>
<td>0.352</td>
<td>0.288</td>
</tr>
<tr>
<td>S x TR</td>
<td>0.444</td>
<td>0.545</td>
<td>0.445</td>
<td>0.373</td>
<td>0.282</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experimental factors</th>
<th>P values for yellowness ratio (b)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b* 504 h</td>
<td>b* 1008 h</td>
<td>b* 1512 h</td>
<td>b* 2016 h</td>
<td>b* 2520h</td>
</tr>
<tr>
<td>Species (S)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Treatments (TR)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.006</td>
<td>0.01</td>
</tr>
<tr>
<td>S x TR</td>
<td>0.071</td>
<td>0.018</td>
<td>0.041</td>
<td>0.095</td>
<td>0.193</td>
</tr>
</tbody>
</table>

4.3.1.1a Lightness (L*)

There were significant effects of the acetylacetonate and UV absorber (HEPBP) on the lightness parameter L* after 1512 h (p<0.05), 2016 h (p<0.05), 2520 h (p=0.051) and 3024 h (p<0.05). Changes in lightness of coated panels pre-treated with manganese acetylacetonate were significantly (p<0.05) lower than those of untreated controls after 2016, 2520 and 3024 hours of exposure of panels to artificial accelerated weathering. Moreover, samples treated with manganese acetylacetonate were darkened significantly (p<0.05) less than panels pre-treated with the other chemicals after 3024 h of artificial weathering. There were no significant (p<0.05) differences in the lightness of the other treated and clear-coated panels and the untreated controls.
Fig. 4.3: Changes in lightness ($L^*$) ratio of clear coated wood panels pre-treated with metal acetylacetonates or the UV absorber HEPBP and untreated controls following artificial weathering for: (a) 2016 h; (b) 2520 h; (c) 3024 h

Fig. 4.4 shows the appearance of untreated controls and panels (Scots pine and yellow cedar) pre-treated with manganese acetylacetonate before artificial accelerated weathering. Manganese acetylacetonate darkened Scots pine and yellow cedar panels. Fig. 4.5 and 4.6 shows the appearance of untreated controls and wood panels pre-treated with manganese acetylacetonate and exposed to 2520 h and 3024 h of accelerated weathering. Both Scots pine and yellow cedar panels pre-treated with manganese acetylacetonate were lighter than untreated controls after accelerated weathering for 2520 h and 3024 h.
Untreated                                Manganese acetylacetonate

a  Scots pine (0 h)                      b  Scots pine (0 h)

c  Yellow cedar (0 h)                    d  Yellow cedar (0 h)

Fig. 4.4: Initial appearance of clear-coated Scots pine and yellow cedar panels: a and c are untreated controls; b and d are panels treated with manganese acetylacetonate

Untreated                                Manganese acetylacetonate

a  Scots pine (2520 h)                   b  Scots pine (2520 h)

c  Yellow cedar (2520 h)                 d  Yellow cedar (2520 h)

Fig. 4.5: Appearance of clear-coated Scots pine and yellow cedar panels after 2520 h of artificial accelerated weathering: a,c are untreated controls; b,d are panels treated with manganese acetylacetonate. Note that Scots pine and yellow cedar panels pre-treated with manganese acetylacetonate are lighter than untreated controls
There were significant effects of wood species on L* after 3024 h of exposure of panels to accelerated weathering (p<0.001). There was no significant (p>0.05) difference in the lightness ratios (L*) of Scots pine and yellow cedar panels after the first 2520 h artificial weathering, but after 3024 h of weathering, the lightness ratio of yellow cedar panels (0.803) was significantly (p<0.05) lower than that of Scots pine (0.767) samples.

A chemical treatments by species interactions on lightness ratios (L*) occurred for samples exposed to accelerated weathering for 504 h (p=0.032), 1008 h (p=0.003) and 1512 h (p<0.044). These interactions occurred because yellow cedar panels treated with manganese acetylacetonate were lighter than Scots pine samples after 504, 1008 and 1512 h of exposure in contrast to controls or samples treated with other photostabilizers, which were darker. Yellow cedar panels pre-treated with titanium acetylacetonate and exposed to accelerated weathering for 504, 1008 or 1512 h were slightly lighter than untreated panels and panels treated with the other photostabilizers.
4.3.1.1b Yellowness (b*) ratio

There were significant effects of the acetylacetonates and the UV absorber HEBP on the yellowness of panels after they were exposed to accelerated weathering for 504 h (p<0.001), 1008 h (p<0.001), 1512 h (p<0.001), 2016 h (p<0.01), 2520 h (p<0.05) and 3024 h (p<0.05). After 504 h of artificial weathering, clear coated panels pre-treated with manganese acetylacetonate, titanium acetylacetonate or titanium acetylacetonate containing HEBP yellowed significantly (p<0.05) less than the untreated controls (p<0.05). Panels pre-treated with DMF yellowed significantly (p<0.05) more than the untreated control after 504 h weathering. After 2016 h weathering, samples pre-treated with titanium acetylacetonate were significantly (p<0.05) less yellow than the untreated controls and also
panels pre-treated with HEPBP or DMF. After 2520 h weathering, panels pre-treated with titanium acetylacetonate yellowed significantly ($p<0.05$) less than untreated panels. Panels treated with HEPBP and DMF were also significantly ($p<0.05$) less yellow than untreated panels, but they were significantly ($p<0.05$) yellower than panels pre-treated with titanium acetylacetonate (Fig. 4.5). After 3024 h weathering, yellowness ratio of panels pre-treated with titanium acetylacetonate was 0.936, indicating that it was effective at restricting the yellowing of wood panels.

![Graphs showing yellowness ratios of panels treated with different agents](image)

**Fig. 4.8**: Yellowness ($b^*$) ratios of clear-coated panels that were untreated or pre-treated with metal acetylacetonates and HEPBP following artificial weathering for: (a) 504 h; (b) 2016 h; (c) 2520 h; (d) 3024 h

Fig. 4.9 shows the appearance of Scots pine panels pre-treated with titanium acetylacetonate and DMF after 2016 h, 2520 h and 3024 h of artificial accelerated
weathering. All photographs of treated and untreated yellow cedar and Scots pine before and after artificial accelerated weathering are appended to this thesis (Appendix 2).

![Titanium acetylacetonate and DMF treated panels](image)

Fig. 4.9: Appearance of clear-coated Scots pine panels that pre-treated with titanium acetylacetonate or DMF and weathered for 2016 h (a, b), 2520 h (c, d) and 3024 h (e, f). Note: Yellowness of panels treated with titanium acetylacetonate is less than that of panels treated with DMF

‘Wood species’ also had a significant effect on yellowing of clear-coated panels during artificial weathering (Fig. 4.10). Yellowness ratios of panels were significantly different after 504 h (p<0.001), 2016 h (p<0.001), 2520 h (p<0.001) and 3024 h (p<0.001). The appearance of the panels is shown in Fig. 4.11. After 504 h, 2016 h, 2520 h and 3024 h of accelerated weathering, yellow cedar panels were significantly less yellow than Scots pine samples, in accord with measurement of the $b^*$ parameter.
Fig. 4.10: Yellowness (b*) ratios of clear-coated Scots pine and yellow cedar panels after artificial accelerated weathering

Fig. 4.11 shows the appearance of clear-coated Scots pine and yellow cedar panels pre-treated with titanium acetylacetonate and exposed to accelerated weathering for 2016 h, 2520 h and 3024 h. Treated yellow cedar panels showed less yellowing than Scots pine (results averaged across treatments).
Fig. 4.11: Appearance of clear-coated Scots pine (left column) and yellow cedar (right column) panels pre-treated with titanium acetylacetonate and exposed to artificial accelerated weathering for 1008 h, 1512 h, 2016 h, 2520 h and 3024 h. Note: Yellow cedar panels are lighter and less yellow than Scots pine panels.

Significant interactions of species x chemical treatments (p<0.05) were observed for the yellowing of panels exposed to 1008 h and 1512 h of artificial weathering. This interaction...
occurred because titanium acetylacetonate was effective at restricting the yellowing of yellow cedar, but it was ineffective at restricting the yellowing of Scots pine (Fig. 4.12). It is noteworthy that titanium acetylacetonate restricted yellowing of yellow cedar panels exposed to 1512 h of accelerated weathering.

