

**HIGH PERFORMANCE CLEAR-COAT
SYSTEMS FOR WOOD USED OUTDOORS**

by

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Abstract

Wood is one of the main materials of choice to reduce the environmental footprint of the building and construction sector. Wood is aesthetically pleasing and hence there is great demand for finishing systems that do not mask wood's color and texture. Unfortunately, clear coatings used on wood outdoors fail within one to two years mainly because of photodegradation of the underlying wood substrate. The performance of clear coatings on wood can be enhanced by photostabilizing the wood before coating or by modifying the clear coating to improve its photostability and flexibility. However, these approaches have seldom been combined. In this thesis I hypothesized that pre-treatments that can photostabilize wood without adversely affecting coating performance could, when combined with state-of-the-art clear coatings, create coating systems that are a significant improvement on those that are currently available. I compared the ability of nine different chemical treatments to photostabilize wood. I examined the effect of the same wood pre-treatments on coating properties (wettability and adhesion) and the permeability of three different coating types. The most effective photostabilizing pre-treatments were benzoyl chloride, vinyl benzoate and chromic acid, and a PF-resin containing a hindered amine light stabilizer. The solvent based polyurethane was more compatible than the water-based acrylic and alkyd coatings with treated wood surfaces. Wood treatments had no effect on coating adhesion, but coating adhesion was highest for the polyurethane. Subsequently, I examined the outdoor performance of seven different clear coatings on photostabilized wood substrates. Benzoyl chloride, vinyl benzoate, chromic acid and the PF-resin/HALS treatments effectively enhanced the clear coat performance during a year-long weathering trial in Australia. Clear coat performance was also improved by using coatings with double the amount of UVA/HALS additives. My findings confirm that clear coat performance on wood exposed outdoors depends on the combination of wood pre-treatment and coating type. I conclude that superior clear coat systems (pre-treatment plus coating) for wood can be developed by combining very effective treatments that can photostabilize wood together with state-of-the-art photostable and flexible clear coatings.

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1. General introduction

1.1 Introduction

The popularity of wood as a building material has been recognized for many centuries (Hodges 1970; Richardson 1993; Ulrich 2008). Wood is popular because of its ease of processing, aesthetic appeal, local availability, generally low cost, and good mechanical strength in relation to its density (Hon & Chang 1984). In recent years another factor has added to the popularity of wood as a building material. Wood requires much lower levels of energy to process than other building materials such as concrete and steel, thus making wood one of the materials of choice to reduce fossil fuel dependency and lower carbon emissions (Buchanan & Levine 1999; Börjesson & Gustavsson 2000). Furthermore, wood is a renewable material with a closed carbon cycle (Buchanan & Levine 1999). As a result of these environmental advantages, wood is increasingly being specified by architects and designers for use in green buildings (Ward 2010a). For example, Ward (2010b) reported on the increased use of wood for school construction in the United States to comply with new environmental regulations for public buildings. Growing demand for wood as a building material has also occurred in the market for cladding (facades). In this market, besides wood's environmental advantages mentioned above, the use of wood is desirable to counterbalance the 'heavy appearance' of steel and glass that are often used to construct modern multi-storey buildings (Forsythe 2007).

Wood is susceptible to fire and deterioration by organisms (fungi and insects), which places it at a disadvantage compared to concrete and steel (Kiguchi & Evans

1998). Wood is also susceptible to weathering when exposed outdoors. Weathering is a term used to define the combined effects of solar radiation (UV and visible), moisture and heat, abrasion due to windblown particles, atmospheric pollutants and certain microorganisms on wood surfaces (Feist 1982; Feist & Hon 1984; Evans 2008). Weathering is driven by the photodegradation of lignin. Degradation of lignin leads to the generation of aromatic and other free radicals, which further breakdown lignin and wood's other main components, cellulose and hemicelluloses (Derbyshire & Miller 1981; Feist & Hon 1984; Evans et al. 1996). Weathering does not affect wood's strength properties, as weathering is limited to the surface. Weathering creates a rough texture at exposed wood surfaces and causes wood to become grey. These changes to the appearance of wood are disliked by most consumers (Derbyshire & Miller 1981; Feist 1982; Feist 1990; Williams 1999). The weathering of wood can be prevented by application of opaque paint prior to outdoor exposure. However, consumers usually prefer clear or semi-transparent coatings that do not completely mask wood's color and texture (Sell & Feist 1986; George et al. 2005). Nevertheless, a major problem with the use of clear coatings is their transparency to UV and visible radiation, which leads to photodegradation of the wood underneath the coating (MacLeod et al. 1995; Singh & Dawson 2003). Most clear coatings fail within a two year time period and are not recommended for use on wood exposed outdoors (Cassens & Feist 1991; MacLeod et al. 1995). This, together with the high maintenance costs of clear-coated wood has resulted in many consumers substituting wood with other materials even though they are 'less green'. For example, in 2009 only 18% of window frames in the European Union were made

from wood whereas 22% were made from aluminum and 56% from PVC (VFF 2011).

Attempts to improve the performance of clear coatings on wood by changing the physical and chemical properties of coatings have met with some success. For example, the addition of organic UV absorbers such as benzotriazoles or inorganic UV absorbers such as titanium dioxide to coatings can improve their outdoor performance on wood (DebRoy 2006; Forsthuber & Gröll 2010). Additives such as hindered amine light stabilizers can also improve the performance of clear coatings on wood outdoors especially when they are combined with UV absorbers (Forsthuber & Gröll 2010). Direct modification of the coating binder to make it photostable has also improved the performance of clear coats. For example, Hon et al. (1985) reported that modification of the binder in an acrylic clear coating with a polymerized hydroxybenzophenone UV absorber increased the performance of that coating on wood surfaces exposed to weathering.

Another route to increasing the performance of clear coatings on wood exposed outdoors is to photostabilize the wood prior to finishing (Black & Mraz 1974; Feist 1979; Derbyshire & Miller 1981). Evidence that photostabilization of wood (prior to coating) will increase the performance of clear coatings on wood is mainly derived from research performed on the use of chromic acid as a pre-treatment prior to finishing. Chromic acid is able to photostabilize lignin and greatly improves the performance of clear coatings on wood during weathering (Black & Mraz 1974; Williams & Feist 1985; Evans & Schmalzl 1989). In fact, chromic acid was used commercially as a pre-treatment in Japan in the 1980s to enhance the weathering

resistance of acrylic-urethane finishes applied to wooden doors (Ohtani 1987). Williams & Feist (1985) reported that clear coatings applied to chromic acid pre-treated wood surfaces showed no sign of degradation after 15 years of outdoor exposure in Madison, Wisconsin. Furthermore, Preston (2010) mentioned in personal conversations that clear coated house sidings pre-treated with chromic acid are still in good condition after 28 years of outdoor exposure. Such high performances from clear coatings on wood pre-treated with chromic acid would certainly meet the requirements for maintenance friendly products in outdoor use. However, the green discoloration of chromic acid treated wood exposed outdoors as well as a high toxicity of chromium VI has prevented the widespread use of chromic acid as a pre-treatment for clear coated wood (Sax 1975; Evans et al. 1992). Further evidence to support the hypothesis that photostabilization of wood surfaces will improve clear coat performance arises from work on the grafting of UV absorbers to wood. This research showed that UV absorbers grafted to wood could photostabilize lignin and improve the performance of clear coatings exposed to artificial and natural weathering (Williams 1983; Kiguchi & Evans 1998). However, the coatings on grafted wood substrates were only exposed to weathering for short periods of time (100 days) and they did not appear to have the longevity of coatings applied to chromic acid treated wood.

1.2 General hypothesis and aims

The research that has been done to enhance clear coat performance on wood exposed outdoors has focussed on modifying the clear coating (use of additives or different binders) or photostabilizing the wood before clear coating.

Relatively little research has been conducted to enhance clear coat performance by combining the two approaches. It seems reasonable to anticipate that this holistic approach to improving clear coat performance will lead to significant improvements in clear coat performance. It has been shown that wood pre-treatments such as chromic acid can improve the performance of clear coatings on wood used outdoors because they can photostabilize lignin (Williams & Feist 1985). Chromic acid pre-treatment also imparted higher dimensional stability and improved wettability to wood surfaces (Black & Mraz 1974; Williams & Feist 1985). Improvements in clear coat performance arising from the use of wood photostabilizing pre-treatments may also depend on the ability of the pre-treatment to modify the wood surface in other ways (wetting and adhesion properties) that enhance wood coating interactions and longevity.

One of the aims of this study was to compare the ability of a range of chemical treatments to photostabilize wood and then determine how these pre-treatments altered various surface properties of wood that influence important coating properties. Furthermore, this study determined which combination of wood pre-treatment and state-of-the-art clear coat was the most durable during a natural weathering trial. The overall aim of this study was to answer the general hypothesis that pre-treatments that can photostabilize wood without adversely affecting coating performance, when combined with state-of-the-art clear coatings, will create coating systems (pre-treatment plus coating) that are a significant improvement on those that are currently available.

1.3 Outline of study

Following this introduction, Chapter 2 reviews relevant literature on the need for coatings as well as the type of clear coatings used on wood exposed outdoors. Chapter 2 also reviews the failure mechanisms of clear coatings on wood exposed outdoors and describes ways of modifying clear coatings to improve their durability. Finally Chapter 2 concludes by describing previous research on the photostabilization and modification of wood surfaces to improve the performance of clear coatings. Chapter 3 compares the ability of nine state-of-the-art wood photostabilizing pre-treatments (including chromic acid) to photostabilize wood. Untreated wood acted as a control. Research in this chapter also examined the effect of wood pre-treatments on the properties of wood surfaces that can influence coating performance, for example, wettability and adhesion. Measurements of the permeability of the three main clear coat types are also included in this chapter because the permeability of coatings can influence their outdoor performance. Experimentation in Chapter 4 combined the wood pre-treatments tested in Chapter 3 and untreated controls with seven state-of-the-art clear coatings and examined the performance of the combinations during 349 days of natural weathering in Southeast Australia. Chapter 5 discusses the results of both experimental chapters, offers suggestions for further research and draws overall conclusions. A better understanding of the influence of wood treatments on coating properties and how they increase the performance of state-of-the-art clear coatings could help manufacturers to design durable clear coat systems for wood used outdoors. Moreover, it could make wood more competitive and cost-effective and help to

satisfy the long-standing market demand for high performance clear coating systems for wood, that will give 10 years maintenance free performance outdoors.

2. Literature review

2.1 Introduction

There is a growing demand for wood as a building material because wood is a renewable resource, but the unpleasant appearance of weathered wood surfaces in combination with high maintenance requirements has limited the use of wood products in exterior applications (Feist & Hon 1984; Buchanan & Honey 1994). The effects of weathering on wood can be reduced by applying coatings to wood. Wood coatings can be either opaque, semi-transparent or transparent (Feist & Mraz 1980). Transparent coatings are increasingly demanded by architects and customers since they retain the natural appearance of wood (Sell & Feist 1986; George et al. 2005). However, transparent coatings applied to wood used outdoors tend to fail prematurely (MacLeod et al. 1995; Singh & Dawson 2003). The durability of clear coatings can be improved using treatments such as the modification of wood with chromic acid or the grafting of UV absorbers that restrict the photodegradation of wood (Williams 1983; Williams & Feist 1985; Kiguchi & Evans 1998). The commercial application of these particular systems has, however, been limited due to their toxicity, impractical application procedures or high costs (Evans et al. 2002; Evans 2009). Nevertheless, there is still great interest in finding treatments that can enhance the durability of clear coats and reduce their high maintenance levels (Evans et al. 2002).

In this chapter, the use of exterior coatings for wood will be reviewed. Emphasis will be placed on the types of clear coats applied to wood, their durability and the mechanisms responsible for their failure when they are used outdoors. In addition, the different ways of improving clear coat durability will be reviewed.

2.2 Use of wood outdoors and the need for coatings

2.2.1 Exterior use of wood

The use of wood outdoors dates back several millennia. In approximately 2500 B.C., wooden boats were built by the Egyptians for the transportation of goods down the Nile (Hodges 1970). Wood was also used by the Romans and Greeks as columns/piles for substructures in their cities. Wooden piles as well as bridges were widely utilized during the empire of Alexander the Great around 350 B.C. (Richardson 1993; Ulrich 2008). At this time, attempts to increase the durability of wood in exterior applications were made. According to Richardson (1993), Alexander the Great ordered the application of olive oil to all exposed wooden structures to protect them from decay. The Roman naturalist Pliny the elder (AD 23-79) recommended the use of cedar oil to prevent wood from rotting (Richardson 1993).

The reasons for using wood in the past were probably similar to those that apply today, and include wood's local availability as a raw material, low cost, good material properties and ease of processing. A more contemporary reason for utilizing wood outdoors is the increasing demand for sustainable and 'environmentally friendly' products. Wood is obtained from a renewable resource, trees, and because of its CO₂ neutrality it is able to meet these demands. All these

characteristics make wood a desirable material for many applications such as siding, windows, garden furniture, boats and buildings (Jones 2004).

In addition, wood is increasingly favoured by architects and designers because it is visually appealing. This trend is particularly apparent in the market for facades where the ability of wood to counterbalance the 'heavy appearance' of glass and steel has led to increased use of wood (Forsythe 2007). This increased market share of wood in the facade market as well as the increasing demand for the use of renewable materials such as wood suggests that protecting the appearance of wood through the use of coatings will become increasingly important in the future (Jones 2004).

2.2.2 The need of coatings for wood used outdoors

2.2.2.1 Decorative purposes

Exterior coatings for wood are required for either decorative or protective purposes, as mentioned above (Nylén & Sunderland 1965; Gaynes et al. 1967; Roberts 1968; Bulian & Graystone 2009). Decorative effects can be achieved with a variety of different classes of coating materials each of which has different opacities; (1) opaque; (2) semi-transparent; and (3) transparent (Bulian & Graystone 2009). Opaque coatings contain pigments which mask the texture and color of the substrate and provide a decorative effect through the color of the pigments (Ali 2005; Talbert 2008; Bulian & Graystone 2009). Semi-transparent coatings contain lower levels of pigments than opaque coatings and do not mask the texture of the substrate. Therefore they create a decorative effect through both color of the

pigments and texture of the underlying substrate (Hall & Giglio 2010). Transparent coatings, on the other hand, impart a decorative effect solely by the formation of a protective overlay that does not completely mask the texture or color of the underlying substrate. Transparent coatings also contain some pigments such as extenders, but less pigment is used and they are more transparent than those used in opaque coatings (Ali 2005; Talbert 2008; Bulian & Graystone 2009). Hence, these pigments and particles do not influence opacity or color, but rather adjust coating properties, such as density and gloss as well as the transmission of ultraviolet (UV) radiation through the coating (Ali 2005; Talbert 2008; Bulian & Graystone 2009).

2.2.2.2 Protective purposes

Coatings can protect wood used outdoors but, their protective effect depends largely on the type of degradation involved as well as on the type of coating that is applied to the wood. Three types of degradation can occur when wood is exposed outdoors: (1) weathering; (2) decay and; (3) attack by insects, marine borers and certain mammals such as birds (Highley 1999).

2.2.2.2.a Weathering

Weathering of wood results from the combined effect of solar radiation (UV, visible, and infrared light), moisture and heat, abrasion due to windblown particles, atmospheric pollutants and microorganisms on wood, as mentioned in Chapter 1 (Feist 1982; Feist & Hon 1984; Evans et al. 2005). Weathering of wood is restricted to the wood surface and, as opposed to decay, it does not greatly affect wood's strength properties (Browne & Simonson 1957; Derbyshire & Miller 1981; Feist

1990). The most notable feature of weathered wood is its rough surface texture and gray color (Sell 1968; Chang et al. 1982; Feist 1982; Feist 1983; Williams 1999; Evans et al. 2005).

Degradation of wood caused by weathering can be reduced by applying a coating to the wood before it is used outdoors. Opaque coatings are the most effective coatings at restricting weathering since they completely mask the substrate (Ali 2005; Feist 2006; Talbert 2008; Bulian & Graystone 2009). Clear coatings are less effective for the reasons outlined above (Section 2.1) (MacLeod et al. 1995; Singh & Dawson 2003; Bulian & Graystone 2009).

2.3 Clear coatings for exterior wood

Clear coatings are, as described previously, a desirable method of finishing wood used outdoors. There are large varieties of clear coats available and various methods of classifying these coatings have been developed. Bulian & Graystone (2009) listed 11 potential classification categories for wood coatings based on generic coating type, solid particle content, appearance, chemistry, solvent technology and end use. One problem with these classifications is that most coating types fit in to more than one category and often this leads to indistinct borders between the coatings. Bulian & Graystone (2009) pointed out that a certain classification of the coating is needed only for descriptive purposes, and other information can be neglected or assumed.