**Fig. 4.12: Changes in yellowness (b*) ratio of pre-treated and clear-coated Scots pine and yellow cedar panels after artificial weathering for 1008 h and 1512 h**

4.3.1.1c Redness (a*)

Redness changes were significantly (p<0.05) different for the two species after 504 h (p<0.001), 1008 h (p<0.001), 1512 h (p<0.001), 2016 h (p<0.001), 2520 h (p<0.001) and 3024 h (p<0.001) of weathering (Table 4.5). Redness ratios of clear coated wood panels during artificial weathering are plotted in Fig. 4.13. Scots pine panels were significantly (p<0.05) redder throughout the weathering trial than yellow cedar panels. The difference in redness of Scots pine and yellow cedar panels became more pronounced after 2016 h of exposure of panels to accelerated weathering.
4.3.1.2 Gloss measurements

Wood species had a significant effect on gloss of clear-coated panels after 2016 h of artificial weathering (p<0.001). The gloss of coated Scots pine panels was significantly higher than that of yellow cedar panels, ([3.042] vs [2.417]). Differences in gloss for all other time periods were not statistically significant. As a result, gloss measurements were not carried out after 2520 h or 3024 h of exposure of samples to accelerated weathering. Gloss of wood panels pre-treated with different photostabilizers, and exposed to artificial accelerated weathering for 2016 h, is shown in Fig. 4.14.

Table 4.6: P values of species (S), metal acetylacetonate treatment (TR) and species x treatments interaction (S x TR) on gloss measured on clear coatings on wood exposed to 3024 hours of accelerated weathering. Measurements were made every 504 hours.

<table>
<thead>
<tr>
<th>Experimental factors</th>
<th>Gloss (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G 0 h</td>
</tr>
<tr>
<td>Species (S)</td>
<td>0.869</td>
</tr>
<tr>
<td>Treatments (TR)</td>
<td>0.9</td>
</tr>
<tr>
<td>S x TR</td>
<td>0.216</td>
</tr>
</tbody>
</table>
The two metal acetylacetonates used as pre-treatments under the polyurethane clear coatings had no consistent effects on the occurrence of film defects in the coatings. Delamination and checking of films occurred more frequently on Scots pine than yellow cedar panels, but defects occurred randomly on all treated and untreated controls for each species.

### 4.3.1.3 Adhesion measurements

Statistical analysis showed significant (p<0.05) effects of chemical treatments on the adhesion of the polyurethane coating to wood exposed to artificial weathering. The HEPBP and manganese acetylacetonate pre-treatments significantly increased the adhesion of the polyurethane clear coating to wood after 3024 h of artificial weathering (p<0.01) (Fig. 4.15). Titanium acetylacetonate and titanium acetylacetonate containing HEPBP were not effective at improving the adhesion of the coating. Results in Fig. 4.15 are averaged across the two species because there was no significant effect of ‘species’ on adhesion and no significant (p<0.05) interaction of species and treatment.
Fig. 4.15: Area of clear coating removed (mm$^2$) from treated and untreated wood panels after they were exposed to 3024 h of artificial weathering

Fig. 4.16 shows the coated wood that was removed from weathered Scots pine and yellow cedar samples by the tape tests. UV radiation damages wood beneath clear coatings (Singh and Dawson 2003), so increased numbers of square pieces of wood (mm$^2$) that are attached to tape sections after adhesion testing indicate lower levels of coating adhesion and vice versa. No wood squares were removed from unweathered controls so the relevant tape sections in Fig. 4.16 are completely transparent. Tape tests on samples pre-treated with DMF removed 83.2% of wood within the adhesion grid indicating poor coating adhesion. The tape sections that contained the lowest number of wood squares were those pulled off from samples pre-treated with HEPBP or manganese acetylacetonate, although there is significant variability between samples (Fig. 4.16).
Fig. 4.16: Wood removed from Scots pine (a) and yellow cedar (b) coated with a polyurethane clear coating and pre-treated with metal acetylacetonates or HEPBP, and subjected to cross-cut adhesion testing.

4.4 Discussion

My results partially support my hypothesis that manganese and titanium acetylacetonate applied as photostabilizing pre-treatments will enhance the performance of a clear polyurethane finish on yellow cedar and Scots pine panels exposed to artificial accelerated
weathering. However, the effectiveness of the pre-treatments varied with wood species, length of time panels were exposed to the weather and the parameters used to assess the performance of the clear coatings. For example, manganese acetylacetonate restricted loss of adhesion of the polyurethane coating whereas titanium acetylacetonate had no such effect. Neither treatment reduced loss in gloss of coatings on panels exposed to accelerated weathering. Both manganese and titanium acetylacetonate restricted colour changes of clear-coated wood panels, but there were significant species x treatment interactions on L* and b* because manganese acetylacetonate was more effective than titanium acetylacetonate at restricting darkening of panels, whereas titanium acetylacetonate was more effective than manganese acetylacetonate at restricting yellowing of panels. It is noteworthy that manganese and titanium acetylacetonate were more effective at restricting colour changes of clear-coated panels than HEPBP, which has performed well as a pre-treatment to enhance the performance of clear finishes on wood (Kiguchi and Evans 1998; Kiguchi et al 2001; Olsson et al. 2014). However, the addition of HEPBP in titanium acetylacetonate did not improve its ability to restrict colour changes possibly because titanium acetylacetonate complexed with HEPBP. There has only been one study that looked at the ability of reactive titanium compounds, including titanium acetylacetonate, to improve the performance of clear-coatings on wood (Evans et al. 2015). This study found that the titanium compounds improved the performance of an alkyd clear coating on western red cedar panels exposed outdoors in Melbourne, Australia for 22 months, but they had no positive effect on the performance of the same coating on radiata pine. My results also indicate that the effectiveness of metal acetylacetonates at improving the performance of a clear polyurethane coating varies with wood species. In particular the compounds appeared to be better at reducing the discolouration of the clear coating on yellow cedar, an extractive-rich species like western red cedar than on Scots pine. It is possible that manganese and titanium acetylacetonate complex and stabilize various extractives in yellow cedar, which has
beneficial effects on the photostability of the wood-clear coating interface. In support of this suggestion, Dost (1959) noted that titanium esters are able to react with extractives in California redwood forming water-insoluble complexes. He went on to suggest that such stabilization of extractives could reduce photodegradation of wood and also retard photodegradation of other wood components (Dost 1959). Manganese acetylacetonate or titanium acetylacetonate did not decrease the checking of clear-coated panels possibly because they were unable to restrict shrinkage of wood. However, they had beneficial effects on clear coating performance in accord with findings in Chapter 3 that they were able to photostabilize wood. HEPBP also had positive effects on coating performance, but it is not available commercially whereas metal acetylacetonates are widely used in industry. Further research is needed to examine the full potential of manganese and titanium acetylacetonate as pre-treatments to improve the performance of clear coatings. Such research would need to examine the effects of wood species on the ability of the metal acetylacetonates to improve clear coatings performance as well as parameters such as level of chemical applied to wood surfaces and reaction conditions.

4.5 Conclusions

Manganese and titanium acetylacetonate had some positive effects on the performance of a clear polyurethane coating on yellow cedar and Scots pine panels exposed to artificial accelerated weathering, as noted above. Therefore, I conclude that there is merit in further experimental work to fully evaluate and optimize the ability of titanium and manganese acetylacetonate (and possibly other metal acetylacetonates tested in Chapter 3) to improve the performance of polyurethane and other clear coatings on wood. I present a possible mechanism to explain how the metal acetylacetonates were able to reduce the discoloration of the coated wood panels, which involves complexation of extractives at wood surfaces. Further research is needed to test whether this mechanism is correct.
5. Surface protection of yellow cedar with titanium acetylacetonate and oils

5.1 Introduction

In Chapter 3, I compared the effects of six metal acetylacetonates on the properties of wood veneers exposed to natural weathering. My results indicated that the metal acetylacetonates differed in their ability to photostabilize veneers. Titanium and manganese acetylacetonate were selected for further testing, based on their ability to photostabilize veneers, their low toxicity and effects on the colour of veneers. Manganese and to a lesser extent titanium acetylacetonate were also effective at improving the performance of a clear film-forming polyurethane finish on wood panels exposed to artificial weathering (Chapter 4). Wood is increasingly being finished with natural oils rather than film-forming finishes, for a variety of reasons (Williams 2010; Egan 2012). Oils can be derived from renewable resources and have a long tradition of use for wood protection (Barry 2013). Oil-based finishes are easily applied to wood and are easy to maintain (Williams 2010). Their performance can be improved using a chromic acid pre-treatment, as noted in Chapter 2 (Black and Mraz 1974; Feist 1979), and manganese, cobalt and zirconium salts accelerate the curing of oils (Lazzari and Chiantore 1999; Mallégol et al. 2016). Metal acetylacetonates are able to react with –OH, -COOH, -NH₂ (Guo 2011), which suggests that they may be able to react with functional groups in wood and also complex with oils, UV absorbers and other compounds, which contain –OH, -COOH or -NH₂ groups. Castor oil has a reactive hydroxyl group, and it may be able to complex with metal acetylacetonates (Naughton 1974; Ogunniyi 2006).