Irrespective of coating type, the four main constituents of clear coatings are binders, pigments, solvents and additives (Nylen & Sunderland 1965; Ali 2005; Talbert 2008; Bulian & Graystone 2009). Binders are the most important constituent

since many properties of the wet and dry coating film are determined by them (Nylen & Sunderland 1965). Binders for wood coatings can be natural polymers or synthetically derived, but both types of binders are referred to as resins (Bulian & Graystone 2009). Various types of synthetic binders are employed in wood coatings and the distinction between them has, according to Roberts (1968), higher significance than the distinction between general coating type and opacity of the coating. Because of the significance of binder and binder-type, clear coatings specified in this chapter will be categorized by binder-type. A short explanation will also be given to the terms varnish and lacquer since they are invariably linked to clear coatings as well as to water-borne coating systems.

2.3.1 Naturally derived binders

Linseed oils and tung oils have been the most commonly used naturally derived binders (Gaynes et al. 1967; Roberts 1968; Feist 2006; Bulian & Graystone 2009). Linseed oils have been widely used on their own as binders, but today they are increasingly used to modify varnishes and alkyd resins (Roberts 1968; Talbert 2008; Bulian & Graystone 2009). Tung oils, on the other hand, have been mainly used in conjunction with other materials such as phenolic resins, and less often as binders on their own (Derksen et al. 1995). Both linseed and tung oils are classified as drying oils because they cure due to a combination of oxidation and polymerization, also referred to as auto-oxidation (Roberts 1968; Talbert 2008; Bulian & Graystone 2009). The main components of drying oils, (>97%), are esters from glycerol and fatty acids, also called glycerides (Nylen & Sunderland 1965; Bulian & Graystone 2009) (Figure 2.1). Other constituents that accompany these

esters such as phospholipids and free fatty acids are eliminated during refining (Bulian & Graystone 2009).

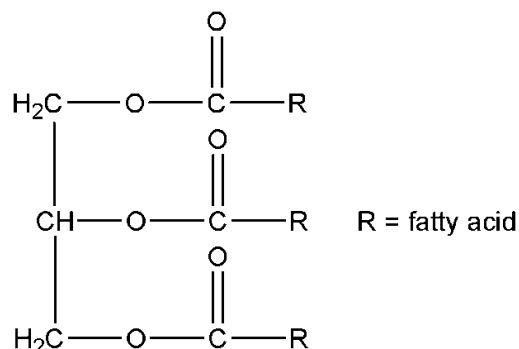


Figure 2.1: Tri-ester of glycerine and an unsaturated fatty acid (Goldschmidt & Streitberger 2003)

Exterior clear coatings based on oil binders penetrate the substrate and therefore they are less prone to failure by cracking and peeling (Black et al. 1979). The service life of oil based clear finishes is only one to two years and therefore they are usually not recommended for outdoor use (Feist 1984; Feist 2006). Furthermore, as Williams (1999) points out, if oil based coatings are to be used outdoors they must contain an adequate amount of mildewcides to prevent premature failure.

Natural resins such as rosin, Congo, Damar, Kauri and Copal were widely used as binders in clear finishes until the late 1940s, but their importance in exterior wood finishes today is negligible (Roberts 1968; Mills & White 1977; Ali 2005; Bulian & Graystone 2009). Natural resins were usually added to varnishes to influence properties such as hardness, gloss and moisture resistance (Roberts 1968). Today the supply of most natural resins has disappeared and they are only used in very special applications (Mills & White 1977).

2.3.2 Synthetically derived binders

Synthetically derived binders were developed in the early 1900s, but only gained industrial importance approximately 50 years later (Nylen & Sunderland 1965; Ali 2005). According to Roberts (1968), synthetic binders are composed of repeating molecular units, which form, depending on their functionality, reactivity and the type of polymerization involved, linear, branched, or cross-linked polymer chains. Molecular units within these polymer chains can exhibit different properties and this enables manufacturers to construct synthetic binders that are customized for particular applications (Nylen & Sunderland 1965). The synthetic binders examined here are the ones most commonly used in exterior wood coatings. Some of the binders are also used in other applications such as adhesives.

2.3.2.1 Alkyd resins

Alkyd resins were one of the first synthetic binders developed for use in coatings (Bulian & Graystone 2009). According to Kienle & Ferguson (1929), alkyd resins include all complexes formed by reactions of polyhydric alcohols and polybasic acids. The most common polyhydric alcohols and polybasic acids for alkyd resins are glycerol and phthalic anhydride, respectively, which were first used by Smith in 1901 (Kienle & Ferguson 1929; Nylen & Sunderland 1965; Roberts 1968). Another polyhydric alcohol used for the production of alkyd resins is pentaerythritol (Roberts 1968; Ali 2005; Bulian & Graystone 2009) (Fig. 2.2). The use of pentaerythritol allows alkyd resins to be synthesized that are faster setting and more durable (Roberts 1968).

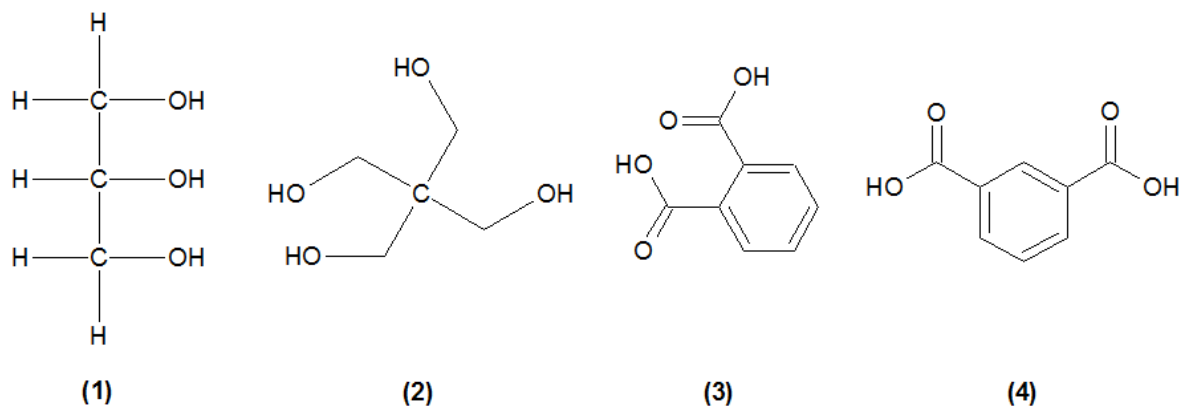


Figure 2.2: Chemicals commonly used to synthesize alkyd resins: (1) Polyhydric alcohols glycerol; (2) Pentaerythritol; (3) Phthalic anhydride orthophthalic acid; (4) Phthalic anhydride isophthalic acid (Bulian & Graystone 2009)

The major disadvantages of alkyd resins synthesized using glycerol and phthalic anhydride are their brittleness and insolubility (Nylen & Sunderland 1965; Roberts 1968; Paul 1985). In the late 1920s, Kienle solved this problem by adding fatty acids and oils to the chemical constituents of the alkyd resin (Paul 1985). Accordingly, the properties and possible end use of alkyd resins are to a large extent influenced by the amount of fatty acids or oils added to the resin (Talbert 2008). Therefore, alkyd resins are generally classified using their oil content. The following classifications can be found in the literature (Gaynes et al. 1967; Dören et al. 1994; Heitkamp & Pellowe 1995; Ali 2005; Talbert 2008; Bulian & Graystone 2009):

- (1) Long oil alkyd: percent of oil or fatty acid > 60%
- (2) Medium oil alkyd: percent of oil or fatty acid = 40-60%
- (3) Short oil alkyd: percent of oil or fatty acid < 40%

A further distinction between alkyds is based on their drying characteristics. Drying alkyds containing higher levels of drying oils (medium to long-oil) cure due to auto-oxidation and this enables a film to form (Ali 2005; Talbert 2008; Bulian &

Graystone 2009). Non-drying alkyds (short-oil) do not dry in air and require heat for curing (Talbert 2008; Bulian & Graystone 2009). The former types of alkyd possess high elasticity and good exterior durability making them suitable for coatings applied to porches, decks, sidings and other architectural applications (Roberts 1968; Ali 2005; Bulian & Graystone 2009). Non-drying alkyds are mainly used as plasticizers for other synthetic resins because they improve the flexibility of the resins by reducing their glass transition temperatures (Talbert 2008; Bulian & Graystone 2009).

2.3.2.2 Acrylic resins

Acrylic resins are the most widely used synthetic binder type for coatings (Linak & Kishi 2010). Acrylic resins can be described as addition polymers made up of esters of acrylic and methacrylic acids (Roberts 1968; Paul 1985; Friel 1995; Talbert 2008) (Fig. 2.3). Acrylic resins utilized by the coatings industry are divided into two types: (1) thermoplastic acrylic resins and (2) thermosetting acrylic resins (Friel 1995; Ali 2005).

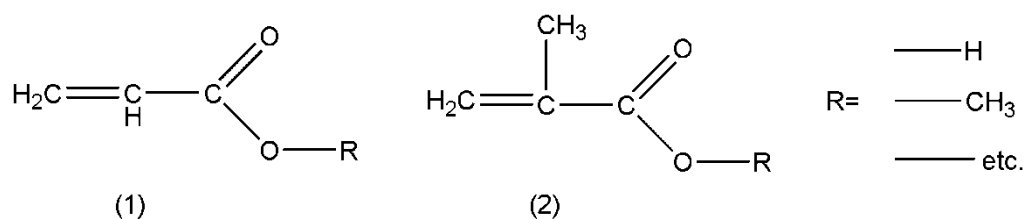


Figure 2.3: Esters of acrylic acid (1) and methacrylic acid (2) (Goldschmidt & Streitberger 2003)

2.3.2.2.a Thermoplastic acrylic resins

Thermoplastic acrylic resins are defined as acrylic polymers carried in a solvent, which form a film due to evaporation of the solvent (Friel 1995). Thermoplastic acrylic resins contain high molecular weight polymers leading to good film properties, but they also need increased amounts of solvents to generate processable viscosity levels (Friel 1995; Ali 2005). Because of restrictions on volatile organic compounds (VOC) Friel (1995) pointed out that the use of intermediate molecular weight polymers as well as the reduction of deleterious low-molecular-weight fractions provides a way of finding a good balance between minimum solvent amount and maximum molecular weight. The use of water as a solvent is another way of lowering VOC levels and has been used in several sectors including those that make architectural and wood coatings (Ali 2005; Bulian & Graystone 2009). Despite these methods of reducing VOCs and the good properties of thermoplastic acrylic resins such as clarity and outdoor durability, the demand for these resins is declining (Ali 2005; Bulian & Graystone 2009).

2.3.2.2.b Thermosetting acrylic resins

Thermosetting acrylic resins are similar to thermoplastic acrylic resins with the exception that the former contain functional groups, e.g. hydroxyl groups, which allow film formation due to cross-linking with other components such as polyisocyanates (Friel 1995; Wicks et al. 1999; Bulian & Graystone 2009). Cross-linking by internal (self) cross-linking also contributes to film formation, however, it is not as common (Wicks et al. 1999; Bulian & Graystone 2009). Generally cross-linking is initiated by heat and takes place after application of the coating, which

enables the use of low molecular weight polymers that are easier to apply (Friel 1995; Ali 2005; Talbert 2008). During cross-linking, low molecular weight polymers are converted into high molecular weight polymers generating the typical properties of thermosetting acrylic resins such as high hardness, good exterior durability and high resistance to solvents and heat (Friel 1995; Ali 2005).

An alternative to cross-linking caused by chemical reactions of functional groups is photochemical cross-linking. During the photochemical activation process, cross-linking of polymers is initiated by free radicals or cations generated by the reaction of photoinitiators with high-energy electromagnetic radiation (Bulian & Graystone 2009). Photoinitiators usually split into radicals by either homolysis or hydrogen abstraction (Goldschmidt & Streitberger 2003). Photochemical activation is often referred to as UV curing, but this only represents radical formation triggered by the absorption of UV radiation by photoinitiators (Pappas 1992).

A further method of radiation curing involves higher energy electron-beams (EB). In contrast to UV curing, EB curing utilizes high-energy electrons and X-rays to excite polymers directly in the resin (Pappas 1992; Norris et al. 2000). Despite the advantages of EB curing, the high capital costs of this technology have prevented its wide-spread use by industry (Pappas 1992; Goldschmidt & Streitberger 2003).

2.3.2.3 Polyurethane resins

Polyurethane (PUR) resins are defined as the product of a polyaddition reaction between isocyanate elements and hydroxyl functional groups (Nylen & Sunderland 1965) (Fig. 2.4). Polyaddition reactions to form PUR resins were discovered by Wurtz in 1848 and started to stimulate industrial interest around 1940

when the German chemist Otto Bayer transferred these reactions to polyfunctional structural elements (Nylen & Sunderland 1965; Goldschmidt & Streitberger 2003).

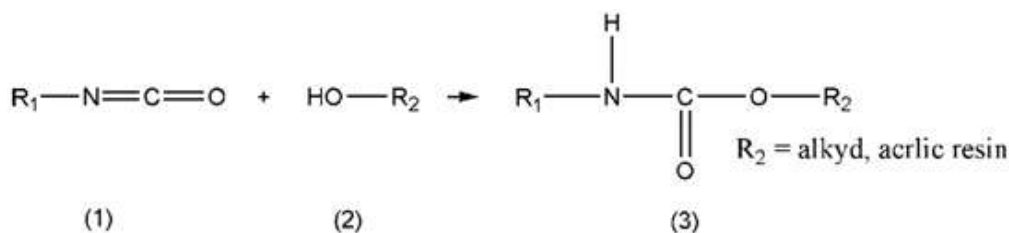


Figure 2.4: Urethane (3) formed by the reaction of isocyanate (1) and alcohol (2) (Goldschmidt & Streitberger 2003)

PUR resins are very reactive at room temperature due to their isocyanate groups (Nylen & Sunderland 1965). The exact rate of reactivity, however, depends on the type of isocyanate employed. Isocyanates can be either aromatic, aliphatic or cycloaliphatic with a corresponding reactivity from highest to lowest, respectively (Müller & Poth 2006). The aromatic isocyanate, toluene diisocyanate (TDI) and the aliphatic isocyanate, hexamethylene diisocyanate (HDI) are the main types of isocyanates used in PUR coatings, and both contain two functional groups which are necessary to achieve good cross-linking of the resin (Müller & Poth 2006; Bulian & Graystone 2009). Besides TDI and HDI there are other diisocyanates used for coatings including diphenylmethane diisocyanate (MDI) and isophorone diisocyanate (IPDI) (Bulian & Graystone 2009). Isocyanates in their unmodified forms are very toxic and can cause respiratory problems or elicit hypersensitivity in people even after short periods of exposure (Nylen & Sunderland 1965). Therefore, isocyanates are usually utilized as oligomers, which are less toxic but still require protective measures by the people handling them (Müller & Poth 2006).

PUR based resins can be divided into three groups which according to Bulian & Graystone (2009) are:

- (1) One-pack materials with isocyanates fully reacted
- (2) One-pack materials with isocyanates initially masked and activated during film formation
- (3) Two-pack materials with separate isocyanates

Two-pack materials are used widely in the coating industry and these require the mixing of both components before application. The first component contains polymers with hydroxyl groups, e.g. alkyds or acrylics, and the second component contains polyisocyanates with at least two isocyanate groups (Bulian & Graystone 2009). Two-pack PUR coatings offer good properties such as excellent chemical and abrasion resistance paired with an optimum balance of hardness and flexibility (Müller & Poth 2006). Additionally when aliphatic polyisocyanates are employed yellowing of the film is strongly reduced (Nylen & Sunderland 1965).

2.3.3 Varnishes

The term varnish is often used colloquially to describe transparent coatings for wooden products. A more specific way to define varnishes is given by Roberts (1968) who states that varnishes are a homogeneous mixture of resin, drying oil, drier and solvent. Varnishes are classified as oleoresinous materials due to the combination of resin and oil. Oleoresinous materials are manufactured by cooking oils together with naturally or synthetically derived resins (Bentley 1999). Many different types of resins can be incorporated into varnishes. According to Gaynes et al. (1967) alkyd resins and phenolic resins have been widely used for many years.

Varnishes based on phenolic resins in particular are characterized by good resistance to heat and chemicals. However, they tend to yellow during outdoor exposure, which has limited their use to interior applications or exterior applications on darker wood species.

The properties of varnishes also depend on the types and amount of oils that they contain. Oils such as tung and linseed are preferred and the durability of varnishes is classified according to the amount of oil they contain (or oil length) (Bentley 1999). Oil lengths for varnishes are specified in gallons of oil used per 100 pounds of resin (Gaynes et al. 1967). Varnishes can contain either short, medium or long oils with oil contents of less than 15 gallons, between 15 and 30 gallons or more than 30 gallons per 100 pounds, respectively (Roberts 1968). Short oils have the fastest drying times whereas long oils have the highest durability and are used in exterior varnishes (Roberts 1968).

2.3.4 Lacquers

Lacquers are commonly applied to wood, but the term causes much confusion (Roberts 1968). This confusion derives mainly from the different definitions for lacquers. For example, Gaynes et al. (1967) mention that for many years the term lacquers solely defined products made with nitrocellulose. The American Society for Testing and Materials (ASTM), however, defined lacquers as coatings which dry by solvent evaporation (Gaynes et al. 1967). In addition to these definitions, the term lacquers has also been used to describe transparent coatings (Bulian & Graystone 2009).