Based on previous studies and my results in Chapter 3, I hypothesize that the combination of metal acetylacetonates and oils (castor oil or linseed oil) or the UV absorber HEPBP (2-hydroxy-4(2,3-epoxypropoxy)-benzophenone), will provide enhanced protection to wood surfaces exposed to the weathering. I test this hypothesis by treating yellow cedar wood (veneers and panels) with titanium acetylacetonate and linseed oil or castor oil and the
UV absorber, HEPBP. The photoprotective effects of the treatments on wood exposed to natural weathering were mainly examined, using methodology described in Chapter 3.

5.2 Materials and methods

The experiments described in this chapter examined the effects of titanium acetylacetonate combined with oils or UV absorber on photo-protection of wood. Initially, the effects of chemical treatments (9 levels) on the photostability of wood veneers (6 blocks) were examined. This preliminary work used the same techniques described in Chapter 3. Subsequently, the effects of chemical treatments (7 levels) on the weathering of wood panels were examined. The following measurements were made: (1) Contact angles of water droplets on panels; (2) Colour changes of panels (ΔL*, Δa*, Δb*, ΔE); (3) Surface erosion. Analyses of variance (ANOVA) for randomized block designs were used to analyse the effects of chemical treatments on the aforementioned properties. ANOVA used Genstat (v. 18) as described in Chapter 3. Significant results (p<0.05) are plotted graphically and error bars (± 2 x SED, or LSD) can be used to compare differences between individual means (Abdi and Williams 2010).

5.2.1 Materials

5.2.1.1 Preparation of 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP)

HEPBP was prepared as described by Manasek et al. (1976). Dihydroxy benzophenone (DHBP, 2,5-Dimethyl-2,5-di(tert.butyldihydroxy)hexane) was reacted with epichlorohydrin (1-Chloro-2,3-epoxypropane) in 2 M KOH at 80°C for 2 h with constant stirring and reflux, which is referred to in Fig. 2.11 (Chapter 2). The reaction product was washed 6 times using deionized water, dried and recrystallized 3 times until a yellow crystalline powder was obtained.

5.2.1.2 Preparation of copper ethanolamine

Copper ethanolamine was prepared as described by Humar et al. (2007). Copper ethanolamine has a ratio of copper to ethanolamine of 1:6 and Cu concentration of 1.0%.
Weight of copper (powder, <425 μm, 99.5% trace metals basis, Sigma-Aldrich) was measured using a digital balance and then added into an excess (1:6) of ethanolamine (2-aminoethanol). The solution was stirred and brushed onto wood panels using a pre-dipped brush. The same amount of copper ethanolamine was applied to all panels that were allocated to castor oil treatments.

5.2.1.3 Preparation of chemical treatments

Linseed oil (raw linseed oil, Recochem) and castor oil (Ricinus Communis (Castor) Seed Oi, Home Health) were bought in retail stores. Titanium acetylacetonate and HEPBP solutions were made by dissolving titanium acetylacetonate and HEPBP in dimethylformamide (DMF) to be consistent with previous experiments. Titanium acetylacetonate and HEPBP were mixed directly with oils to make combination treatments with the concentrations listed in Table 5.1.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Concentration of solutions/% (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor oil</td>
<td>*</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>*</td>
</tr>
<tr>
<td>Titanium acetylacetonate</td>
<td>2</td>
</tr>
<tr>
<td>HEPBP</td>
<td>2</td>
</tr>
<tr>
<td>Ti+castor oil</td>
<td>2</td>
</tr>
<tr>
<td>Ti+linseed oil</td>
<td>2</td>
</tr>
<tr>
<td>Ti+castor oil+HEPBP</td>
<td>2</td>
</tr>
<tr>
<td>Ti+linseed oil+HEPBP</td>
<td>2</td>
</tr>
<tr>
<td>Control (untreated)</td>
<td>*</td>
</tr>
</tbody>
</table>

* : Not applicable

5.2.1.4 Preparation of wood veneers and panels

Yellow cedar veneers were prepared as described in Chapter 3. Ten veneers from each of six parent blocks of wood were selected at random and allocated to the nine chemical treatments listed in Table 5.1 (50 veneers for each of the nine treatments, 450 veneers in total). Oven-dried weights of individual veneers were measured as described in Chapter 3, except they were dried to a constant weight at a lower temperature of 80°C for 3 hours rather
than 105°C for 2 hours. Five veneers, as one batch and allocated to different treatments, were fixed using butterfly clips to separate glass plates measuring 39.5 x 20 cm. Veneers were treated with the required amount of chemical (8.55 mg/cm²) using a pre-dipped paint brush. Treated and untreated veneers were air-dried for three hours. The oven-dried weights of both treated and untreated veneers were measured as described above. Veneers were conditioned at 20 ± 1°C and 65 ± 5% r.h. relative humidity for five days and their thicknesses were measured using a digital micrometer (Lorentzen and Wettre HWS 5781, Sweden).

Wood panels measuring 75 mm (width) x 17 mm (thickness) x 150 mm (length) were sawn from five separate yellow cedar boards as recommended by European Standard EN 927-6 (British Standard 2008). Panels were planed with a Martin planer (Martin T44) and hand-sanded with 220 grit sandpaper (1948 Siaflex aluminum oxide, Sia abrasives). They were conditioned at 20 ± 1°C and 65 ± 5% r.h. relative humidity for seven days. The density and growth rate of wood used to prepare different boards (Table 5.2) was measured using the same methods described in Chapter 3.

<table>
<thead>
<tr>
<th>Board Number</th>
<th>No. of growth rings/cm</th>
<th>Basic density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9-17</td>
<td>0.3769</td>
</tr>
<tr>
<td>2</td>
<td>15-39</td>
<td>0.4063</td>
</tr>
<tr>
<td>3</td>
<td>10-18</td>
<td>0.3860</td>
</tr>
<tr>
<td>4</td>
<td>19-35</td>
<td>0.4295</td>
</tr>
<tr>
<td>5</td>
<td>7-12</td>
<td>0.3519</td>
</tr>
</tbody>
</table>

The wood panels were randomly allocated to the 7 treatments (5 panels per treatment) (Table 5.3). A paint brush was used to apply 8.55 mg/cm² of chemical onto each panel. Wood panels that were allocated to castor oil-containing treatments were first pre-treated with copper ethanolamine because castor oil is used in combination with copper-amine as a protective treatment for wood. Panels pre-treated with copper ethanolamine were air-dried for 30 minutes and conditioned in the same environment as described above. All panels were then brush-coated with their respective oil treatments (8.55 mg/cm²), air-dried for three hours and then stored in a conditioning room, as above for seven days.
Table 5.3: Compounds and concentrations of solutions used to treat wood panels

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Concentration/% (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor oil (CuEa)</td>
<td>1</td>
</tr>
<tr>
<td>Titanium acetylacetonate</td>
<td>2</td>
</tr>
<tr>
<td>HEPBP</td>
<td>2</td>
</tr>
<tr>
<td>Ti+castor oil (CuEa)</td>
<td>2</td>
</tr>
<tr>
<td>Ti+castor oil+HEPBP (CuEa)</td>
<td>2</td>
</tr>
<tr>
<td>Copper ethanolamine (aq.)</td>
<td>1</td>
</tr>
<tr>
<td>Control (untreated)</td>
<td>*</td>
</tr>
</tbody>
</table>

5.2.2 Weathering trials

Forty five treated and untreated veneers from each block were fixed to individual glass plates and secured in place using opaque Perspex strips and butterfly clips, as described in Chapter 3 (90 veneers in total per treatment) (Fig. 5.1). The remaining 45 treated and untreated veneers from each block were stored in a constant climate room and acted as controls. Veneers were exposed above ground, oriented horizontally (0°) in Vancouver, Canada (49° 15' 54.51" N, 123° 15' 7.27" W, 87 m elevation) for 50 days from April 14th to June 3rd, 2016 (Fig. 5.1). Weathered veneers were removed from glass plates and conditioned as above for seven days. Oven-dried weights of weathered veneers were measured and weight losses of treated and untreated veneers were calculated as described in Chapter 3.
Fig. 5.1: Method of exposing treated and untreated yellow cedar veneers to the weather

The end grain of wood panels were sealed with epoxy resin (Part A: epoxy resin, Part B: hardener, System Three) and both sides of the panels were coated with an opaque sealer-primer (Zinsser & Co Bulls-Eye 1-2-3 Qt. Primer Sealer/Stain Killer). A rectangular stainless steel mask measuring 13 mm x 40 mm with a circular opening (10 mm in diameter) was screwed onto the surface of each panel (Fig. 5.2). Specimens were exposed in Vancouver on a weathering rack at 45 degrees to the vertical from April 14th to October 15th, 2016 (Fig. 5.3). Information on the weather during the weathering trial was obtained from Environment Canada (Table. 5.4).
Fig. 5.2: Steel mask secured onto the surface of a wood panel. Scale bar = 10 mm