A more adequate definition of lacquers is that they are easy to apply, fast drying coatings, which can be dissolved in their original solvents (Roberts 1968). Lacquers can be clear or opaque, applied by several techniques, be either water or solvent borne and contain any type of binder (Roberts 1968).

2.3.5 Water-borne clear coatings

Water-borne coatings have generated considerable interest in the past two decades. The reasons for this interest has been the need for companies to lower emissions of volatile organic compounds (VOC) and the low cost of water compared to organic solvents (Müller & Poth 2006). Despite these advantages, water-based coatings also have some operational disadvantages such as the need for increased drying energy, longer flash-off times, less efficient substrate wetting and in the particular case of wood, grain raising (Dören et al. 1994; Müller & Poth 2006; Bulian & Graystone 2009).

Water-based coatings can contain any type of binder including those used in solvent-based coatings (Bulian & Graystone 2009). The difference between water-borne and solvent based coatings is that the latter are true solutions, whereas water-based coatings can be a solution, a colloid or a dispersion. The type of system employed in water-borne coatings appears to be dependent on the nature of the binder that is utilized. According to Dören et al. (1994), solution, colloid and dispersions are generally classified using particle size which is as follows:

Solution	0.001 μ m	(water soluble)
Colloid	0.001-0.1 μ m	(colloidal dispersion)
Dispersion	> 0.1 μ m	(aqueous emulsion)

It has been reported that the dry film properties of water-based coatings are similar to those of solvent based-coatings although differences exist in the rheology of the liquid (Bulian & Graystone 2009). Müller & Poth (2006) pointed out that some water-soluble resins generate water-sensitive dry films and their use is therefore restricted to that of additives or co-binders.

2.4 Durability and failure mechanisms of clear coatings

The durability of clear coatings used on wood surfaces in exterior applications is poor, as mentioned in Chapter 1. According to Cassens & Feist (1991) clear coatings usually fail within two years of exterior exposure. Similar findings have also been reported by Feist (1997). Hence, clear coatings are not recommended for use on wood exposed outdoors (Ashton 1980; Cassens & Feist 1991; Dawson et al. 2008).

The main reason for the poor durability of clear coatings used on wood outdoors stems from the penetration of the coating by UV and visible light and degradation of the underlying wood (MacLeod et al. 1995). To overcome this problem, attempts have been made to reduce the transmission of radiation through clear coatings or increase the photostability of the underlying wood.

There are different mechanisms that cause the failure of clear coatings used on wood outdoors. These failure mechanisms can be caused by different factors or combinations of them, including problems resulting from application of the coating, physical and chemical properties of the coating, wrong choice of coating type and inadequate quality and design of the wooden structure (de Meijer 2001; Weldon 2002).

2.4.1 Delamination

Delamination is one of the typical ways that clear coatings fail when they are used on wood exposed outdoors (H.E. Ashton 1967). Delamination is characterized by the peeling, flaking and lifting-off of the clear coat from the surface of wood (Fig 2.5).



Figure 2.5: Clear coat delamination on wood samples (left) and a wooden window frame (right). Note the grey discoloration of the wood

During exposure tests of clear coated wood performed by the California Redwood Association in the 1950s it was noticed that delamination of clear coats took place at the wood-coating interface rather than in the coating itself (Estrada 1967). Recently, Singh & Dawson (2003) confirmed this observation. They observed that the delamination of clear coatings is mainly caused by separations of individual wood cells close to the surface. These findings were derived from light microscope photographs of the wood-clear coat interface. These photographs showed parts of separated wood cells which were still attached to the underside of the delaminated coating (Fig 2.6). Singh & Dawson (2003) also observed that separation of wood cells was caused by photodegradation of lignin in the middle lamellae of cells.

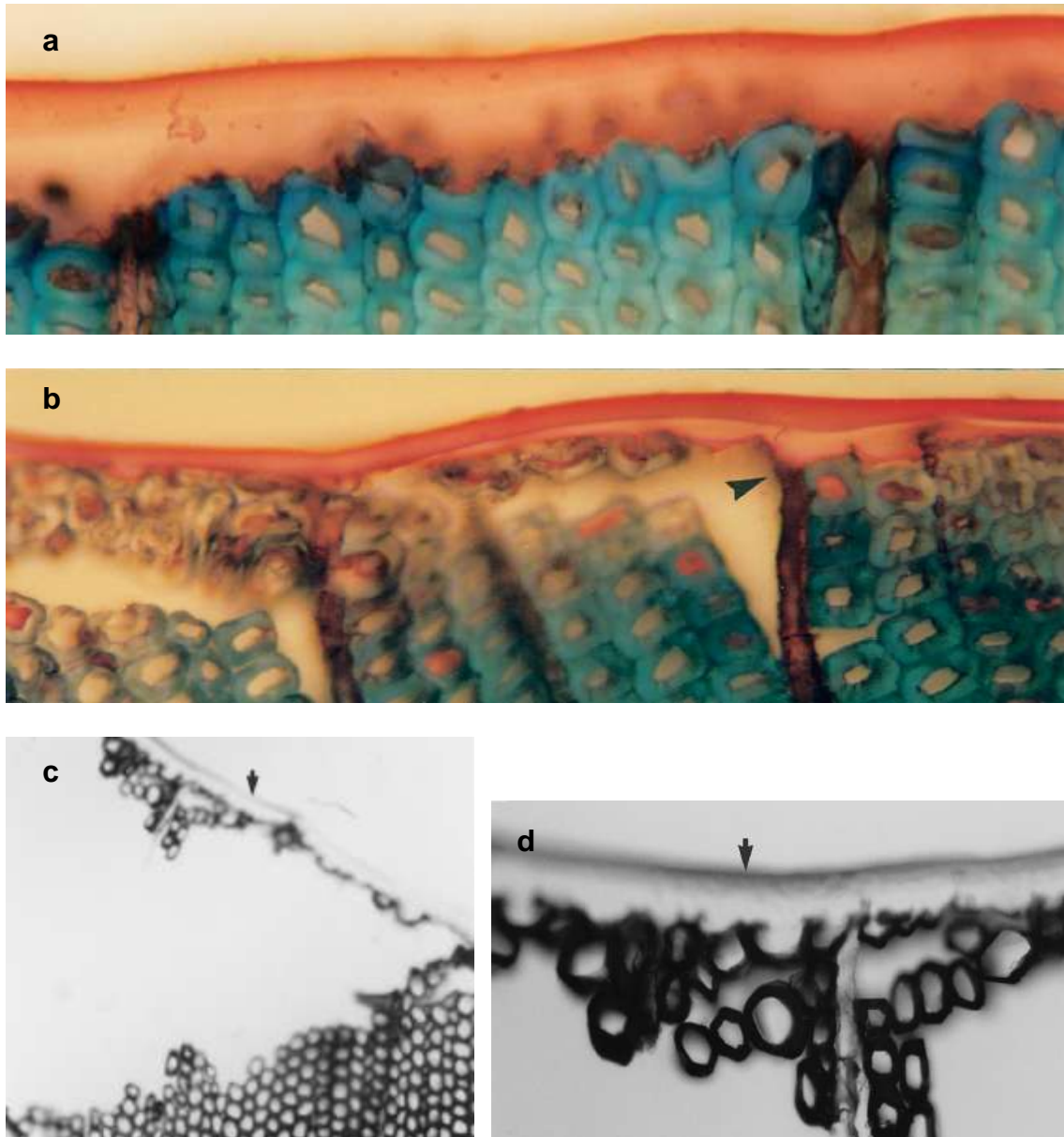


Figure 2.6: Light microscope photographs of transverse sections of coated wood. a: intact coating in close contact to the wood surface; b: detached weathered surface cells and coating parts; c: detached coating with separated wood cells attached to the underside of the coating; d: magnification of detached coating and wood cells (arrow) shown in figure c (adapted from Singh & Dawson 2003)

2.4.2 Cracking

According to Ashton (1967) cracking is another common mechanism responsible for the failure of clear coats on wood used outdoors. There are different

theories about why cracks form in coatings. Floyd (1983) assumed that cracks are caused by dimensional changes in wood that generate stresses in the coating. He further assumed that certain parts of the coating film, such as voids, would concentrate these stresses leading to the initiation of cracks in the coating. These assumptions partially accord with the findings of Ashton (1967) who reported that cracks in clear coatings developed due to the formation of small 'craters' on the surface, which eventually increased in size and developed into cracks running parallel to the grain direction.

Changes in the glass transition temperatures (T_g) of coatings have been suggested as being involved in the development of cracks in coatings. For example, Podgorski et al. (1996) showed that during artificial and natural weathering, cracking of an exterior wood coating was correlated with an increase in the T_g of the coating. However, the addition of UV absorbers to the coating reduced T_g and also the amount of cracks that developed (Podgorski et al. 1996). Therefore, it was suggested that coatings with a low T_g were more flexible and less susceptible to cracking (Podgorski et al. 1996). To ensure adequate flexibility of coatings Podgorski et al. (1996) suggested that the T_g of the coating should be kept below 30°C. Schmid (1988) suggested a T_g of 0-10°C was necessary to maintain coating flexibility for a period of 10-20 years.

Lack of coating flexibility prevents stresses from being relieved by the development of strains in the coating and hence the stresses are relieved by the formation of cracks (Weldon 2002). An experiment by Ashton (1979), however, suggested the opposite. He found that clear alkyds performed worse than short oil

phenolics even though the latter are much less flexible. Hence, Ashton (1979) concluded that flexibility of a clear coating is less important for its durability than water vapor permeation or transmission.

2.4.3 Discoloration

The most obvious example of discoloration of clear coatings during outdoor exposure is the yellowing of PUR coatings (McGinnis 1960). Such yellowing is caused by the formation of peroxides, particularly in coatings containing unsaturated fatty acids. Those fatty acids oxidize the aromatic isocyanates to create colored compounds (Nylen & Sunderland 1965). Aliphatic isocyanates are, as mentioned above, less sensitive to this problem and thus they have been widely employed in PUR coatings (Nylen & Sunderland 1965). Hence, color differences in varnishes containing aliphatic isocyanates were attributed to photo-discoloration of the wood underneath the coating rather than to discoloration of the coating (Yalinkiliç et al. 1999). Similar conclusions have been drawn by MacLeod et al. (1995). They exposed coated and uncoated Western red cedar (*Thuja plicata* Donn ex. D.Don) panels outdoors under a range of cut-off filters. They found that panels coated with a soft-latex based acrylic polymer showed the same severe discoloration at the wood surface as uncoated panels indicating that the coating itself was not responsible for discoloration.

2.4.4 Blistering

Very little research has been carried out on the blistering of clear-coated wood used outdoors. One exception is the work of Pereira & Eusébio (2006) who

examined the blistering behaviour of several wood varnishes exposed to artificial weathering. They found that varnishes without additives, such as UV absorbers (UVA) and hindered amine light stabilizers (HALS), showed less blistering during exposure to fluorescent UV radiation (QUV) and filtered xenon-arc radiation (Xenotest) than varnishes containing these additives. Since blistering represented only one of several assessment criteria for the overall evaluation of varnish performance, Pereira & Eusébio (2006) did not examine in detail the factors responsible for the formation of the blisters. There has not been any other research that specifically examined the formation of blisters on clear-coated wood used outdoors. However, the FPL (1966) stated in a research-note about the finishing of exterior plywood that penetrating finishes such as water-repellents and oils are unaffected by failures such as blistering because they are unable to form a film. The advantage of penetrating clear finishes over film-forming clear finishes was also noted by Laughnan (1956). He pointed out that penetrating clear finishes fail less often than film-forming clear coats and require less maintenance than film-forming clear coats, which makes them the preferred choice for wood exposed outdoors.

2.5 Durability increase of clear coatings through coating alterations

The poor durability of clear coatings on wood exposed outdoors has, as mentioned previously, prevented the wide-spread use of clear coatings for exterior applications (Ashton 1980). According to Hayoz et al. (2003), however, the demand for durable (exterior) transparent coatings that do not obscure wood's color and texture has been increasing. Hence, companies have sought to accommodate this demand by developing more durable clear coats. For example, many clear coats

now contain UVA's and other additives to help screen solar-radiation before it reaches and damages the wood (Hayoz et al. 2003).

2.5.1 Additives

Additives are classified as substances that are added to coatings in small quantities and are capable of modifying one or more properties of the coating [(EN971) cited in (Bulian & Graystone 2009)]. Additives can influence wet film properties, the film formation of the coating itself as well as dry film properties (Bulian & Graystone 2009). The additives discussed in the following sections are designed to inhibit photodegradation of coatings.

2.5.1.1 UV absorbers

2.5.1.1.a Organic UV absorbers

Organic UV absorbers (UVA) are designed to absorb damaging UV radiation and convert radiation energy into heat by means of cis-trans isomerisation or intermolecular hydrogen transfer, also known as tautomerism (Wicks et al. 1999) (Fig 2.7). UVA are able to prevent free radical formation as well as protecting themselves against photodegradation due to these energy conversion processes (DebRoy 2006). UVA can be used in protective overlays such as coatings, but they can also be incorporated into the substrate itself (Gantz & Summer 1957).

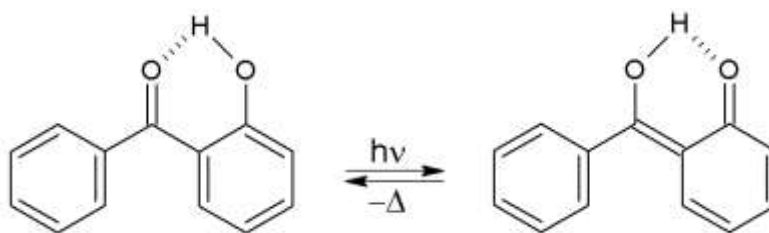


Figure 2.7: Conversion of radiation energy by tautomerism of a typical UV absorber, 2-hydroxybenzophenone (Wicks et al. 1999)

Organic UVA such as benzophenones (BP) and benzotriazoles (BTZ) have a limited light-fastness, but because of their broad absorption spectra and translucency they are widely added to clear coatings (DebRoy 2006). When organic UVA started to be used to improve the light stability of textiles, plastics and coatings, derivatives of benzophenones were thought to be the most efficient UV absorbers (Gantz & Summer 1957). Approximately 10 years later Rothstein (1967) compared four different UVA in combination with four different clear wood coatings and found that benzotriazoles were the most effective. In addition to this finding, he found that alkyd varnishes were the most compatible with UVA, and length increases of their alkyl or alkoxy side chain improved the compatibility of the UVA with all four coatings. Recently another type of organic UVA, the hydroxyphenyltriazines (HPT), has been found to be very effective at improving the light stability of automotive and wood coatings (DebRoy 2006) (Fig 2.8).

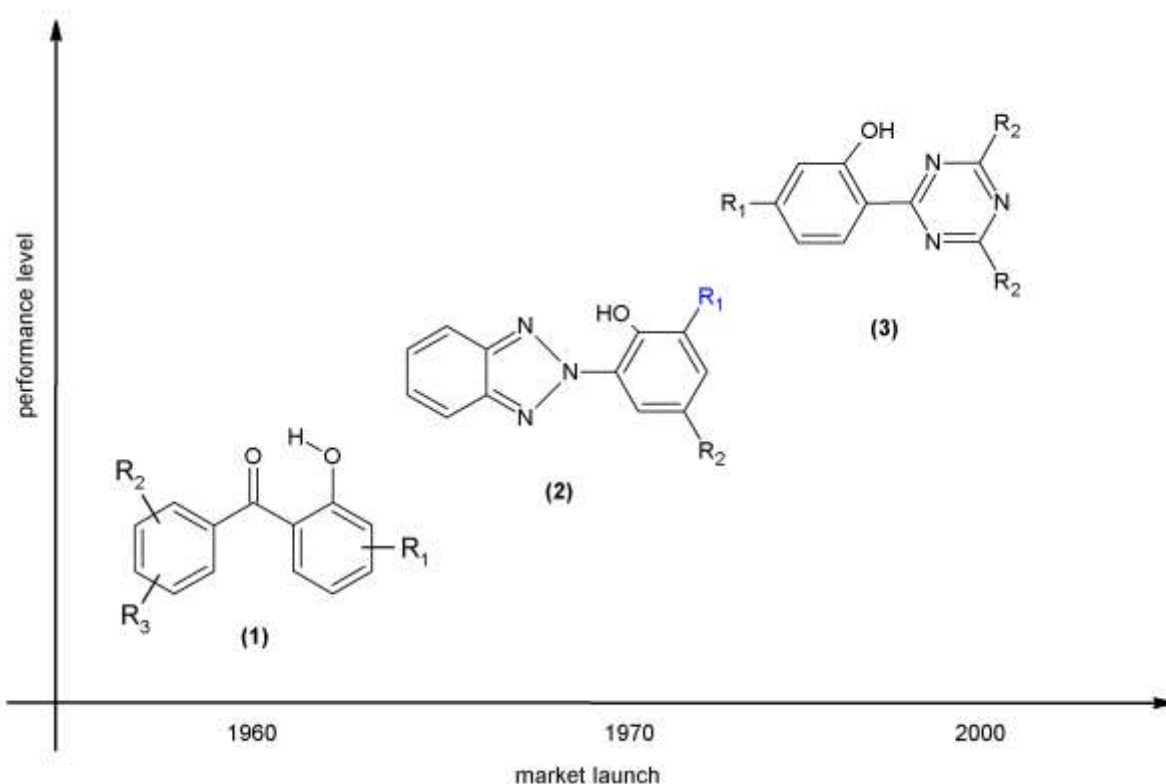


Figure 2.8: Performance level and approximate market launch of benzophenone (1), benzotriazole (2) and hydroxyphenyltriazine (3) derivatives (Wicks et al. 1999; DebRoy 2006)

2.5.1.1.b Inorganic UV absorbers

Inorganic UVA include pigments such as titanium dioxide (TiO_2) and iron (III) oxide (Fe_2O_3) which have good light fastness and permanence (DebRoy 2006). TiO_2 is mainly derived from rutile which contains 96% of the desired white pigment and is the most stable form of TiO_2 (Carp et al. 2004). Fe_2O_3 is one of the three main iron oxides, and is mainly derived from the mineral hematite, but it can also be manufactured by chemical processes such as the heat treatment of iron (II) sulphate (Leskelä et al. 1984; Daintith 2004).

TiO_2 is usually added to clear coatings as ultrafine particles. Fe_2O_3 is added to coatings in the form of so-called transparent, lightly coloured Fe_2O_3 pigments

(Bittler & Ostertag 1980; Daniel et al. 2004). The pigment size of TiO_2 and Fe_2O_3 is limited to a maximum of approximately 15-50nm to increase their transparency in coatings (Allen et al. 2002). Furthermore, size limitations of TiO_2 and Fe_2O_3 shift their scattering ability to shorter wave-length regions, which makes them more effective against UV degradation (Allen et al. 2002). TiO_2 and Fe_2O_3 are able to protect materials against photodegradation by UV absorption and scattering of UV radiation (Hocken et al. 1999). Nevertheless, Aloui et al. (2007) reported that transparent Fe_2O_3 caused discoloration of clear-coated wood during artificial weathering. This finding accords with those of Allen et al. (2002). They noted that Fe_2O_3 also discolored coatings exposed to weathering. In contrast, Allen et al. (2002) reported that clear-coated wood containing TiO_2 performed well during artificial weathering. Similar results were also obtained by Forsthuber & Gröll (2010). They also found that TiO_2 was the best additive at preventing the discoloration of clear-coated wood exposed to artificial weathering in a xenon arc weatherometer.

2.5.1.2 Hindered amine light stabilizers

HALS are derivatives of 2,2,6,6-tetramethylpiperidine (TMP), which act as a free-radical scavenger and hence inhibit autoxidation (Wicks et al. 1999; DebRoy 2006) (Fig 2.9). The first TMP derivative was synthesized by Neiman et al. (1962) by oxidizing triacetone-amine and hydroperoxides in the presence of tungsten, molybdenum or vanadium salts.

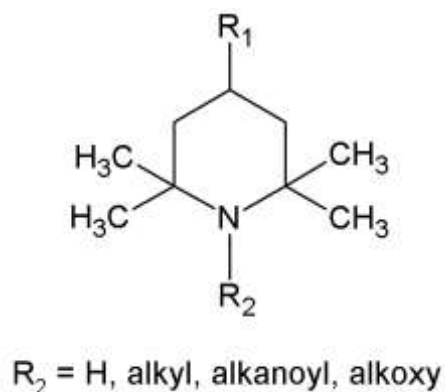


Figure 2.9: Chemical structure of 2,2,6,6-tetramethylpiperidine (Wicks et al. 1999)

HALS are often used in combination with UVA due to their synergistic effects on photostabilization (Toda et al. 1985). For example, Forsthuber & Gröll (2010), reported that HALS protected the surface of coatings, but they were also able to inhibit the photo-oxidation of UVA. As a result, acrylic based clear wood coatings containing UVA/HALS combinations were protected from photodegradation. In addition to this finding, they observed that the combination of a HALS with a UVA strongly reduced the discoloration of the wood beneath the coating.

The mechanisms responsible for the photoprotective effects of HALS are complex and not completely understood (Hawkins 1984). One of the mechanisms that is favoured in the literature involves the Denisov-cycle. In this cycle nitroxyl radicals and aminoethers are formed from HALS followed by the reformation of nitroxyl radicals as described in Figure 2.10 (DebRoy 2006).

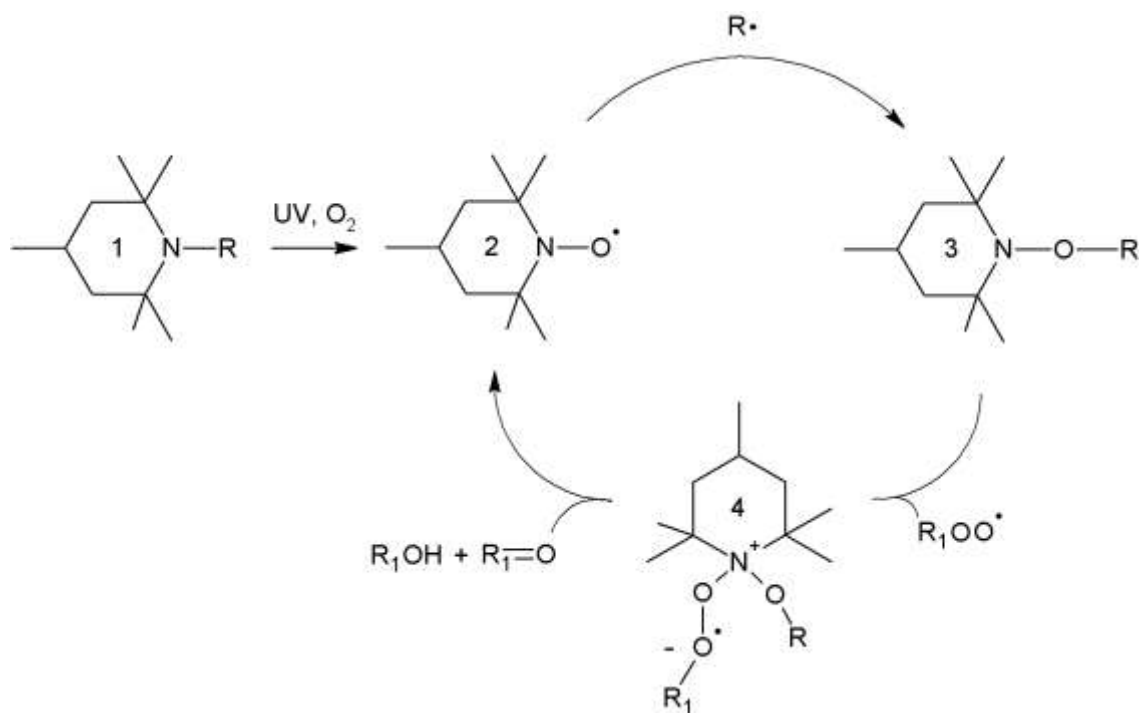


Figure 2.10: Denisov cycle as illustrated by DebRoy (2006); The transformation of HALS (1) to nitroxy radicals (2) is followed by radical trapping under the formation of aminoethers (3); subsequent reactions lead to an intermediate product (4) which transforms back into nitroxy radicals (2)

Allen (1986) mentioned that the Denisov-cycle cannot be the sole mechanism responsible for the photoprotective efficiency of HALS. He suggested that side reactions contributed to the effectiveness of the cyclic mechanism to compensate for the deficiency of nitroxyl radicals competing with oxygen for the scavenging of alkyl radicals (Allen 1986). Beside such side-reactions, Bortolus et al. (1992) discovered that HALS can stabilize polymers by quenching the singlet excited state of aromatic hydrocarbons.

2.5.2 Changes in coating thickness

The effect of film thickness on the performance of coatings was first examined by Schuh & Theuerer (1937). Their research used biennial outdoor and

indoor tests, and included 13 different coatings applied to brass sheets. Their results revealed that the durability of coatings depended on a combination of film thickness and coating type. For example, long-oil varnishes performed better when thick films were applied to the metal substrate, whereas thick short-oil varnish coatings tended to fail (Schuh & Theuerer 1937).

Laughnan (1956) also examined the effects of film thickness on the durability of house paints on wood siding. He found that the application of thicker coatings in the form of two coating layers extended the maintenance intervals of house paints. However, he also pointed out that excessively thick paint films should be avoided. Feist (1994) also found that two layers of transparent wood finishes outperformed one coating layer. Additionally he observed that semi-transparent stains applied to rough sawn wood surfaces performed better than the same coatings applied to smooth wood surfaces. Feist (1994) attributed this finding mainly to the fact that a thicker coating film was applied to the rough wood surface.

2.5.3 Binder alterations

An alternative method of increasing the durability of coatings is to modify the binder. Hon et al. (1985) demonstrated that a transparent acrylic wood coating with a binder containing an internal UV absorber performed very well. The modified binder photostabilized the underlying wood and protected the coating as well. The modified acrylic binder was created in two main steps. The first step included the grafting of 2,4-dihydroxybenzophenone (2,4-DHBP) to glycidyl methacrylate which resulted in the formation of the intermediate product 2-hydroxy-4(3-methacryloxy-2-hydroxy-propoxy) benzophenone (HMHBP) (Fig 2.11). The second step included the

polymerization of HMHBP in tetrahydrofuran resulting in the formation of poly(HMHBP), which was used as the modified binder.

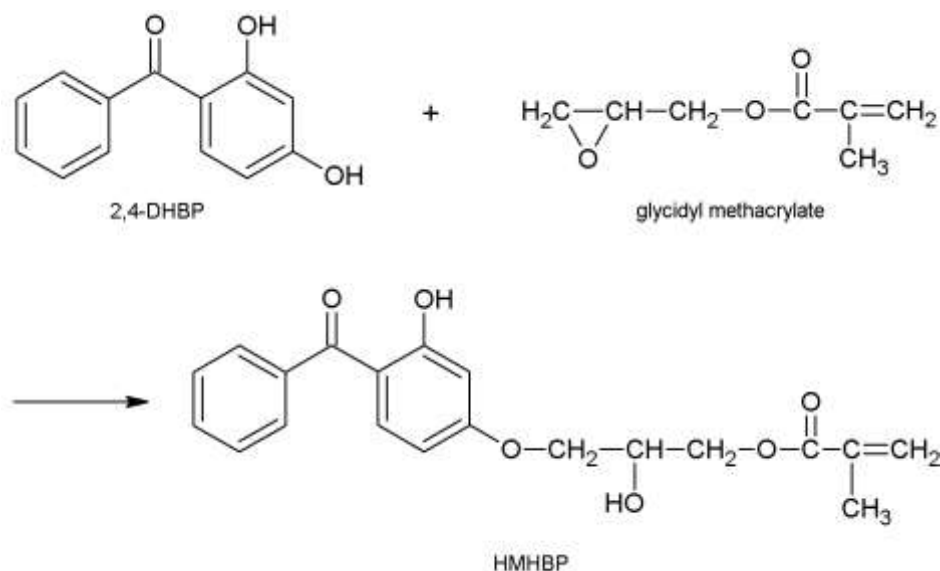


Figure 2.11: Reaction scheme for the formation of 2-hydroxy-4(3-methacryloxy-2-hydroxypropoxy) benzophenone (HMHBP)

Hon et al. (1985) also tested HMHBP copolymerized with alkyl methacrylate (1:1 w/w). The resulting copoly(HMHBP) produced the same levels of color stabilization and brightness retention as poly(HMHBP).

Another type of binder modification that can create highly durable coatings involves the copolymerization of coating binders with fluorine compounds (Munekata 1988; Iezzi et al. 2000; Asakawa 2003). According to Barry (2008) fluoroacrylates are the longest commercially available binder in this class. Fluoroacrylates are defined as copolymers made up of acrylic monomers and monomers containing fluorinated side chains (Wood 2002) (Fig. 2.12). As reported by McKeen (2006) fluoroacrylates belong to the group of partially fluorinated polymers because they

can contain atoms such as hydrogen and chlorine, unlike fluoropolymers, which contain solely carbon and fluorine atoms.

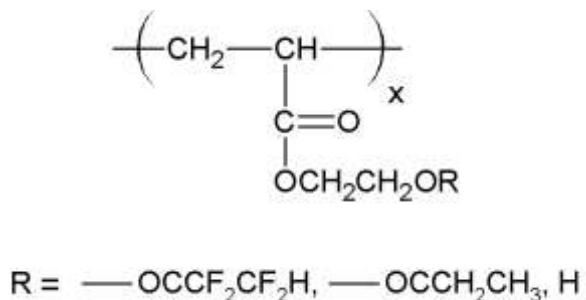


Figure 2.12: Example of a fluoroacrylate

The improved thermal and photochemical resistance of fluoroacrylates is mainly attributed to the introduction of fluorinated groups (Brady 1990). This finding has also been confirmed for other fluorinated coatings such as fluorinated PUR, fluorinated ethylene vinyl ether (FEVE) and poly(vinylidene fluoride) (PVDF). Nevertheless, all fluorinated coatings need a certain percentage of unfluorinated structural units, e.g. acrylic monomers or PUR monomers, in order to maintain important coatings properties such as adhesion and solubility in common solvents (Chiantore et al. 2000; Iezzi et al. 2000). Unfluorinated structural units have a negative influence on the long term stability of fluorinated coatings (Chiantore et al. 2000). Therefore their selection is a key factor affecting the durability of fluorinated coatings and an optimal balance of fluorinated and unfluorinated structures has to be found. Additionally, when fluorinated polymers are used as a clear coating it is still necessary to include UVA in the formulation because UV radiation can still decompose the underlying substrate (Asakawa 2003).

2.6 Durability increase of clear coatings through substrate alterations

Alterations to coatings such as the addition of UVA or HALS have improved the durability of both wood substrates and clear coatings (Rogez 2002). These stabilizers are not completely effective, however, at protecting the substrate, in part, because the stabilizers are susceptible to photodegradation and thermal degradation (Gensler et al. 2000). An alternative way to increase clear coat performance on wood substrates was suggested by Black & Mraz (1974), Feist (1979) and Derbyshire & Miller (1981). They all suggested that the key to successful clear coat performance is to photostabilize the wood prior to finishing. Many attempts have been made since to develop wood stabilizing pre-treatments, but only a few treatments can effectively photostabilize wood (Evans 2009). Furthermore, only a small number of these treatments have been tested in combination with clear coats.

2.6.1 Treatments with known effects on clear coat stabilization

2.6.1.1 Chromic acid

Aqueous chromium trioxide (CrO_3), also known as chromic acid, is a remarkably effective treatment that can inhibit the photodegradation of wood (Williams & Feist 1984). Chromic acid treated wood showed less springwood erosion during artificial weathering than untreated specimens (Black & Mraz 1974). Evans & Schmalzl (1989) showed that chromic acid treatment of wood restricted weight losses of wood veneers during weathering, suggesting that it could also photostabilize lignin. FTIR spectroscopy confirmed that chromic acid treatment

photostabilized lignin in wood veneers exposed to natural weathering (Evans et al. 1992). Williams & Feist (1985) also found that chromic acid imparted dimensional stability to wood and greatly improved the water repellency of the wood surface.

Hon & Chang (1985) first suggested that the stabilizing effects of chromic acid treated wood were due to the formation of photostable lignin-chromium complexes. Hon & Chang (1985) also suggested that photostability results from the formation of complexes between chromic acid and phenolic hydroxyl groups, which are capable of transferring or emitting energy from the modified wood surface. This explanation does not seem plausible because other metal compounds can react with phenolic hydroxyl groups and they do not photostabilize wood. A more likely explanation is that the oxidation of lignin phenol groups and the formation of chromium (III) quinone complexes accounts for the excellent photostability of wood modified by chromic acid (Schmalzl et al. 2003).

Chromic acid pre-treatment of wood significantly improves the performance of clear coatings (Williams & Feist 1985). For example, clear coatings applied to chromic acid pre-treated wood surfaces showed no sign of degradation after 15 years of outdoor exposure in Madison, Wisconsin (Williams & Feist 1985). Preston (2010) mentioned in personal conversations that clear coated house siding pre-treated with chromic acid were still in good condition after 28 years of exterior exposure (Fig. 2.13).



Figure 2.13: Left: Retention of clear finish on wood treated with chromic acid (c/o Sam Williams, US FPL); Right: Clear finish on chromic acid treated radiata pine after 28 years exterior exposure (c/o Alan Preston, Viance)

The commercial application of chromic acid to treat wood has been limited, except in Japan where the Yamaha Corporation pre-treated wooden doors with chromic acid to enhance the weathering resistance of acrylic-urethane finishes (Ohtani 1987). One of the reasons for the limited use of chromic acid as a wood pre-treatment is the initial brown discoloration of the wood surface that slowly changes to green when chromium VI compounds are reduced to lower valence states (Evans et al. 1992). Furthermore, chromic acid is toxic and carcinogenic like other chromium VI compounds (Sax 1975).