Fig. 5.3: Natural weathering of treated and untreated yellow cedar panels

Table 5.4: Record of the weather in Vancouver during the exposure trial of yellow cedar panels (April 14th to October 14th 2016)

<table>
<thead>
<tr>
<th>Month</th>
<th>Maximum Temperature</th>
<th>Minimum Temperature</th>
<th>Total Rainfall</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>27.4 °C</td>
<td>6.5 °C</td>
<td>11.2 mm</td>
</tr>
<tr>
<td>June</td>
<td>27.6 °C</td>
<td>7.8 °C</td>
<td>122.4 mm</td>
</tr>
<tr>
<td>July</td>
<td>26.0 °C</td>
<td>9.2 °C</td>
<td>93 mm</td>
</tr>
<tr>
<td>August</td>
<td>26.3 °C</td>
<td>13.5 °C</td>
<td>8.3 mm</td>
</tr>
<tr>
<td>September</td>
<td>29.8 °C</td>
<td>10.4 °C</td>
<td>32.2 mm</td>
</tr>
<tr>
<td>October</td>
<td>21.1 °C</td>
<td>3.9 °C</td>
<td>155.1 mm</td>
</tr>
</tbody>
</table>
5.2.3 Characterization of veneers and test panels exposed to natural weathering

Measurements were carried out on weathered wood veneers and controls as described in Chapter 3 (as follows): (1) Weight losses of veneers; (2) Erosion of veneers; (3) Tensile strengths of veneers; (4) Hydrophobicity of veneers; (5) Colour of veneers ($\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta E$). Measurements of weight and tensile strength losses of veneers and colour changes of veneers used the same techniques described in Chapter 3, except veneers were over dried at 80°C prior to and after weathering and rather than 105°C.

Hydrophobicity of veneers was measured using a goniometer (KSV CAM 101) as described in Chapter 3, except water droplets on veneers were imaged every 16 ms for 124 frames and then, one frame every 1s for 2400 frames.

Colour and contact angle measurement on wood panels were carried out before and after weathering using a template as described in Chapter 4. The template was used to ensure that measurements were carried out at exactly the same location both before and after weathering. Confocal profilometry (Altisurf 504®, ALTIMET, France) was used to analyse and visualise the erosion of wood specimens after weathering (Hazneza and Evans 2016). After outdoor exposure, the stainless steel masks were removed from panels. Linear profile scans were performed on each panel. Three 13 mm line scans were made on each panel, which crossed both eroded and uneroded sections under the areas beneath the masks. Step height differences due to erosion were analysed in PaperMap 3.2.0 (Digital Surf 2004) and exported to Excel, using the same method described in Chapter 3. In addition, an area measuring 13 x 13 mm within each area was scanned using the following parameters: 3 mm (3024 μm to 92 nm) probe with 3 mm/s scanning speed. Surface maps of these eroded areas were analysed in PaperMap 3.2.0 (Digital Surf 2004). PaperMap was also used to quantify the erosion of panels during exposure to natural weathering (Jamali and Evans 2011).

Veneers samples were prepared for scanning electron microscopy using the same methods described in Chapter 3. Wood specimens measuring 3 mm x 3 mm were cut from eroded and uneroded areas within treated and untreated wood panels exposed to natural
weathering for 6 months. Veneer sections and solid wood samples measuring 3 mm x 1 mm were glued onto aluminium stubs using Nylon nail polish as an adhesive. Specimens were coated with a thin layer of gold as described in Chapter 3 and examined using a Zeiss UltraPlus field emission scanning electron microscope operating at an accelerating voltage of 5 kV. SEM images of the surface of treated and untreated veneers and solid wood blocks (weathered and unweathered) were saved as TIFF files.

5.3 Results

5.3.1 Photoprotective effects of titanium acetylacetonate, HEPBP and oils on wood veneers

The results of statistical analyses of experimental results are summarised in Table 5.5. There were significant effects of treatments on weight loss (p<0.001), tensile strength (p<0.001), contact angle (p<0.001) and colour changes (p<0.001) of yellow cedar veneers exposed to natural weathering for 50 days.

Table 5.5: Effects of chemical treatments on the weight losses, tensile strengths, contact angles, colour changes, and the erosion of yellow cedar veneers exposed to natural weathering

<table>
<thead>
<tr>
<th>Response Variables</th>
<th>Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight losses</td>
<td>***</td>
</tr>
<tr>
<td>Colour changes</td>
<td>L*</td>
</tr>
<tr>
<td></td>
<td>***</td>
</tr>
<tr>
<td></td>
<td>a*</td>
</tr>
<tr>
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<td>--</td>
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<tr>
<td></td>
<td>b*</td>
</tr>
<tr>
<td></td>
<td>***</td>
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<tr>
<td></td>
<td>ΔE</td>
</tr>
<tr>
<td></td>
<td>***</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Unweathered</td>
</tr>
<tr>
<td></td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Weathered</td>
</tr>
<tr>
<td></td>
<td>***</td>
</tr>
<tr>
<td></td>
<td>Ratios</td>
</tr>
<tr>
<td></td>
<td>***</td>
</tr>
<tr>
<td>Contact angle</td>
<td>Unweathered</td>
</tr>
<tr>
<td></td>
<td>***</td>
</tr>
<tr>
<td></td>
<td>Weathered</td>
</tr>
<tr>
<td></td>
<td>***</td>
</tr>
<tr>
<td></td>
<td>Ratios</td>
</tr>
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<td></td>
<td>***</td>
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</tbody>
</table>

*=p<0.05 **=p<0.01 ***=p<0.001

5.3.1.1 Effect of chemical and oil treatments on weight losses of veneers

Titanium acetylacetonate, HEPBP and oils had significant effects on weight losses of veneers during weathering (Fig. 5.5). All treatments except castor oil significantly reduced
weight losses of veneers, and the addition of oil to titanium acetylacetonate further reduced weight losses (Fig. 5.4). Castor oil on its own was not effective at reducing the weight loss of veneers during weathering (Fig. 5.4), whereas linseed oil significantly (p<0.05) reduced weight losses.

![Graph showing weight loss of various treatments](image)

Fig. 5.4: Weight losses of yellow cedar veneers treated with titanium acetylacetonate, castor oil, linseed oil and HEPBP and exposed to the weather in Vancouver for 50 days. The photoprotective effects of chemical and oil treatments can be assessed with reference to weight losses of untreated controls (UNT)

### 5.3.1.2 Effect of chemical and oil treatments on tensile strength of veneers

The chemical treatments had no significant effect (p>0.05) on tensile strength of yellow cedar veneers before weathering, but had a highly significant effect (p<0.001) on the strength of veneers after weathering. However, only veneers treated with titanium acetylacetonate or HEPBP were significantly stronger after weathering than untreated controls (Fig. 5.5). The strength of veneers treated with linseed oil and its various combinations after weathering were similar to that of the untreated controls (Fig. 5.5a). In contrast, veneers treated with castor oil, and its combinations were significantly (p<0.05) weaker than untreated controls. Ratios of tensile strength of veneers before and after weathering are compared in Fig. 5.5b. The results are similar to those of the tensile strength of veneers after weathering (Fig. 5.5a). The only difference is that
HEPBP is ineffective at reducing tensile strength losses when results are expressed as ratios rather than as absolute strength values. Tensile strength ratios confirm that castor oil had a negative effect on tensile strength of veneers exposed to weathering.

Fig. 5.5: Tensile strength of treated and untreated yellow cedar veneers exposed to the weather in Vancouver for 50 days. The photoprotective effects of the metal acetylacetonates can be assessed with reference to tensile strengths of untreated controls (UNT)

5.3.1.3 Effect of chemical and oil treatments on water repellency of veneers

Chemical treatments had significant effects on the contact angles of water droplets on veneers before and also after veneers were weathered (p<0.001). Before weathering, untreated veneers had an initial contact angle of greater than 90°. HEPBP and titanium acetylacetonate significantly increased the initial contact angles of water droplets on veneers. However, castor oil reduced contact angles of water droplets on veneers (Fig. 5.6a). After veneers were weathered, the contact angles of water droplets on untreated veneers decreased and were lower than 90°. The contact angles of water droplets on treated veneers were all significantly greater than those on untreated (weathered) veneers, with the exception of most treatments containing linseed oil (Fig. 5.6b).
Fig. 5.6: Contact angles of water droplets on treated and untreated yellow cedar veneers before (a) and after (b) exposure of veneers to the weather for 50 days in Vancouver. The hydrophobic effects of the metal acetylacetonates can be assessed with reference to those of similarly exposed untreated controls.