Attempts to find other less toxic metal compounds that are as effective as chromic acid at photostabilizing wood have not been successful. Schmalzl & Evans (2003) compared the photostabilizing effects of titanium, zirconium and manganese compounds applied to radiata pine veneers. Their results after 35 days of natural weathering in Canberra, Australia showed that manganese III acetate dihydrate and

potassium permanganate where the most effective treatments followed by some titanates. The manganate treatments were able to restrict weight losses of veneers during weathering and were much more effective than chromic acid controls in restricting tensile strength losses. Titanates were not able to restrict weight losses and their ability to restrict tensile strength losses was lower than that of the manganate treatments. Zirconium treatments were the least effective, but caused less discoloration of the wood than titanates and also the manganese compounds (Schmalzl & Evans 2003).

2.6.1.2 Grafted UVA

The grafting of UVA to wood was first described by Williams in the early 1980s. Williams (1983) synthesized 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone (HEPBP), as described in Manasek et al. (1976). HEPBP was then grafted to the surface of western red cedar specimens (Fig. 2.14).

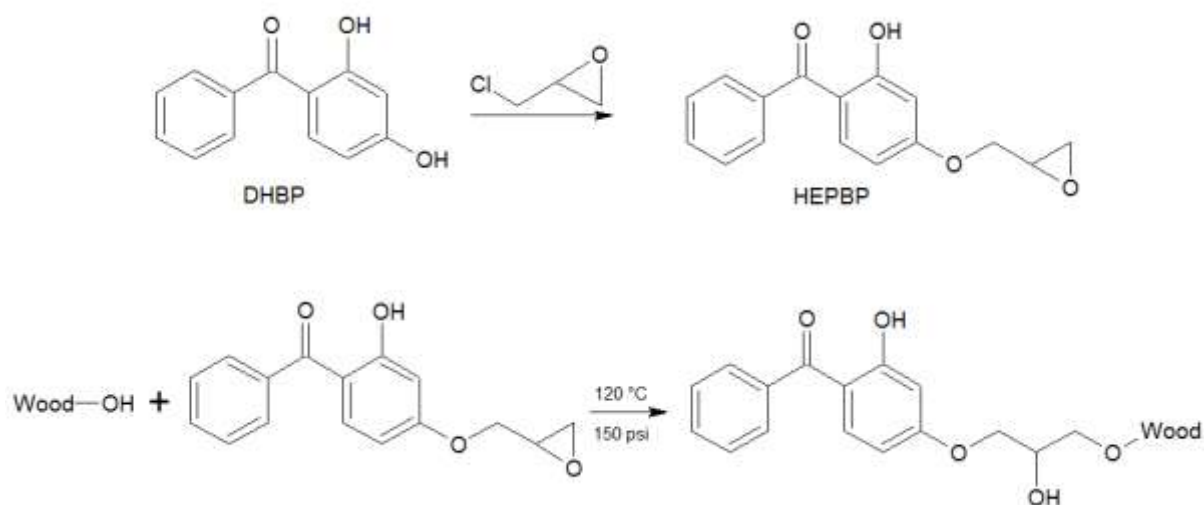


Figure 2.14: Synthesis of 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone (HEPBP) and its reaction with wood

HEPBP was effective at reducing the erosion of springwood in specimens exposed to accelerated weathering. Furthermore, grafting of HEPBP to wood also extended the service life of two coatings, a commercial spar varnish and an exterior grade polyurethane, applied to western red cedar.

Kiguchi & Evans (1998) extended Williams' research by comparing the photoprotective effects of grafted HEPBP with those of chromic acid. Weight loss measurements of treated veneers during a natural weathering trial in Canberra, Australia indicated that the grafting of HEPBP was as effective as chromic acid at restricting weight losses of wood veneers. Additionally, the tensile strength of grafted wood veneers exposed to weathering was superior to those of similarly exposed chromic acid treated veneers. Kiguchi & Evans (1998) also showed that grafting with HEPBP improved the performance of two types of clear coats (Fig. 2.15).

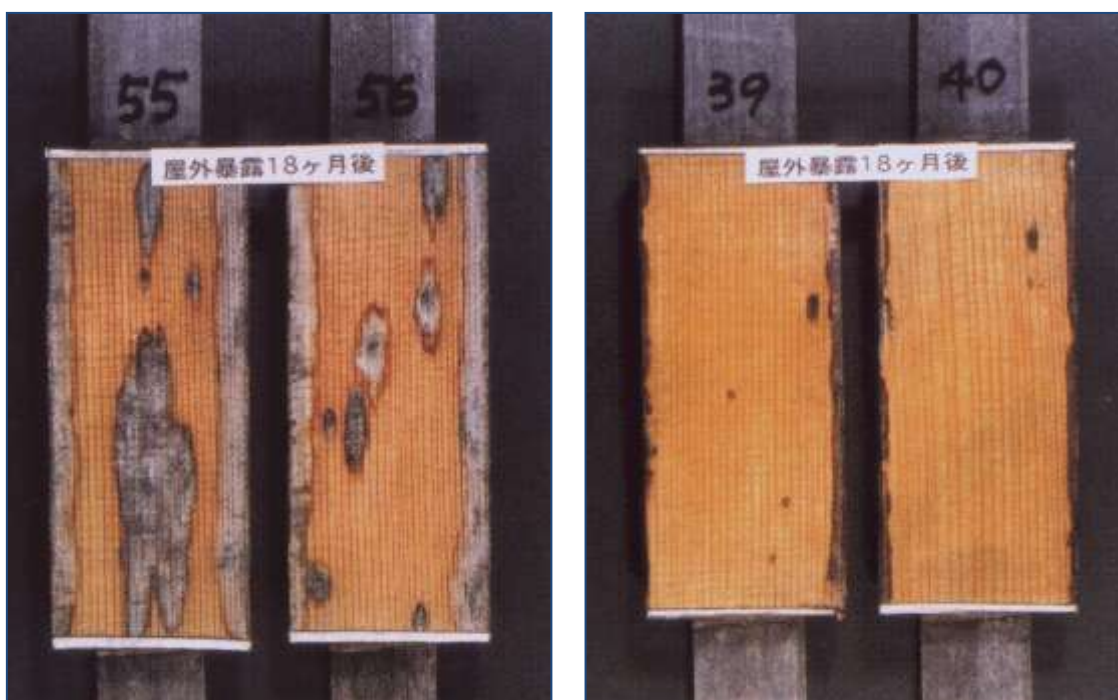


Figure 2.15: Performance of clear finishes on untreated controls (left) and 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone (HEPBP) grafted wood (right) (c/o Makoto Kiguchi)

An alternative to grafting using UVA containing epoxy groups has been the use of UVA containing an isocyanate group. For example, Grelier et al. (1997) grafted several isocyanate derivatives to the surface of Grand fir (*Abies grandis* Douglas ex D. Don) wood, European oak (*Quercus robur* L.) wood and medium density fiberboard (MDF) using a microwave. The grafted hydroxyl phenyl benzotriazole UV absorber (HPBT) 2-[(2-benzotriazinyl)-4-hydroxy-5-tert-butylphenyl]ethylisocyanate had the best photostabilizing effect on both Grand Fir wood and European oak wood. Grafting significantly reduced the total color change (ΔE) of treated wood after eight hours of exposure to UV light. HPBT by itself was less effective at reducing discoloration of MDF boards but showed better performance in conjunction with polyethylene glycol (PEG) and HALS. The beneficial effect of combining HPBT with PEG and HALS was also observed on Grand Fir and European oak samples.

Grafting of UVA containing an isocyanate group, and a polystyrene-maleic anhydride copolymer containing polyethylene glycol chains and a hydroxyphenylbenzotriazole absorber was also effective at reducing the photo-discoloration of wood samples (Grelier et al. 2007). Grafting of this complex polymer to Scots pine (*Pinus sylvestris* L.) samples led to good color retention of uncoated samples and improved adhesion of acrylic finishes on the modified surface after samples were exposed to accelerated weathering. Nevertheless, the color stability of the finished samples was less than that of unfinished samples (Grelier et al. 2007).

2.6.1.3 UVA/HALS combinations

UVA and HALS are widely incorporated into clear coatings to improve their coating durability as well as the durability of the wood substrate against photodegradation, as mentioned above (Rogez 2002; Evans et al. 2005). Chang et al. (1998) used UVA and HALS as a photostabilizing treatment for wood. They pre-treated the surface of Taiwanian (*Taiwania cryptomeriodes* Hay.) heartwood with the UVA Tinuvin 1130 and the liquid HALS Tinuvin 292 prior to the application of a PUR coating containing Tinuvin 1130. Weathering of the specimens in a fluorescent weathering device for 96 hours revealed that discoloration of the wood was significantly reduced by the pre-treatment and modified coating.

Pre-treatment of radiata pine (*Pinus radiata* D. Don) samples with a 2% aqueous solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl followed by the application of a transparent long oil alkyd containing UVA and HALS was able to restrict the photo-induced discoloration of the wood (Schaller & Rogez 2007). Exposed wood panels had lost very little of their original color and no coating defects were present after 18 months of outdoor exposure in Switzerland (Schaller & Rogez 2007). George et al. (2005) also suggested that impregnation of wood surfaces with HALS prior to the application of a clear coat containing UVA could be a useful strategy for protecting wood from photodegradation and enhancing the performance of clear coats used outdoors.

A completely different approach to enhancing clear coat performance with combinations of UVA and HALS was examined by de la Caba et al. (2007). They impregnated a composite panel consisting of a cellulose fibre core and Ayous

(*Triplochiton scleroxylon* K. Schum.) wood faces, with phenol-formaldehyde resin that contained UVA and HALS. Half of the resin treated panels were coated with a PMMA coating before they were exposed together with uncoated panels in a xenon arc weatherometer. Results after 3000 hours of weathering showed that resin treated panels containing the PMMA topcoat performed better than the uncoated samples and no cracks or loss of gloss were observed.

2.6.1.4 Polyethylene glycol treatments

Polyethylene glycol (PEG) is a white, wax-like polymer that has a wide variety of uses (Mitchell 1972). PEG is able to reduce the face checking of wood during seasoning and it can dimensionally stabilize wood by bulking fibers (Stamm 1959). Because of these properties, PEG is a valuable stabilizing treatment for carvings and other archeological artifacts (Mitchell 1972).

According to Ohkoshi (2002), PEG can also photostabilize lignin, although degradation and leaching of PEG over time limits the effectiveness of the treatment. Nevertheless, application of a top coat can prevent leaching of PEG and, as reported by Kiguchi et al. (1997), pre-treatment of Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) plywood with a 10% solution of PEG prevented film failure of clear coatings when the coated plywood was exposed outdoors for two years.

2.6.2 Treatments with presumed effects on clear coat stabilization

2.6.2.1 Benzoyl chloride

Esterification of Scots pine veneers with benzoyl chloride (Fig. 2.16), shows great promise at protecting wood surfaces from photodegradation. Benzoyl chloride

was highly effective at preventing weight losses of wood veneers exposed to both artificial and natural weathering (Evans et al. 2002). Scanning electron microscopy showed that benzylation was able to restrict the degradation of the lignin-rich middle lamella during weathering. FTIR spectroscopy confirmed that benzylation was able to photostabilize lignin in wood exposed to natural weathering. Electron spin resonance spectroscopy indicated that the photostabilization of lignin was due to the ability of benzoyl groups to inhibit the generation of free radicals (Evans et al. 2002). High levels of photostability were found for veneers modified to high weight gains.

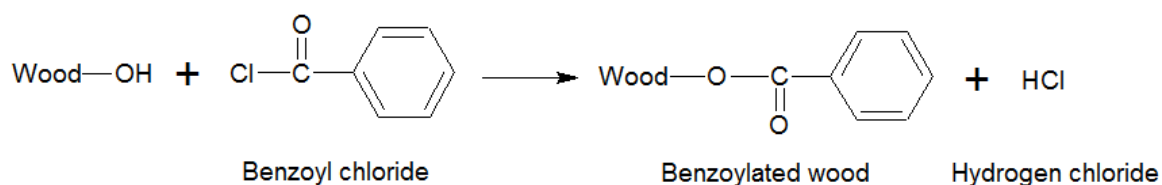


Figure 2.16: Esterification of wood with benzoyl chloride

Subsequently, Pandey & Chandrashekar (2006) found that esterification of Chir pine (*Pinus roxburghii* Sargent) wood with benzoyl chloride reduced the photo-discoloration of samples exposed to UV-light (Fig. 2.17).

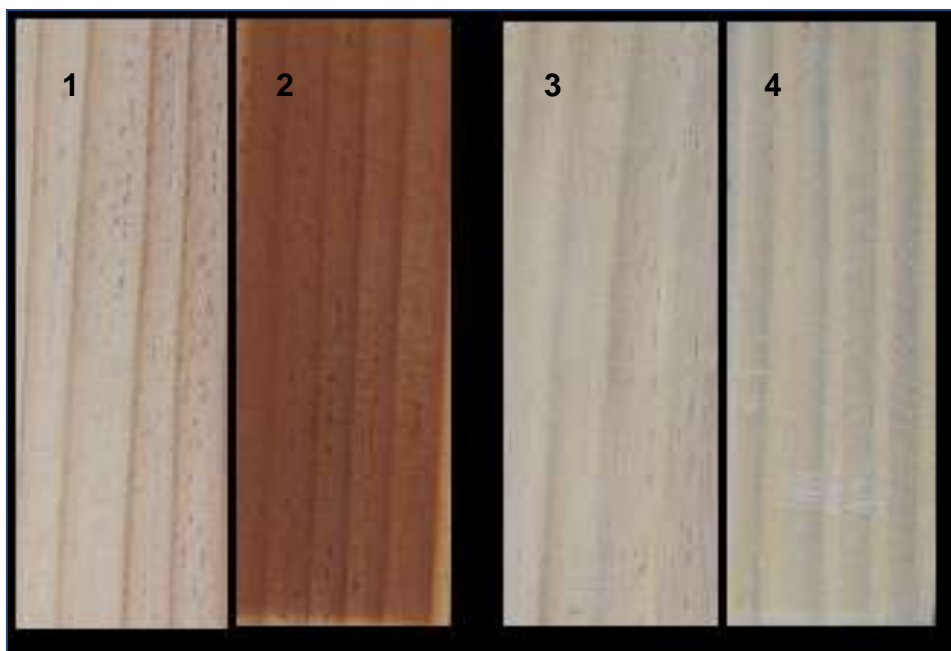


Figure 2.17: Effect of color stabilization on benzoylated Chir pine wood: 1: unexposed, unmodified sample; 2: exposed, unmodified sample; 3: unexposed, benzoylated sample; 4: exposed, benzoylated sample (c/o Krishna Pandey)

Because of its excellent ability to photostabilize wood, benzoylation might be an effective pre-treatment for enhancing the durability of clear finishes on wood (Evans et al. 2002). Nevertheless, no research has been carried out to investigate whether benzoylation can improve the durability of clear coats on wood.

2.6.2.2 Vinyl benzoate

Very recently, Jebrane et al. (2009) found that esterification of wood with the aromatic vinyl ester, vinyl benzoate (Fig. 2.18), was effective at protecting wood from photodegradation.

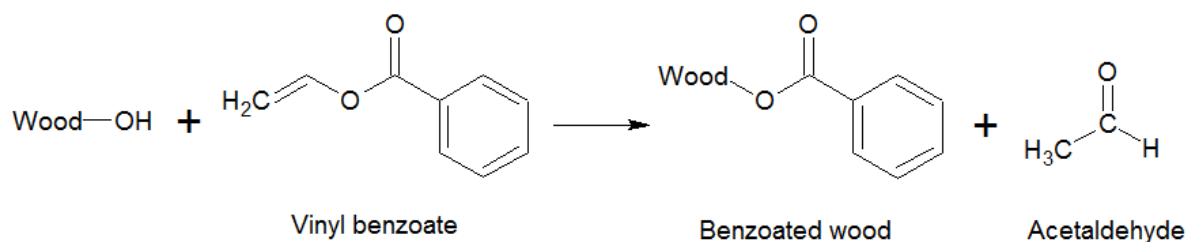


Figure 2.18: Esterification of wood with vinyl benzoate

Vinyl benzoate was able to restrict weight and tensile strength losses of treated veneers exposed to natural weathering, which indicates that the treatment was able to photostabilize lignin and cellulose to some extent (Jebrane et al. 2009). The photoprotective effects of vinyl benzoate treated veneers were positively correlated with the weight gains of the treated veneers (up to a maximum weight gain of approximately 30% based on the initial unreacted, oven-dry weight of veneers). Other aromatic vinyl esters such as vinyl cinnamate and vinyl-4-T-butylbenzoate were less effective at preventing photodegradation of wood veneers (Jebrane et al. 2009).

Vinyl benzoate treatment of wood to high weight gains appears to be a good pre-treatment for wood products used outdoors that need to be resistant to weathering (Jebrane et al. 2009). Treatment of wood with vinyl benzoate might also improve of clear coat durability, but no research has been performed to test this hypothesis.

2.6.2.3 Phenol-formaldehyde resins

Phenol-formaldehyde resins (PF) are polymers formed by polycondensation reactions between phenols and formaldehyde solutions (Fig 2.19) (Ibeh 1998).

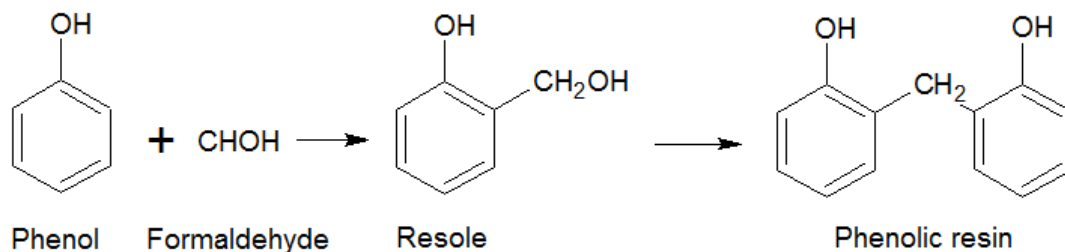


Figure 2.19: Principle of polymerizing a phenol with formaldehyde to form intermediate resoles. Further polycondensation of resoles results in the formation of a thermoset phenolic resin. Note: The process shown represents resole phenol-formaldehyde resins and usually leads to the formation of large 3-dimensional phenolic resin networks

The two main types of PFs are resol resins and novolak resins. According to Ibeh (1998) there are several differences between resol and novolak as follows:

Table 2.1: Differences between resol and novolak phenol-formaldehyde resins

	Resol	Novolak
Production	One-stage resin produced by using alkaline catalysts Produced via B-staging	Two-stage resin produced by using acidic catalysts Produced by prepolymerization
Properties	Usually liquid after production Shelf life of less than a year Split off water when curing Methylol-bearing resins Phenol to formaldehyde ratio: 1: 0.35-0.6	Usually solid after production Infinite shelf life Twice as dimensionally stable as resol Split off ammonium when curing Non-methylol bearing resins Phenol to formaldehyde ratio: 1: 0.7-0.9
Application	Typically used for casting and bonding	Mainly used for molding compounds

The first pre-treatment of wood with PF was carried out by Baekeland (1909), the inventor of the Bakelite process. He pre-treated wood with PF by both dipping and coating and subsequently cured the resin using heat. After the treatment, Baekeland (1909) reported that the modified wood was resistant to boiling water, most solvents and chemical solutions. Further research on wood pre-treated with PF was done by Stamm & Seborg (1936). They found that PF-resins were able to reduce the swelling and shrinking rates of wood. Moreover, Stamm & Seborg (1939) found that treatment of Douglas-fir plywood with PF significantly reduced the checking of face plies during natural weathering. The treatment also improved the decay resistance of wood. The ability of PF to stabilize wood was later explained by its ability to physically block hydroxyl groups (Stamm & Baechler 1960).

Sudiyani et al. (1999), treated albizia (*Paraserianthes falcataria* (L.) I. Nielsen) and sugi (*Cryptomeria japonica* D. Don) wood blocks, with a low molecular weight PF. The treatment was able to significantly reduce the discoloration (ΔE) of specimens during one year of natural weathering and 1,080 hours of artificial weathering. Furthermore, the treatment helped to reduce weight losses of wood blocks due to photodegradation as well as weight losses due to decay.

De la Caba et al. (2007) also found that resin treated composite panels top-coated with a PMMA coating performed better than uncoated samples. Presumably, treatment of wood with PF could enhance the performance of clear coats. However, de la Caba et al. (2007) ascribed the photoprotective effect that they observed to the UVA and HALS. Therefore, investigations of the ability of PF-resins or PF modified with UVA and HALS to photostabilize wood have not been carried out.

2.6.2.4 Reflectors

Very little research has been carried out on the ability of reflectors such as TiO_2 to photostabilize wood and enhance the performance of clear coatings. Blackburn et al. (1991) reported that small amounts (0.5-1.0%) of micronized TiO_2 were able to protect wood surfaces when applied solely or in combination with iron oxide. Because iron oxides alter the natural appearance of wood, there has also been interest in the use of zinc oxides as photoprotective agents for wood (Schulte 2001). Zinc oxides may be better than TiO_2 at protecting materials against long-wave UVA radiation and they impart less white coloring at given concentrations (Pinnell et al. 2000). There has also been interest in using other rare metal oxides such as cerium oxide as photoprotective wood pre-treatments (George et al. 2005). For example, recently, Liu et al. (2010) examined the photostability of yellow cedar (*Chamaecyparis nootkatensis* (D.Don) Spach) veneers pre-treated with micronized iron oxide or cerium oxide nanoparticles. Iron oxide was the most effective treatment at preventing weight and tensile strength losses of veneers exposed to 30 days of natural weathering in Vancouver, Canada. Veneers treated with iron oxide showed the least discoloration during weathering, although previous experiments, which examined the color retention of clear coatings containing, reported otherwise (Allen et al. 2002; Aloui et al. 2007). Cerium oxide nanoparticles were not effective at restricting the weight and tensile strength losses of wood veneers and were clearly less effective than conventional photostabilizers such as UVA/HALS and micronized iron oxide. Cerium oxide nanoparticles were also ineffective at preventing the photo-discoloration of exposed veneers.

2.7 Summary

Photodegradation of wood leads to an unpleasant discoloration and roughening of wood surfaces exposed outdoors (Sell 1968; Chang et al. 1982; Feist 1982; Feist 1983; Williams 1999; Evans et al. 2005). Photodegradation of wood can be blocked by painting the wood with an opaque coating (MacLeod et al. 1995). Clear coatings on the other hand, are unable to protect wood from photodegradation and usually fail within a period of two years of exposure (Cassens & Feist 1991).

Due to the high demand for clear coated exterior wood products (claddings, window frames etc.) many wood pre-treatments and clear coat modifications have been tested for their ability to improve the photostability of wood and coatings, respectively. Nevertheless, as can be seen from this literature review, relatively few pre-treatments and coating modifications were able to enhance the photostability of wood, and there has been little attempt to combine effective wood pre-treatments with durable state-of-the-art clear coats. Hence, this thesis tries to rectify this deficiency. The research seeks to combine the most effective photostabilizing wood pre-treatments with state-of-the-art modified clear coatings in order to significantly improve the performance of clear coatings on wood, as mentioned in Chapter 1.

3. Effect of wood treatments on photo-stability, surface wetting and coating adhesion (experiment 1)

3.1 Introduction

Only a limited number of chemical treatments are able to photostabilize lignin (Evans 2008). The most effective photostabilizing treatment, which is known to significantly improve clear coat performance, is chromic acid. Despite the known ability of chromic acid and some of the other treatments to photostabilize wood, comparisons of their effectiveness have not been carried out. Furthermore, information on how some of these treatments influence clear coat performance is lacking. Chemical modification with some of these different treatments, such as benzoyl chloride and vinyl benzoate, may influence the surface properties of wood that affect coating performance.

The research in this Chapter compared the ability of different chemical modification treatments to photostabilize lignin and how the same treatments influenced wood surface and coating properties such as wettability and adhesion. The aim was to determine which treatments were the best at photostabilizing wood and examine how these treatments altered various properties that influence coating performance.

3.2 Materials and methods

3.2.1 Photostability of chemically modified wood

3.2.1.1 Experimental design and statistical analyses

A randomized complete block (RCB) design with one fixed factor (chemical treatment) was used to examine the effect of different treatments on the photostability of wood. Specimens were cut from six different wood blocks (experimental blocks), to provide replication at the higher level. An appropriate analysis of variance (ANOVA) was carried out to assess the effect of chemical modification on the response variables: weight loss, tensile strength loss and erosion. Statistical computation was performed using Genstat 12.1 (VSN International 2009) with the significance level α defined at 0.05. Prior to statistical analyses, diagnostic checks were performed to determine whether data conformed to the underlying assumptions of ANOVA, i.e., normality and equal variance of residuals. Significant results ($p < 0.05$) are plotted graphically and least significant difference (LSD) bars can be used to compare differences between individual means. Appendix 1 contains a complete record of all statistical analyses that were performed.

3.2.1.2 Sample preparation

3.2.1.2.a Wood blocks and veneers

Six yellow cedar (*Chamaecyparis nootkatensis* [D. Don] Spach) wood blocks measuring 100 mm (longitudinal) x 30 mm (tangential) x 35 mm (radial) were cut from different boards representing six unique experimental blocks. Wood blocks were then machined into a t-shape using an Altendorf F45 table saw to allow 35 mm wide and approximately 100 µm thick radial oriented veneers to be cut from the blocks (Fig. 3.1). These t-shaped wood blocks were pressure impregnated with distilled water in a glass vacuum chamber (approx. 2.5 litre volume) at 0.1 bar for a minimum of 36 hours to soften the wood blocks and make it easier to microtome them. During the impregnation process each t-shaped wood block was weighed down with a stainless steel weight (approx. 200g).

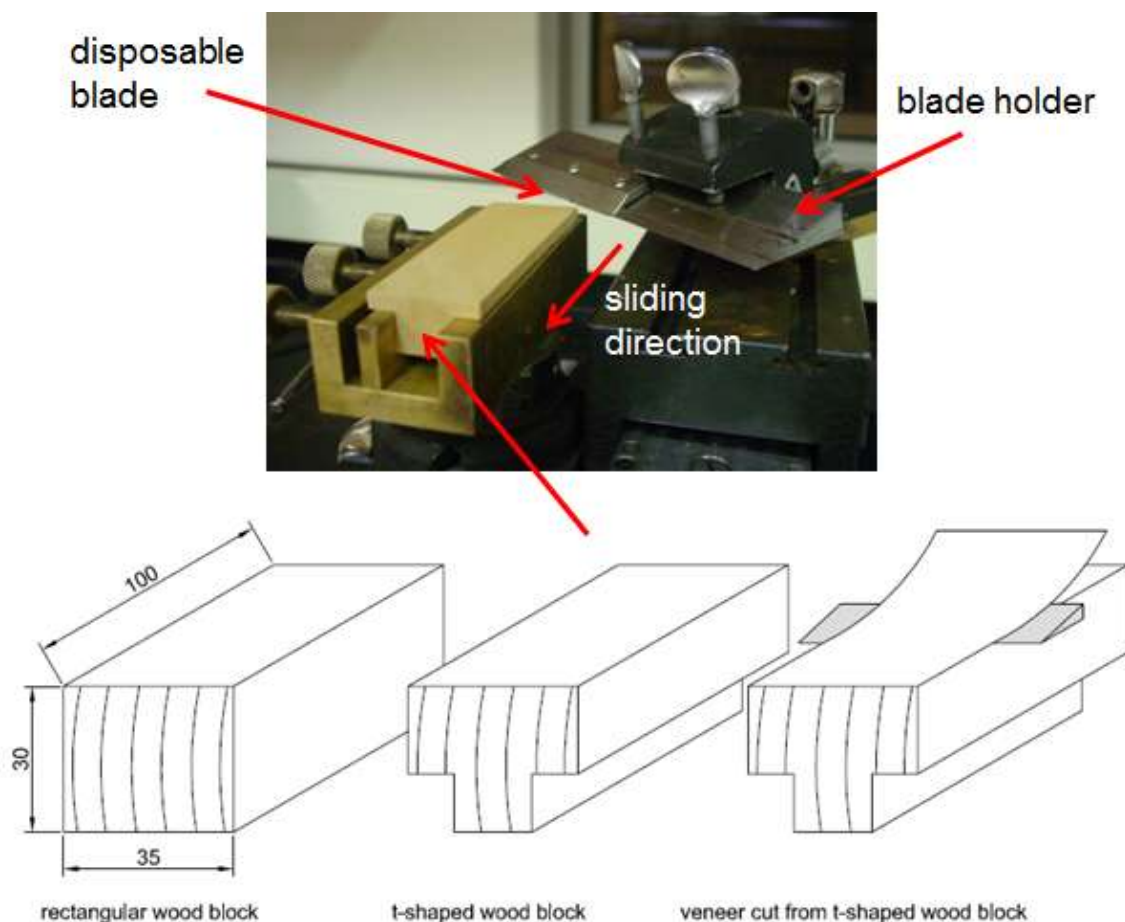


Figure 3.1: Sliding microtome with t-shaped wood block (top). Preparation of wood blocks and cutting scheme of 35 mm wide radially oriented veneers (bottom)

Ten veneers 90-110 μm thick were cut from each of the six t-shaped wood blocks using a Spencer Lens microtome. The microtome was equipped with a blade holder (Feather, No. 160) and disposable microtome blades (Feather, Type S35). Veneers were clamped on glass backing plates and put into a conditioning room at 20 ± 1 $^{\circ}\text{C}$ and $65 \pm 5\%$ r.h. for four days. Veneers from each block were grouped into batches of ten, stored in paper envelopes and kept in a conditioning room (as above) for an additional ten days. Prior to any chemical modification veneers were Soxhlet extracted with a mixture of toluene/ethanol/acetone (4:1:1 v:v:v; all industrial

grade) for four hours and then oven dried at $105\pm 5^{\circ}\text{C}$ for 2.5 hours. Veneers were then cooled for 10 minutes in a desiccator over silica gel and their weights were measured using a digital scale (A&D GR-200). The thickness of each veneer was measured with a digital micrometer (Lorentzen and Wettre, Type 222).

3.2.1.2.b Wood modification

The nine different chemical treatments were each randomly assigned to ten veneers within each block. The remaining unmodified veneer (within each block) was used as an untreated control (UC). After chemical modification, veneers were stored in a conditioning room for two days and then oven-dried and re-weighed, as above. Weight gains of veneers due to chemical modification are expressed as a percentage of their oven-dry, unreacted, veneer weight. Veneers were chemically modified with the following chemicals (Table 3.1):

Table 3.1: Chemicals used to modify wood veneers

No	Treatment	Abbreviation
1	Benzoyl chloride	BC
2	Chromic acid	CA
3	Cerium oxide nanoparticles	CNP
4	Phenol resin	PF
5	Phenol resin with water soluble hindered amine light stabilizer (HALS)	PFH
6	Phenol resin with polyethylene glycol (PEG)	PFP
7	UV absorber and solvent soluble HALS	UVH
8	UV absorber and HALS (as for 7) and yellow iron oxide	UVHIO
9	Vinyl benzoate	VB

Each of the chemical treatments involved different processing steps. The steps involved in the different treatments are described below.

Benzoyl chloride treatment

Veneers were grouped in batches of three and placed separately into 60 mL test tubes. A solution containing 4 mL benzoyl chloride (Acros Organics reagent grade) and 40 mL pyridine (Fisher Scientific reagent grade) was added to each test tube to fully submerge the veneers, as described by Evans et al. (2002). Test tubes were covered with aluminum foil and placed in an oil bath for three hours at 65°C. Veneers were then Soxhlet extracted in acetone (industrial grade) for one hour to remove any unreacted chemicals.

Chromic Acid treatment

An aqueous solution containing 5% w/w chromium trioxide was prepared in a glass bowl. Veneers were dipped into the solution for five seconds and air dried for one hour. Air dried veneers were then oven dried for 15 minutes at $105 \pm 5^\circ\text{C}$.

Cerium oxide nanoparticle treatment

A cerium nanoparticle dispersion (6.7% w/w in water), doped with 10% w/w titanium dioxide (TiO_2), was diluted to a 2% (w/w) dispersion. The dispersion was applied to the veneers with a medium-hard paintbrush. Treated veneers were air-dried for one hour followed by fifteen minutes oven drying at $105 \pm 5^\circ\text{C}$.

PF-resin treatments

An aqueous PF-resin solution (Arclin, Inc.) with a concentration of 48% (v/v) was diluted with distilled water to create a 12% (v/v) solution. Veneers were immersed in this solution for 15 minutes, and then air-dried for 15 minutes.

Subsequently, these veneers were oven-dried at $150 \pm 5^{\circ}\text{C}$ for an additional 15 minutes (in order to cure the PF-resin). The treatment procedures for veneers treated with PF-resin containing PEG (PEG 1000 10% v/v) and PF-resin containing HALS (Lignostab 1198, 2% w/w) were the same as that for veneers treated with PF-resin alone.

UVH treatments

A solution of UVA (Ciba-Geigy Tinuvin 384, 2% v/v) and HALS (Ciba-Geigy Tinuvin 292, 2% v/v) in acetone (industrial grade) was prepared. The solution was brushed onto the veneers with a medium-hard paint brush. Veneers were then air-dried for 20 minutes and then oven dried at $105 \pm 5^{\circ}\text{C}$ for 15 minutes.