When contact angles are expressed as ratios of angles after weathering to those before weathering, results indicate veneers treated with castor oil became more hydrophobic during weathering (Fig. 5.7). In contrast, contact angles ratios of other treated veneers and untreated controls decreased during weathering indicating that veneers became less hydrophobic.

Fig. 5.7: Ratios of contact angles (weathered/unweathered) of treated veneers and untreated control after veneers were exposed to the weather in Vancouver for 50 days.

There were no time to <90° values for untreated controls because they had initial contact angles less than 90°. The time taken for contact angles of water droplets on weathered veneers to decrease below 90° (t<90°) was not significant (p>0.05), but there was a significant effect of treatment alone on t<90° of unweathered veneers (Fig. 5.8). The time
(t<90°) for veneers treated with titanium acetylacetonate (1965s) was significantly (p<0.05) longer than those of other treated veneers (Fig. 5.8).

![Graph showing time (t < 90°) for water droplets on unweathered veneers to decrease below 90°. Veneers treated with castor oil, castor oil with titanium acetylacetonate, castor oil and titanium acetylacetonate with HEPBP are excluded since their initial contact angles were lower than 90°.](image)

**Fig. 5.8:** Time taken for water droplets on unweathered veneers to decrease below 90°. Veneers treated with castor oil, castor oil with titanium acetylacetonate, castor oil and titanium acetylacetonate with HEPBP are excluded since their initial contact angles were lower than 90°

**5.3.1.4 Effect of chemicals and oil treatments on colour of veneers**

Linseed oil and the treatments containing titanium acetylacetonate made wood yellower (Fig. 5.9). Veneers also yellowed significantly after exposure to the weather, as expected. Veneers treated with titanium acetylacetonate and also the untreated controls became darker than other treated veneers after weathering (Fig. 5.10).
Fig. 5.9: Appearance of yellow cedar veneers treated with titanium acetylacetonate, oils and HEPBP before veneers were exposed to the weather

Chemical treatments containing oils had significant effects on the lightness ($L^*$) ($p<0.001$), yellowness ($b^*$) ($p<0.001$) and Delta E ($p<0.001$) of veneers after weathering.

Fig. 5.10: Appearance of yellow cedar veneers treated with titanium acetylacetonate, oils and HEPBP after veneers were exposed to the weather in Vancouver for 50 days
Titanium acetylacetonate significantly (p<0.05) restricted the changes in L* during weathering even though weathered veneers that were initially treated with titanium acetylacetonate appeared to be darker than other veneers as noted above (Fig. 5.10). For example, veneers treated with titanium acetylacetonate had a lightness ratio of 0.874 compared to a lightness ratio of 0.813 for untreated controls. The lightness values of veneers treated with castor oil and combinations, and also linseed oil containing titanium acetylacetonate were significantly (p<0.05) lower than those of the untreated control (Fig. 5.11). Wood veneers yellowed when exposed to the weather as expected, but veneers treated with titanium acetylacetonate yellowed more than untreated veneers. Castor oil and linseed oil combinations with titanium acetylacetonate and HEPBP were ineffective at restricting the yellowing of veneers during natural weathering (Fig. 5.12).

![Fig. 5.11: Changes in lightness (L*) of treated veneers and untreated controls after veneers were exposed to 50 days of weathering in Vancouver](image-url)
Fig. 5.12: Changes in yellowness (b*) of treated veneers and untreated controls after veneers were weathered in Vancouver for 50 days

Chemical treatment with oils was ineffective at reducing total colour change (ΔE) of veneers during weathering. Titanium acetylacetonate significantly (p<0.05) increased the colour change (Delta E) of veneers because of the pronounced effect it had on the yellowness of veneers (Figs. 5.12 and 5.13).

Fig. 5.13: Total colour change of treated veneers and untreated controls after they were exposed to 50 days of natural weathering in Vancouver

5.3.1.5 Scanning electron microscopy (SEM) of wood veneers

Micro-checking of bordered pits occurred at the surfaces of untreated veneers exposed to natural weathering as also noted in Chapter 3 (Fig. 5.14). Colonization of veneer surfaces by mould also occurred (Fig. 5.14d).
Fig. 5.14: Scanning electron microscope photographs of the surface of untreated veneers before and after exposure to the weather for 50 days in Vancouver; a,b: unexposed; c,d: exposed. Note micro-checking of bordered pits in c, and d (arrowed) mould fungi colonizing the surface of veneers in d (arrowed)

Veneers surfaces treated with HEPBP contained needle-shaped structures, possibly recrystallized HEPBP (Fig. 5.15a). Micro-checking of bordered pits was observed at HEPBP-treated veneers surfaces exposed to natural weathering, but it was less pronounced than that at the surfaces of untreated wood surfaces (Fig. 5.15a, b). The surface of wood treated with linseed oil was coated with oil and, as a result, it was difficult to see the bordered pits (Fig. 5.15c). Wood treated with linseed oil was degraded during weathering, but the degradation was less pronounced than that at untreated wood surfaces (Fig. 5.15d). The addition of titanium acetylacetonate and HEPBP to linseed oil had little beneficial effect at restricting damage to veneers exposed to natural weathering.
Fig. 5.15: Scanning electron microscope photographs of the surface of veneers treated with HEPBP (a,b) or treated with linseed oil containing titanium acetylacetonate (c,d) before and after exposure to the weather for 50 days in Vancouver; a,c: unexposed; b,d: exposed.

There was no difference in SEM images of wood treated with castor oil, and its various combinations. SEM images of wood veneers treated with castor oil and combinations showed areas that were filled with oil (Fig. 5.16a,b). After these veneers were exposed to the weather, large numbers of holes developed in wood cell walls (Fig. 5.16c,d) (Fig. 5.17a,b,c,d).
Fig. 5.16: Scanning electron microscope photographs of the surface of veneers treated with castor oil before and after exposure to the weather for 50 days in Vancouver; a,b: castor oil treated, unexposed; c,d: castor oil treated, exposed
Fig. 5.17: Scanning electron microscope photographs of the surface of veneers treated with castor oil combinations after exposure to the weather for 50 days in Vancouver; a,b: castor oil and titanium acetylacetonate treated, exposed; c,d: castor oil, HEPBP and titanium acetylacetonate treated, exposed

5.3.2 Photoprotective effects of titanium acetylacetonate, HEPBP and castor oil on wood panels

The results of statistical analyses of experimental results for parameters used to assess the weathering of solid wood panels are summarized in Table 5.6. The treatments had significant effects on contact angle (p<0.001), erosion and colour changes (p<0.001) of panels.
Table 5.6: Effects of chemical treatments on the weight losses, tensile strengths, contact angles, colour changes, and the erosion of wood panels after natural weathering

<table>
<thead>
<tr>
<th>Response Variables</th>
<th>p values</th>
</tr>
</thead>
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<tr>
<td>Colour changes</td>
<td></td>
</tr>
<tr>
<td>L*</td>
<td>***</td>
</tr>
<tr>
<td>a*</td>
<td>--</td>
</tr>
<tr>
<td>b*</td>
<td>***</td>
</tr>
<tr>
<td>Ratios</td>
<td>***</td>
</tr>
<tr>
<td>Contact angle</td>
<td></td>
</tr>
<tr>
<td>Unweathered</td>
<td>***</td>
</tr>
<tr>
<td>Weathered</td>
<td>***</td>
</tr>
<tr>
<td>Ratios</td>
<td>***</td>
</tr>
<tr>
<td>Erosion</td>
<td>--</td>
</tr>
</tbody>
</table>

*** = p<0.001

5.3.2.1 Effects of treatments on colour

Copper ethanolamine on its own made wood panels bluer as expected (Fig. 5.1b). Oil made them yellower (Fig. 5.18). After untreated panels were exposed outdoors to the weather, they lost their yellowness and became grey as expected (Fig. 5.18). Panels treated with titanium acetylacetonate and HEPBP retained their yellowness after weathering, particularly panels treated with titanium acetylacetonate. Wood panels treated with castor oil became darker and blotchy with black-blue stains after they were exposed outdoors (Fig. 5.18). All scanned images of treated and untreated wood samples before and after weathering are appended to this thesis (Appendix 3).
Unweathered                          Weathered

a  Untreated control

b  Copper ethanolamine

c  HEPBP

d  Titanium acetylacetonate

e  Castor oil
Wood panels treated with oil and its combination with titanium acetylacetonate and HEPBP were significantly darker ($L^*$), yellower ($b^*$) and redder ($a^*$) than other panels (both treated and untreated). All of the treatments changed the initial colour of wood panels (before weathering) (Figs. 5.18 and 5.19). Panels treated with HEPBP and titanium acetylacetonate were darker and yellower than untreated panels. There were no significant ($p>0.05$) differences in the colour of wood treated with castor oil, and its various combinations and titanium acetylacetonate (refer to Fig. 5.21). After weathering, wood panels treated with castor oil, and its combinations with titanium acetylacetonate and HEPBP were significantly ($p<0.05$) darker than untreated panels (Fig. 5.19). All treated panels were redder and yellower than untreated panels after weathering (Fig. 5.20). Panels treated with castor oil and its combinations had higher yellowness and redness, but lower lightness than those of other treated panels (Figs. 5.19 and 5.20).
Fig. 5.19: CIE colour parameters of treated and untreated wood panels before weathering (L* = lightness; a* = redness; b* = yellowness).

Fig. 5.20: CIE colour parameters of treated and untreated wood panels after weathering (L* = lightness; a* = redness; b* = yellowness).

The changes in L* (lightness), a* (redness) and b* (yellowness) of panels during weathering are also expressed as the ratios of colour parameters after weathering to those of initial parameters (before weathering). The castor oil, castor oil containing titanium acetylacetonate and castor oil containing titanium acetylacetonate and HEPBP darkened the panels (before weathering) (Fig. 5.18) and although the treated panels became darker during weathering, lightness ratios are lower than those of other treated panels. In contrast, panels treated with titanium acetylacetonate and HEPBP became darker during weathering. Titanium acetylacetonate and HEPBP restricted the reddening and yellowing of wood during weathering, but the panels were not as dark as those treated with castor oil solutions (Fig. 5.21).
5.3.2.2 Effects of treatments on water repellency of wood panels

Panels treated with titanium acetylacetonate, HEPBP or CuEa had significantly (p<0.05) higher initial contact angles than the untreated controls (Fig. 5.22). Castor oil containing titanium acetylacetonate and castor oil containing titanium acetylacetonate and HEPBP also significantly increased the hydrophobicity of wood surfaces, but they were less effective than titanium acetylacetonate, HEPBP or CuEa (Fig. 5.22). After weathering, contact angles on panels treated with castor oil solutions were significantly (p<0.05) higher than those on untreated wood and also panels treated with titanium acetylacetonate, HEPBP or CuEa (Fig. 5.23). Panels treated with titanium acetylacetonate, HEPBP and CuEa exposed to the weather had significantly (p<0.05) higher contact angles than similarly exposed untreated panels.

Fig. 5.21: Ratios of CIE colour parameters of treated and untreated wood samples after weathering (L* = lightness; a* = redness; b* = yellowness)
Changes in contact angles of water droplets on panels as a result of weathering are expressed as the ratios of initial contact angles after weathering to those of contact angles before weathering (Fig. 5.24). The decrease in contact angles of water droplets on wood treated with titanium acetylacetonate and HEPBP were significantly (p<0.05) greater than those of droplets on untreated wood. Contact angles of water droplets on panels treated with castor oil solutions all increased significantly (p<0.05) as a result of weathering. Hence, the ratios of contact angle of water droplets on wood treated with the combinations of castor oil with titanium acetylacetonate and HEPBP were all higher than 1, one (Fig. 5.24).
Fig. 5.2: Changes in contact angles ratios of water droplets on treated and untreated wood panels exposed to natural weathering for 6 months in Vancouver

5.3.2.3 Surface confocal profilometry

Statistical analyses of erosion data showed that there was a significant (p<0.05) difference in erosion of treated and untreated panels after the panels were exposed to natural weathering for 6 months. The average erosion of treated samples was significantly (p<0.05) lower than that of untreated controls (p<0.001) ([10.63] vs [24.96]). Panels treated with HEPBP also eroded significantly (p<0.05) less than the untreated controls, but showed greater erosion than samples treated with oil and titanium acetylacetonate combinations. Panels treated with titanium acetylacetonate, and castor oil solutions eroded less than the untreated controls and panels treated with copper ethanolamine or HEPBP, but there was no significant difference (p>0.05) in the ability of these four treatments to restrict erosion of panels (Fig. 5.25).
Fig. 5.25: Erosion (step height difference) of treated and untreated yellow cedar panels after panes were exposed to natural weathering for six months in Vancouver

Fig. 5.26 shows profilometry images of masked areas on treated and untreated panels exposed to 6 months of natural weathering. The images confirm that titanium acetylacetonate and titanium acetylacetonate combined with castor oil and HEPBP reduced the erosion of wood during weathering. Untreated controls had larger height differences as can be seen on the surface map, than panels treated with titanium acetylacetonate and its combinations with castor oil and HEPBP. All profilometry images can be found in Appendix 4. The erosion on untreated surfaces was more consistent across the unmasked area than that at treated wood surfaces. For example, consistent erosion of earlywood and latewood in the unmasked area on the untreated controls occurred (Fig. 5.26d), whereas erosion is much more patchy in treated samples (Fig. 5.26 a,b,c).
(a) Titanium acetylacetonate            (b) Titanium acetylacetonate and castor oil

(c) Titanium acetylacetonate, castor oil
and HEPBP                            (d) Untreated control

Fig. 5.26: Profilometery images of masked areas on treated and untreated wood panels exposed to natural weathering for 6 months in Vancouver

5.3.2.4 Scanning electron microscopy (SEM) of wood panels

SEM images of treated and untreated wood panels exposed to natural weathering did not provide insights into why some treatments were more effective than others, although I noted that panels treated with castor oil and combination were covered with surface mould (Fig. 5.27) whereas wood panels treated with titanium acetylacetonate and HEPBP were less affected by mould (Fig. 5.27). All SEM images are appended to this thesis (Appendix 3).
Fig. 5.2: Scanning electron microscope photographs of the surfaces of wood panels after panels were exposed to the weather for 6 months in Vancouver. a: untreated control; b: treated with titanium acetylacetonate containing castor oil and HEPBP; c: treated with titanium acetylacetonate; d: treated with titanium acetylacetonate containing HEPBP

Since wood samples treated with oil combinations were covered with mould, samples were sectioned obliquely with a razor blade to observe the underlying wood surfaces as shown in Fig. 5.28. Degradation of tracheid walls beneath the layer of mould can be observed, as arrowed in Fig. 5.28.
Beneath the surface layer of mould, I observed holes in the cell walls of tracheids in panels treated with castor oil combinations (Fig. 5.29). These holes resembled those observed in oil-treated veneers exposed to natural weathering (compare to photos here with those in Fig. 5.16).

**Fig. 5.29:** Scanning electron microscope photographs of wood panel surfaces (a): treated with castor oil containing titanium acetylacetonate and (b) treated with castor oil containing titanium acetylacetonate and HEPBP after exposure to the weather for six months in Vancouver

### 5.4 Discussion

The results in this chapter partially support my hypothesis that combinations of oils and UV stabilizers (including titanium acetylacetonate) will enhance the photoprotection of wood pre-treated with titanium acetylacetonate. Castor oil and linseed oil had beneficial effects on the weight losses of veneers treated with titanium acetylacetonate and exposed to natural
weathering. Castor oil also restricted the losses of water repellency of titanium acetylacetonate treated veneers exposed to the weather. Linseed oil and castor oil reduced the colour changes of veneers treated with titanium acetylacetonate. However, castor oil increased the tensile strength losses of veneers during weathering, possibly because it led to the development of holes in cell walls of wood exposed to the weather. My results show that titanium acetylacetonate reduced the erosion of wood panels, but it was less effective at increasing the water repellency of the wood. The addition of castor oil to titanium acetylacetonate increased the water repellency of panels, as expected, and restricted the losses of water repellency of panels compared to the panels simply treated with titanium acetylacetonate. There was no significant effect of addition of HEPBP on the effectiveness of titanium acetylacetonate. In summary, oils combined with titanium acetylacetonate were generally a better protective treatment for wood exposed to the weather than titanium acetylacetonate on its own (with the exception of tensile strength losses when titanium acetylacetonate was combined with castor oil and the negative effects of oils on growth of mould at wood surfaces). In contrast, addition of HEPBP to titanium acetylacetonate had few beneficial effects.

Metal acetylacetonates and other transition metal compounds are able to oxidize and polymerize castor oil. Hence, they have been used as catalysts to improve the drying rate of oils and increase the stability of oils (Koritala 1985; Soucek et al. 2012). Hydroxylated castor oil can be reacted with titanium isopropoxide to form films with good hardness, tensile strength and adhesion to an aluminum surface, according to Martinelli et al. (2009). Titanium bis(acetylacetonate) has been used to create coatings from linseed oil and sunflower oil. The tensile strength, tensile modulus and the thermo-oxidative stability of such coatings are similar to oil coatings cured with driers (Tuman and Soucek 1996). These studies suggest that transition metal compounds are able to improve the performance of oils. There is some evidence for such an effect here. Titanium acetylacetonate increased the water repellency of wood treated with castor oil when wood was exposed outdoors. Titanium acetylacetonate had
a beneficial effect on the ability of castor oil to restrict weight losses of wood veneers, as mentioned above. The same effect did not occur with linseed oil. This discrepancy might have occurred because castor oil unlike linseed oil has a hydroxyl group on its polymer chains which may have been able to react with wood or titanium acetylacetonate.