The UVHIO treatment was applied as a two-stage treatment. The first stage involved the UVA/HALS treatment (above). In the second stage, a distilled water-based solution of the yellow iron oxide (Johnson Matthey Ceramics PW601, 2% w/w) was applied as above for the UVH solution. However, air-drying was extended to one hour due to the slower evaporation rate of the distilled water.

Vinyl benzoate

Veneers were grouped in batches of four to five to obtain a dry wood weight of approximately 1g. Batches of veneers were placed into separate 100 mL test tubes equipped with a Soxhlet adaptor. A solution containing 60 mL dimethylformamide (DMF) carrier solvent (Fisher scientific reagent grade), 0.45 g potassium carbonate catalyst (Alfa Aesar, anhydrous 99%), and 12.6 mL vinyl benzoate (Alfa Aesar reaction agent, 1.52 mol/l carrier solvent) was added to the test tube. DMF was dried over molecular sieves (4 \AA) and potassium carbonate as

well as calcium chloride were dried for 24 hours at $105 \pm 5^{\circ}\text{C}$ in order to create anhydrous reaction conditions. The proportions of these compounds were the same as those used by Jebrane et al. (2009), but the quantities were tripled to fully immerse veneers in solution. The test tube was placed in a stainless steel pot containing silicon oil at $90 \pm 5^{\circ}\text{C}$. Veneers were reacted with solution of vinyl benzoate for 3 hours. A magnetic stirrer was added to the test tube to create a more even distribution of the catalyst. The test tube was fitted with a condenser containing a calcium chloride drying tube, as suggested by Jebrane et al. (2009). Reacted veneers were Soxhlet extracted with distilled water for one hour and then with a mixture of toluene/ethanol/acetone (4:1:1 v:v:v) for 2 hours to remove the catalyst and any unreacted chemicals.

3.2.1.3 Natural weathering

Modified veneers were cut in half and laid across glass baking plates (750 mm in length x 120 mm in width). Two glass strips, approximately 20 mm wide, ran along the entire length of each glass plate so that veneers could be easily secured to the glass plate with alligator clamps (Fig. 3.2). The glass strips were covered with black polyethylene, multi-purpose tape (Scotch), which protected the ends of the veneers from weathering. The other halves of each of the veneers acted as a control and were kept in paper envelopes and stored in a conditioning room for the duration of the weathering trial.

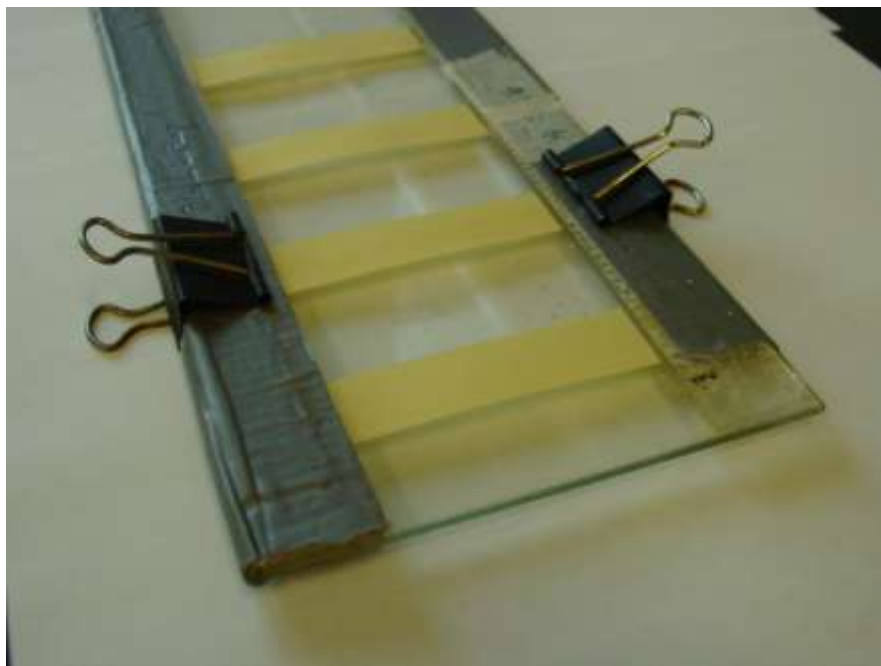


Figure 3.2: Veneers clamped onto glass backing plates. Note the glass strips that hold veneers in place were covered with black tape

Modified veneers and unmodified controls were exposed horizontally and facing south for 35 days in Vancouver, Canada. Samples were conditioned, as above for two weeks, after the exposure trial.

3.2.1.4 Weight, tensile strength, and erosion measurements

Conditioned, weathered veneers and the unweathered control were oven-dried at $105 \pm 5^{\circ}\text{C}$ for 2.5 hours, cooled for 10 minutes in a desiccator over silica gel and weighed as described previously. Weight losses that occurred during weathering were calculated using treated veneer weights. Veneers kept in the conditioning room for the duration of the weathering trial acted as controls. Weight losses of veneers exposed to weathering have been shown to be a good indicator of lignin photodegradation (Evans & Schmalzl 1989).

Veneers were reconditioned for a period of five days prior to tensile strength measurements. Tensile strength tests were carried out with a Pulmac paper tester at zero-span using a clamping pressure of 65 psi (Fig. 3.3). This clamping pressure was the optimum for the testing of the 100 μm thick yellow cedar veneers used for the weathering trial.



Figure 3.3: Pulmac paper tester used for tensile strength tests (left) and a close-up of the jaws of the device (right)

Tensile strengths of veneers after testing were calculated by dividing the maximum load (kg) at failure by the cross sectional dimension (mm^2) of each veneer (Evans & Schmalzl 1989). The ratio of tensile strengths after weathering to the initial tensile strengths of unweathered samples was calculated and used as a measure of strength loss during weathering. Strength losses of veneers during weathering reflect the depolymerisation of cellulose due to photodegradation (Ifju 1964; Derbyshire & Miller 1981). Strength losses of weathered veneers can be compared to those of unweathered treated controls kept in the conditioning room.

The erosion of wood from veneers during weathering, was assessed using one of the halves of each of the veneers remaining after strength testing. The veneer half was fixed to a glass microscope slide using double-sided tape. The slide was placed on the table of a Cotec non-contact confocal white light profilometer (AltiSurf 500). A linear profile scan was performed using a 3 mm (3000 μm to 92 nm) probe (Fig. 3.4).

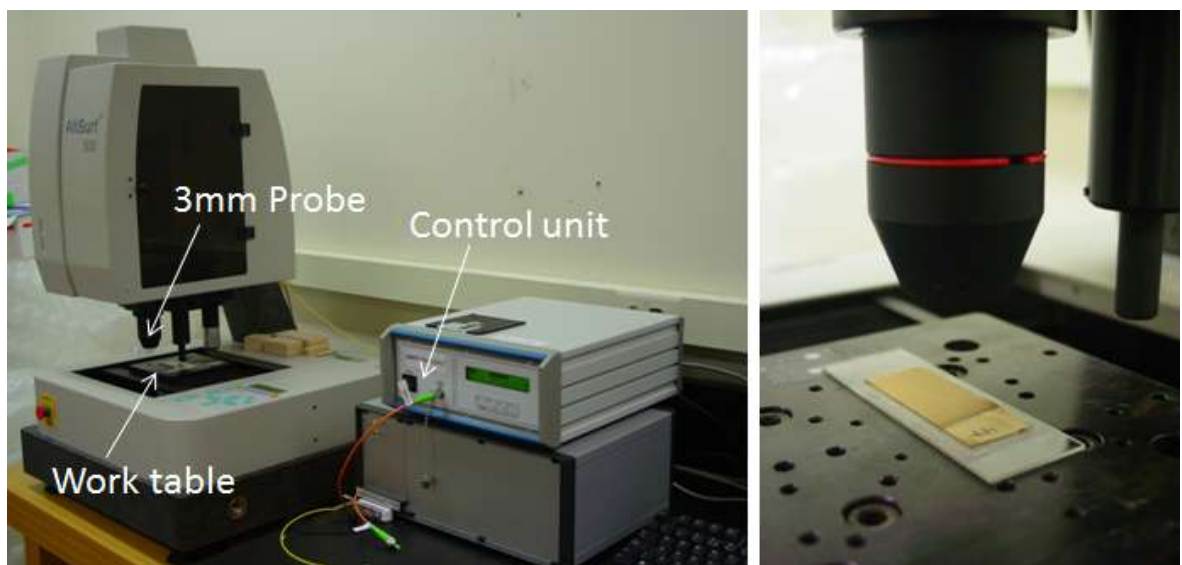


Figure 3.4: Non-contact confocal profilometer used to assess the erosion of veneers after natural weathering (left) and close-up of the 3 mm probe and a microscope slide with one of the veneers (right)

The profile scan traversed one of the earlywood zones in each veneer and had a total length of 17 mm. Each traverse scanned approximately 13 mm of unmasked, eroded wood, and approximately 4 mm of wood that had been masked (Fig. 3.5). The spacing between measuring points was 30 μm and the measuring speed of the probe was 6 mm/s.

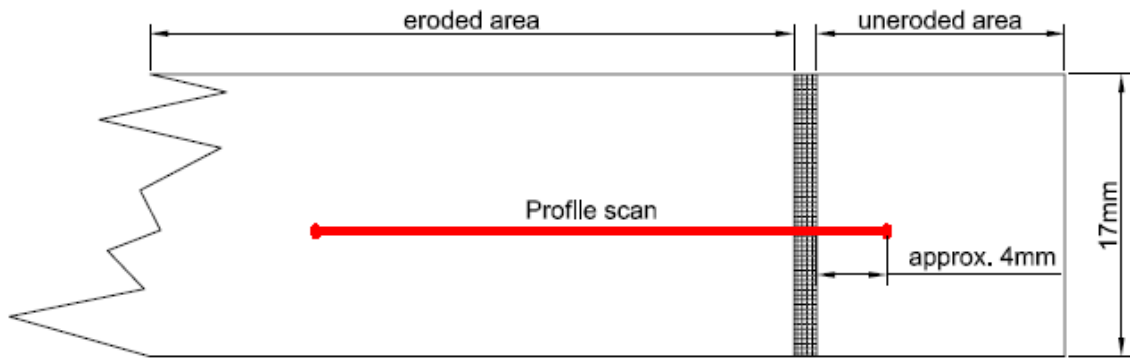


Figure 3.5: Diagram of the dimensions of the veneer sample and profile scan performed after veneers were exposed to natural weathering

The profiles generated by the profilometer were analyzed in PaperMap 3.2.0 (Digital Surf 2004), and two areas of interest, eroded and uneroded, were defined for each profile. All data points from each profile (561) were then exported to Excel 2007 (Microsoft Corporation 2006) and the average profile height of both areas of interest was calculated. Subtraction of the average height of the eroded profile from the average height of the uneroded profile produced a measure of the erosion of the veneers during weathering (Fig. 3.6).

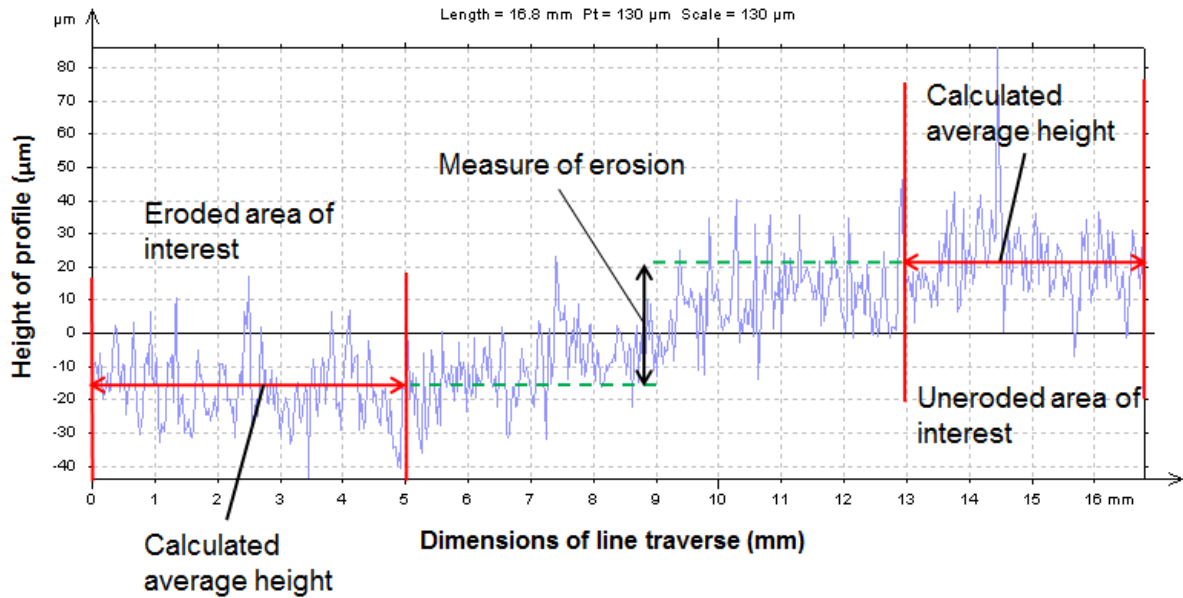


Figure 3.6: Line traverse used to determine the erosion of weathered veneers

3.2.2 Coating properties

3.2.2.1 Experimental design and statistical analyses

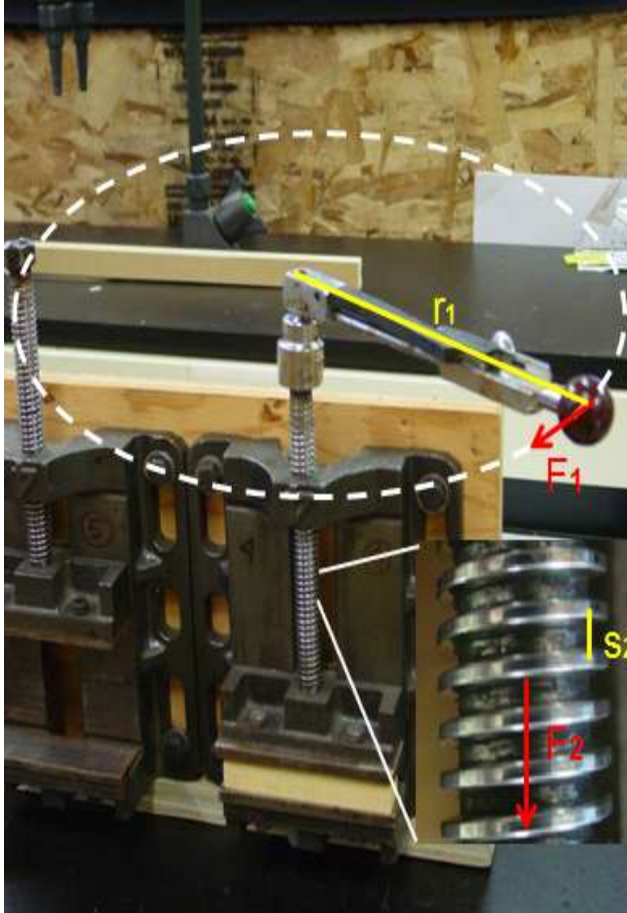
A factorial experiment was designed to examine the effect of two fixed effect factors: (1) Treatment (nine chemical treatments and an untreated control); (2) Coating (Acrylic, Alkyd, PUR) on wood surface and coating properties. Veneer samples were cut from six different yellow cedar wood blocks (experimental blocks) and the first experimental factor was randomly assigned to veneers in each block. Each of these veneers was subdivided into three equal sized areas and each area was randomly allocated to one of the three different coating types. The resulting split-plot design accounted for random variation between blocks (1-6) and between and within veneers. ANOVA was performed (as above) to assess the effect of fixed

and random factors on contact angle of each coating, and coating adhesion (tensile stress and wood failure).

A second experiment examined the permeability of the different coatings. The three coating types mentioned above were randomly applied to a total of ten glass plates (2 coatings on the front of each glass plate and 1 coating on the back). The resulting randomized complete block design (RCB) examined the effect of one fixed factor (coating type) on coating permeability. ANOVA was carried out to assess the effect of coating type on coating permeability. Statistical computation as well as the presentation of the results are the same as those described above in Section 3.2.1.1. Appendix 2 contains a complete record of all statistical analyses that were performed.