Other combinations of treatments have been used to protect wood surfaces. For example, heat treatment is able to improve the weathering resistance of wood on its own (Vernois 2001; Rapp and Sailer 2004; Esteves and Pereira 2008). However, oils have been combined with heat treatment to provide better protection to wood during accelerated weathering (Miklečić et al. 2010). For example, Miklečić et al. (2010) found that oils such as universal oil, thermowood oil and teak oil restricted colour changes and checking of heat treated wood exposed to natural weathering. The combination of thermal modification and oil treatment also increases the biological resistance of wood (Miklečić et al. 2010). Another notable example of combinations of chemicals that can act in concert and synergistically to protect wood surfaces is UV absorber (UVA) and hindered amine light stabilizer (HALS) combinations. The combination of a UVA and HALS provides synergistic photo-protection to wood and coatings according to Avar and Bechtold (1999) and Forsthuber and Grüll (2010). When UV absorbers and HALS are used together in coatings, UVA reduces light reaching the wood substrate while HALS trap free radicals. Hence, blends of UV absorbers and HALS give better stabilization of wood and coatings than either of the additives on their own (Ávár and Bechtold 1999).

One unexpected finding in this chapter was that wood treated with castor oil (before weathering) was not water repellent (θ>90°), but it became water repellent (θ>90°) after panels were weathered outdoors. Castor oil is a non-drying oil, and it may not have cured before exposure (Naughton 1979). Wet oil on wood surfaces leads to contact angles of less than 90° according to Cassie and Baxter (1944). During weathering, castor oil may have cured forming dehydrated castor oil which has water resistance as good as tung oil (Weiss 1971). As a result, dehydrated castor oil is used in varnish and resin systems to improve
water repellency, gloss and chemical resistance of castor oil-based finishes (Ogunniyi and Njikang 2016; Bishai and Hakim 1995). One way of producing dehydrated castor oil is to cross-link hydroxyl groups on castor oil. For example, β-Ketoester synthesized from t-Butyl acetoacetate and xylene was mixed with castor oil to develop a cured castor oil or acetylacetonated castor oil (Trevino and Trumbo 2002). Acetylacetonated castor oil was used as a coating and examined for gloss and hardness resistance. However, there is no indication from my results that titanium acetylacetonate enhanced the water repellency of oil treated surfaces because wood treated with castor oil on its own and then weathered was as water repellent as surfaces treated with castor oil and titanium acetylacetonate.

Another expected effect of castor oil on wood surfaces was the greater losses of tensile strength of veneers treated with castor oil and exposed to weathering compared to those of similarly exposed untreated veneers. Castor oil treated wood developed holes in wood cell walls during weathering suggesting it might accelerate the photodegradation of wood. Such an effect would account for the increased losses in tensile strength of castor oil treated veneers exposed to natural weathering. Johnson et al. (2003) tested fatty acids on photodegradation of Azadiractin-A exposed to UV radiation. They conclude that saturated fatty acids, for example fatty acids on castor oil, accelerate the photodegradation of Azadiractin-A. Castor oil has three points of functionality, namely carboxyl group, hydroxyl group and unsaturation point (Naughton 1974; Ogunniyi 2006), and its reactive properties might account for its effects on tensile strength of veneers and structure of wood cell walls. Wood panels treated with castor oil and its combinations were covered with mould after weathering, as expected.

Clearly the reaction of castor oil and wood needs further study to better understand why water repellency of wood treated with castor oil improved during weathering, and why it appears to accelerate photodegradation of wood. Mould caused dark stains on wood surfaces, which is undesirable. However, mould might act as a ‘biofilm’ to protect wood surfaces against weathering (Sailer et al. 2010). There is little evidence for this effect from my results.
because there was micro-checking of wood beneath surfaces that were covered with mould. However, oil treatments are being used to encourage the growth of mould and yeasts at wood surfaces to provide protection to wood surfaces. For example, van Nieuwenhuijzen et al. (2015) used linseed oil on wood surfaces and exposed wood to natural weathering. The melanized fungi *Aureobasidium* spp. covered wood surfaces after natural weathering. van Nieuwenhuijzen et al. (2015) concluded that the surface layer of fungi were acting as a biofinish to protect wood surfaces, and also stain the wood

### 5.5 Conclusions

Oils when combined with titanium acetylacetonate provided additional protection to wood surfaces, most notably water repellency. However, oils were unable to photostabilize wood, and there is evidence that castor oil accelerated photodegradation of wood veneers exposed to weather. More research is needed to investigate this unwanted effect of castor oil on the photostability of wood. Titanium acetylacetonate was as effective at restricting photodegradation of wood as the benzophenone UV absorber HEPBP. The effectiveness of titanium acetylacetonate-oil treatments could be improved by optimizing the treatment process, perhaps by taking steps to polymerize castor oil and titanium acetylacetonate.
6. General Discussions, Conclusions and Suggestions for Further Research

6.1 Discussions

In the introduction to this thesis, I hypothesized that metal acetylacetonates will protect wood from photodegradation on their own or in combination with other protective systems, such as clear finishes, oils and UV absorbers. Results from my three experimental chapters will be discussed together to indicate whether this general hypothesis can be supported. Overall, metal acetylacetonates were able to photostabilize wood surfaces and in some cases the effectiveness of the acetylacetonates was improved by combining them with other protective systems.

Results in Chapter 3 showed that metal acetylacetonates were able to restrict photodegradation of wood veneers to various degrees depending on the metal in the coordination complex and the parameters used to assess photodegradation of veneers. Titanium and manganese acetylacetonate were selected for further testing because they were able to photostabilize wood, have lower toxicity than some other metal acetylacetonates, and did not greatly discolour wood surfaces (unlike iron). Nickel acetylacetonate was also effective, but has high toxicity (Bhattacharjee and Chaudhuri 1989). Iron acetylacetonate photostabilized wood and was the most effective acetylacetonate at protecting lignin from photodegradation. However, iron and chromium acetylacetonate significantly discoloured wood surfaces, which is undesirable for protection systems designed to improve the performance of clear coatings. Cobalt acetylacetonate had little ability to photostabilize wood veneers exposed to the weather. Cobalt acetylacetonate crystallized at wood surfaces and this may have contributed to its inability to photostabilize wood. Manganese and titanium acetylacetonate were tested as photoprotective primers for a polyurethane clear coating on yellow cedar and pine panels in Chapter 4. These acetylacetonates restricted colour changes of panels during artificial accelerated weathering and results suggested that titanium acetylacetonate was more effective at restricting yellowing of cedar than it was at restricting yellowing of pine. There was a beneficial effect of manganese acetylacetonate on the
adhesion of the polyurethane clear coating on yellow cedar and pine panels. Chapter 5 did not compare the effectiveness of different metal acetylacetonates at photostabilizing panels exposed to the weather, but results showed that titanium acetylacetonate can significantly reduce the erosion of wood samples exposed to the weather, confirming results in Chapter 3 that it can photostabilize wood. One noteworthy difference in the ability of metal acetylacetonates to photostabilize wood was noted in Chapter 3, where it was observed that iron acetylacetonate was better at photostabilizing lignin than the other metal acetylacetonates. Iron acetylacetonate discoloured wood surfaces which is undesirable in photoprotective systems used with natural finishes. However, iron acetylacetonate might have potential as a stain on its own because other iron compounds, for example, iron sulphate are used as stains to give wood the appearance of weathered wood (Stephen 2005).

Overall, my results point to significant differences in the ability of metal acetylacetonates to photostabilize wood and therefore act as protective treatments for wood either directly or in combination with other systems, for example clear coatings or oils. My findings accord with a study by Osawa and Aiba (1982) who found that there were differences in the ability of metal acetylacetonates to photostabilize PVC. They did not explain their observations, but my results and those of others suggest why some of the metal acetylacetonates may be more effective at photostabilizing wood than others.

Metal acetylacetonates are able to crosslink with -OH and -COOH (Guo 2011) suggesting that they can potentially react with hydroxyl groups in wood. The -OH groups on lignin are more reactive than those on holocellulose (Haykir-Acma et al. 2010) and it is possible, as pointed out in Chapter 3 that the formation of metal complexes with lignin accounts for the increased photostability of wood treated with metal acetylacetonates. Differences in the reactivity of metal acetylacetonates with wood and the stability of any complexes formed may account for why some metal acetylacetonates were more effective at photostabilizing veneers than others. There is some evidence to support this suggestion from research on the reactions of metal acetylacetonates with polymers. For example, McNeill and
Liggat (1991) investigated the effects of cobalt and manganese acetylacetonate on thermal stability and degradation mechanism of PMMA (poly(methyl methacrylate)). They found that cobalt acetylacetonate was less able to complex the ester groups in PMMA than manganese acetylacetonate. Chromium acetylacetoante is more reactive than cobalt and rhodium acetylacetonate with acids according to Collman (1965). In addition, Siddiqi et al. (2007) showed that chromium acetylacetonate is more stable than iron, nickel and manganese acetylacetonate at the same temperature.

In addition to differences in the ability of the various acetylacetonates to photostabilize wood my results in Chapter 4 indicate that their effectiveness varies with species (yellow cedar vs Scots pine). This finding accords with previous research that showed that reactive titanium compounds were more effective at improving the exterior performance of an alkyd clear coat on western red cedar compared to radiata pine (Evans et al. 2015). Dost (1959) suggested that reactive titanium compounds are able to modify extractives in California redwood, forming water repellent complexes. Both western red cedar and the yellow cedar examined here are richer in extractives than Pinus species (Barton and MacDonald 1971; Barton 2007), which might explain why titanium acetylacetonate performed differently on yellow cedar compared to Scots pine (Chapter 4).

Metal acetylacetonates have numerous commercial applications as described in Chapter 2, and there are some applications of metal acetylacetonates that are related to wood protection. For example, titanium acetylacetonate can be used with paints and coatings to improve their adhesion, water repellency and scratch resistance (Nestler and Barfurth 1986; Barfurth et al. 1990). Zirconium and aluminum acetylacetonates have been widely used in adhesives as catalysts and crosslinking agents (Clair 2003; Czech and Wojciechowicz 2006). Furthermore, metal acetylacetonates can be used as catalysts to increase the curing rate of oils and improve the stability of oils (Soucek et al. 2012; Koritala 1985). Metallic salts of manganese, cobalt and zirconium are used as driers to accelerate the curing of oils (Lazzari and Chiantore 1999; Mallégol et al. 2016). My results in Chapter 5 showed some beneficial
effects of combining titanium acetylacetonate and oils on the weathering resistance of yellow cedar exposed outdoors. However, such beneficial effects were offset by increased colonization of wood surfaces by mould fungi. Overall, the use of metal acetylacetonates to improve the performance of coatings rather than oil-based treatments appears to be more promising. Metal acetylacetonates can be applied as a primer prior to the application of coatings on wood, in order to photostabilize wood surfaces and improve various performance attributes of coatings such as service life and adhesion. My results and those of others suggest that such an application may be more successful on extractive-rich wood species. Additionally, metal acetylacetonates could be added directly into coating systems to act as catalysts or cross-linking agents to improve the elasticity, water repellency and scratch resistance of the coatings. Hence, I conclude that metal acetylacetonates have the potential to work on both wood and coatings together, which could lead to enhanced performance of coatings.

Another potential application of metal acetylacetonates suggested by my results is as a primer (tannin blocker) to reduce extractive staining of opaque finishes. It is possible that metal acetylacetonates applied to extractive-rich woods could complex with extractives and prevent them from migrating through paint films and marring the appearance of finished wood surfaces. Composite pigments have been used to stop the migration of water-soluble tannin (Nordyke and Spangenberg 1974; Meyer and Stevens 1980), and there are a variety of products containing for example, titanium dioxide (Blumenfeld 1930), magnesium hydroxide, Mg(OH)$_2$ (Meyer and Stevens 1980) that claim to reduce the extractive staining of paints.

One unexpected finding from my research was that castor oil accelerated the photodegradation of wood. Holes developed in the cell walls of wood veneers and panels treated with castor oil and its combinations and exposed to natural weathering. Because of this, the tensile strength of veneers was significantly lower than those of other veneers after they were exposed to natural weathering. The mechanism responsible for this effect needs to be understood because castor oil is a component of water repellents used to treat wood.
(Naughton 1974). Castor oil is used in the synthesis of polyurethane adhesives because of polyhydroxyl on its chains (Somani et al. 2003; Yeganeh and Hojati-Talemi 2007), and its reactive nature may explain why castor oil degraded wood, when it was exposed to natural weathering.

6.2 Conclusions

My results partially support my general hypothesis that metal acetylacetonates can protect wood from photodegradation on their own or in combination with other protective systems, particularly clear finishes, oils and UV absorbers. However, the ability of metal acetylacetonates to photostabilize wood and reduce the photodegradation of lignin varied depending on the metal in the coordination complex. I provide an explanation for how metal acetylacetonates are able to photostabilize wood, but suggest that further research is necessary to fully understand why some metal acetylacetonates were more effective than others. Titanium and manganese acetylacetonate improved the performance of a clear polyurethane coating on Scots pine and yellow cedar panels exposed to artificial accelerated weathering. The acetylacetonates were more effective at improving the performance of the coating on yellow cedar than on Scots pine. I conclude that metal acetylacetonates have potential as photoprotective primers for clear coatings applied to wood, and suggest that they may be more suitable as primers for extractive-rich species such as yellow cedar and possibly western red cedar. The effectiveness of titanium acetylacetonate at restricting the weathering of wood was enhanced by combining it with linseed oil or castor oil, but there were negative effects of the oils on the properties of treated veneers and panels exposed to natural weathering. Hence, I conclude that metal acetylacetonates have greater potential as photoprotective primers for coatings rather than as components of oil-based finishes. Finally, I conclude that metal acetylacetonates have potential practical applications in other areas. For example, iron acetylacetonate was the most effective treatment at photostabilizing lignin, and because it imported a dark colour to wood surfaces, it could be used as a stain to give wood a weathered appearance.
Two unexpected findings from my research that are relevant to wood protection are that the hydrophobicity of castor-oil treated wood surfaces improved when they were exposed outdoors and, secondly castor oil appears to accelerate the photodegradation of wood. Further research is needed to better understand these phenomena and fully explore the potential of metal acetylacetonates as protective treatments for wood.

6.3 Suggestions for further research

My results show that the ability of metal acetylacetonates to photostabilize wood surfaces differs depending on the metal in the acetylacetonate. The different metal acetylacetonates need further studies on their reactivity and stability of acetylacetonate to better understand how they are able to photostabilize wood. Such research might also provide evidence for the reaction mechanism of metal acetylacetonates with wood. In addition to photostabilizing lignin in wood, metal acetylacetonates may be able to stabilize extractives in wood. The hypothesis needs further research to investigate the ability of metal acetylacetonates to complex and stabilize lignin or extractives. If the latter then metal acetylacetonates might act as a tannin blocker to reduce discolouration of paints applied to wood surfaces. It might also be interesting to compare the ability of iron acetylacetonate to stain wood with those of other iron treatments that are used to help wood achieve a weathered look.

The concentrations of metal acetylacetonates that are most effective at photostabilizing wood need to be determined. Higher concentrations of metal acetylacetonates might be more effective at reacting with wood and protecting wood surfaces from weathering. The effectiveness of titanium acetylacetonates at improving the performance of clear coatings requires testing of additional clear coating types such as acrylic and alkyd coatings etc. Vollmer (2011) investigated the exterior performance of different combinations of clear coats such as acrylic, polyurethane and alkyd coatings, and various pre-treatments. He concluded that pre-treatments performed differently with the different types of clear coatings.
Thus further research is needed to better understand the interactive effects of metal acetylacetonates pre-treatments on the performance of coatings on wood.

Finally, the accelerated degradation of wood treated with castor oil was unexpected, as mentioned above. Further research is needed to better understand the chemical basis for the reaction of wood with castor oil. My results also suggest that various types of oils performed differently at wood surfaces. Additional oils need to be tested on their own and in combination with metal acetylacetonates and possibly biocides to develop an effective oil-based exterior finish for wood exposed outdoors.
References


Appendices

Appendix 1 - SEM images and FTIR spectra, Chapter 3

(a) SEM images of untreated and treated veneers before and after exposure

![SEM image](image1)

(b) FTIR spectra of untreated and treated veneers before and after exposure

![FTIR spectra](image2)

More SEM images and spectra for all treated were saved on a hard drive.
Appendix 2 - Images of wood panels, Chapter 4

Scanned images of treated and untreated wood veneers and panels before and after exposure to natural weathering

More scanned images were saved on a hard drive.
Appendix 3 - SEM images and scanned images, Chapter 5

(a) SEM images of treated and untreated veneers and wood panels before and after exposure to natural weathering

(b) Scanned images of treated and untreated veneers and wood panels before and after exposure to natural weathering

More SEM images and scanned pictures were saved on a hard drive.
Appendix 4 - Profilometery images of masked and unmasked (eroded) areas on of treated and untreated wood panels exposed to six months of natural weathering, Chapter 5

Titanium treated wood panel after 6 months of weathering

HEPBP treated wood panel after 6 months of weathering

More profilometry images were saved on a hard drive.