3.2.2.1.a Veneered wood blocks

A total of 120 yellow cedar veneers were cut from six t-shaped wood blocks and chemically modified as described previously in Section 3.2.1.2. Modified veneers were glued to Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) blocks, measuring 100 mm (length) x 35 mm (width) x 10 mm (height), with polyvinyl acetate glue (carpenters white glue). To ensure adequate adhesion of glued veneers to Douglas-fir blocks, samples were placed between the jaws of small presses and a torque wrench was used to apply pressure to the jaws of each press (Fig. 3.7). Samples were pressed for one hour using a pre-determined pressure. The maximum torque needed to reach this pre-determined pressure was calculated as follows (Fig 3.7):



$$P = F_c/A \rightarrow F_c = P \times A$$

with clamping pressure $P = 0.33 \text{ N/mm}^2$;
sample area $A = 3500 \text{ mm}^2$; and

F_c = clamping force

$$\rightarrow F_c = 0.33 \times 3500 = \mathbf{1,155 \text{ N}}$$

$$F_R = \mu \times F_N$$

with $F_R = F_c$; $F_N = F_2$; and friction
coefficient $\mu = 0.11$

$$\rightarrow F_2 = F_c / \mu = 1,155 / 0.11 = \mathbf{10,500 \text{ N}}$$

Due to the balance of forces it is
valid that $F_1 \times s_1 = F_2 \times s_2$; $s_2 = 3 \text{ mm}$

with $s_1 = r_1 \times 2\pi$ and with $M_1 = F_1 \times r_1$

$$\rightarrow M_1 \times 2\pi = F_2 \times s_2$$

$$M_1 = (F_2 \times s_2) / 2\pi = (10,500 \times 0.003) / 2\pi$$

$$\mathbf{M_1 = 5 \text{ Nm}}$$

\rightarrow The torque applied to ensure adequate
clamping pressure was 5 Nm

Figure 3.7: Screw clamp used for pressing glued veneer samples

Sixty veneers were glued to separate Douglas-fir blocks measuring 250 mm (length) x 35 mm (width) x 10 mm (height). After all veneers and blocks were prepared and glued, they were stored in a conditioning room for one week.

3.2.2.1.b Coating of wood blocks

Each veneered wood block was subdivided into three areas and each area was coated with one of the three different types of clear coating (Table 3.2). The clear coats were applied with a HVLP (High Volume Low Pressure) spray gun from Graco (Air Pro; tip size 1.4 mm), which was connected to a pressure pot from Lemmer. Each coating was applied as a single film only to avoid adhesive failures

between first and second coats. The acrylic and alkyd coatings were ready-to-use-systems, whereas the PUR coating had to be prepared by mixing the sealer (IS 207) and catalyst (C 207) in a ratio of 1:1 (v:v) (Table 3.2). After coating, samples were stored in a conditioning room for a minimum of one week.

Table 3.2: Coating types that were tested for their adhesion to modified wood

Binder	Company	Water based	Solvent based	Wet film thickness	Application pressure
Acrylic	Akzo Nobel	x		130 µm	12 psi
Alkyd	Akzo Nobel	x		130 µm	18 psi
PUR	ICA		x	100 µm	10 psi

3.2.2.1.c Test dollies

Individual aluminum test dollies with a diameter of 20 mm were glued onto each of the three areas with the samples prepared for the adhesion test, i.e. 180 dollies were used in total (Fig 3.8). Dollies were bonded to the coatings using two drops of an ethyl cyanoacrylate (Krazyglue) adhesive. Immediately after the adhesive was applied, dollies were clamped under pressure for ten minutes, as in Section 3.2.2.1.a. The maximum torque applied per dolly was 2.5 Nm.



Figure 3.8: Dollies glued to a veneered sample for the adhesion test

3.2.2.2 Wettability tests

Contact angle measurements were carried out with a goniometer (KSV CAM 101) to determine the wettability of the coatings on modified veneer surfaces. The goniometer contained three main components: (1) a height adjustable stage to hold the veneered wood blocks; (2) a syringe containing the coating; (3) a digital camera on the opposite side of the sample stage to image coating droplets (Fig. 3.9). Droplets were imaged every 16 ms for the first 52 frames and then every 1s for an additional ten frames (frames 53-62). The droplet size that was placed on each coated specimen was 5 μL .

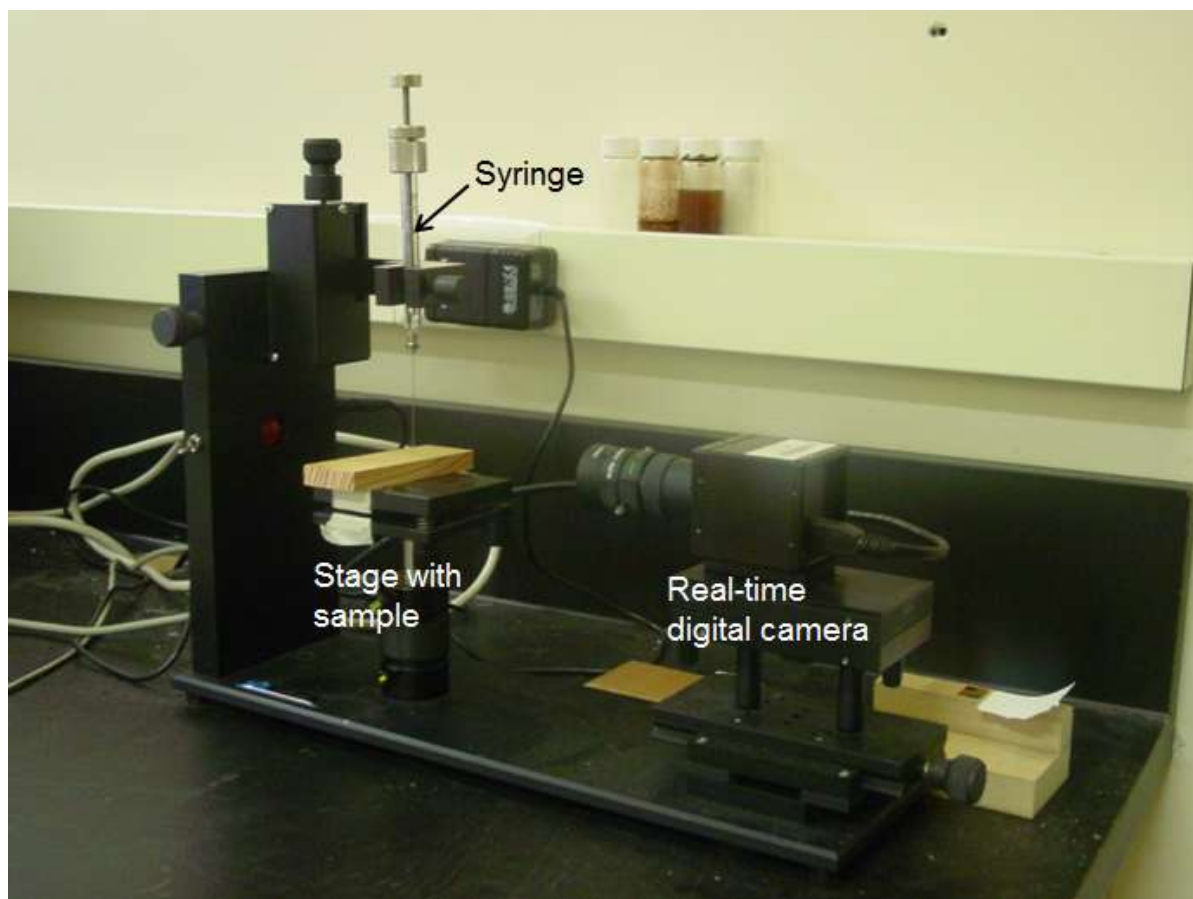


Figure 3.9: KSV goniometer and its three main components

The ninth frame (0.144s) from each test was used to calculate contact angle that the coatings made with modified veneer surfaces, including adjustment of the baseline (Fig. 3.10). Left and right contact angles were averaged to obtain a mean contact angle for each test. The software used for calculating contact angles of droplets was CAM 200 (KSV Instruments 2007).

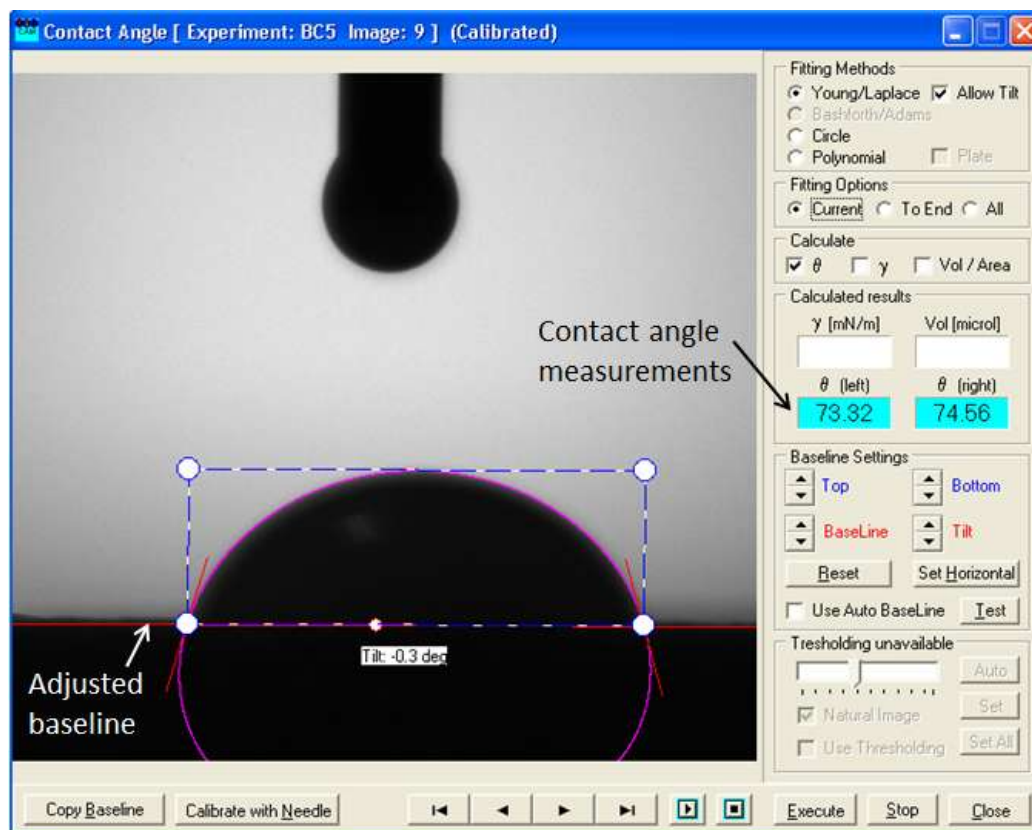


Figure 3.10: Contact angle measurement on a coating droplet using CAM 200 software

3.2.2.3 Adhesion tests

Adhesion tests were carried out using the pull-off-test method (ASTM 2009)¹. The device used to pull off the dollies and measure coating adhesion was a universal strength tester (Instron, model 4202). The cross-head speed used during testing was 2.54 mm/min. A specially designed cardan joint was connected to the universal tester to ensure that shear forces did not have a large influence on the adhesion results (Fig 3.11). Prior to the pull-off-test, each test area was isolated with a cylindrical cutting tool around the circumference of the dollies. Results of the adhesion tests were saved in the software Series IX (Instron 2002) as maximum

¹ The pull-off-test method assessed coating adhesion and percentage wood failure was used as an indicator of the quality of adhesion

load (kilogram Force). Maximum load was converted into tensile stress (N/mm^2), prior to statistical analyses by multiplying the maximum load in kilogram by the gravitational acceleration (9.81 m/s^2), and the division of the resulting product by the area of the dolly in square millimetres.



Figure 3.11: Instron universal tester with control unit (left). Cardan joint used to avoid shear forces (right)



Specimens were examined for the type of failure that occurred during the pull-off tests. Each dolly was overlaid with a transparent circular grid divided into 16 areas, as shown in Figure 3.12.

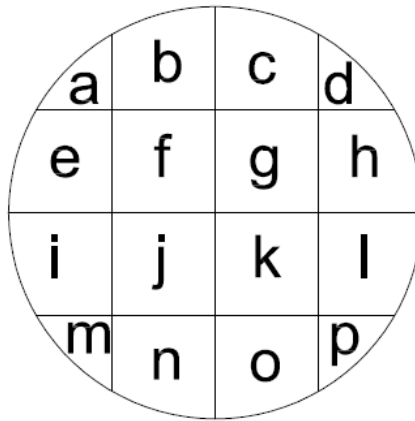


Figure 3.12: Circular grid used to define and quantify failure of coatings on modified veneer surfaces

In each of the 16 areas on the transparent grid the mode of failure of the specimen was recorded. Failure was classified as follows:

- (1) Wood failure: Cohesive failure of wood block and adhesive failure between veneer and wood block
- (2) Dolly failure: Adhesive failure between coating and dolly



Figure 3.13: Typical failure types of samples after adhesion testing using the pull-off method. From left to right: Cohesive failure of wood block; adhesive failure between veneer and wood block; adhesive failure between coating and dolly

The type of failure in each of the 16 grids was estimated visually and summed to obtain an estimate of the total amount of wood failure and dolly failure in each sample. Wood failure was used for analysis of variance.

3.2.2.4 Permeability tests

The permeability of the three different coatings was measured because the permeability of coatings generally influences their exterior performance (Ashton 1964). The coatings were applied to glass plates with a Gardner (BYK) step gap film applicator. The film applicator created four areas with different wet film thicknesses (200 μm , 150 μm , 100 μm , 50 μm) as shown in Figure 3.14. The films were air-dried for 24 hours and a 5 μL droplet of distilled water was placed on the coating using a Gilson (P20) micropipette. The water-droplet was immediately covered with a 20 mL glass vial to reduce evaporation of the droplet. The time it took for the droplet to completely disappear from the surface of the coating was used as a measure of coating permeability.

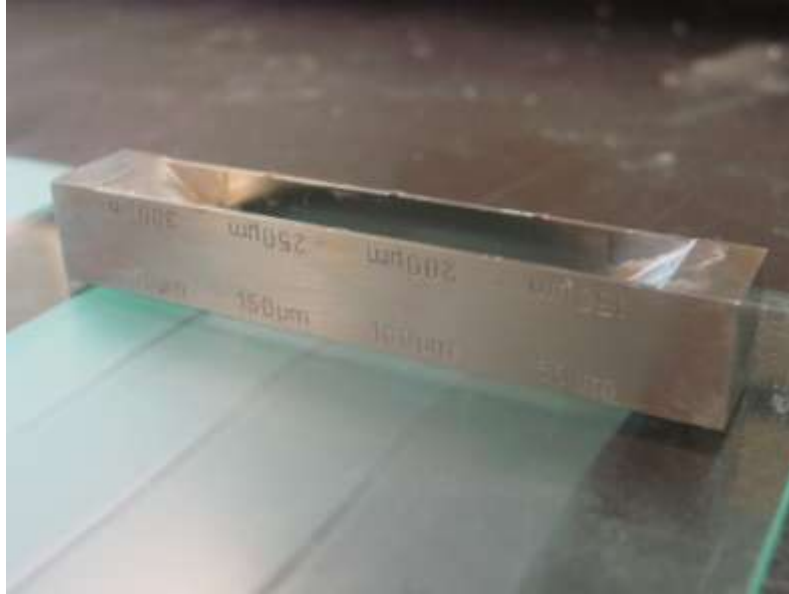


Figure 3.14: Step gap film applicator used to produce 200 µm, 150 µm, 100 µm and 50 µm thick films (left to right)

3.3 Results

Table 3.3 summarizes the effects of and interactions between experimental factors on wettability, adhesion and permeability.

Table 3.3: Effects of chemical treatments on the weight loss, tensile strengths and tensile strength ratios, and the erosion of modified veneers exposed to natural weathering for 35 days

Experimental Factors	Response variables				
	Weight loss	Tensile strength unweathered	Tensile strength weathered	Tensile strength ratios	Erosion
Treatment (T)	***	***	***	***	***

*** = $p < 0.001$

Table 3.4: Effects of and interactions between chemical treatments and coating types on coating properties

Experimental Factors	Response variables			
	Wettability	Tensile stress (Adhesion) +	Wood failure (Adhesion)	Permeability
Treatment (T)	*	NS (0.435)	*	n/a
Coating (C)	***	***	***	**
T x C	***	NS (0.490)	*	n/a

* = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$; NS = not significant ($p > 0.05$), + converted max. load from pull-off-test method in N/mm²

3.3.1 Effect of chemical modification on the weight loss of veneers

Chemical treatment had a highly significant ($p < 0.001$) effect on the weight loss of wood veneers exposed to natural weathering (Table 3.3). Figure 3.15 compares the weight losses of different treated veneers (including untreated veneers) after exposure to 35 days of natural weathering. Veneers treated with benzoyl chloride (BC) had the lowest weight losses followed by those treated with chromic acid (CA) or vinyl benzoate (VB). Weight losses of veneers treated with PF/HALS (PFH) or PF-resin (PF) were significantly ($p < 0.05$) higher than those of veneers treated with BC, CA or VB, but were significantly lower than the weight losses of the untreated control. The PF treatment containing PEG (PFP) was not effective ($p > 0.05$) at preventing weight losses, and veneers treated with PFP showed slightly higher weight losses than untreated veneers. The UVA/HALS treatment (UVH) was also ineffective ($p > 0.05$) at restricting weight losses of veneers, however, the addition of yellow iron oxide to the UVH treatment (UVHIO) improved the ability of the treatment to restrict losses in weight of veneers during

weathering. Accordingly, veneers treated with UVHIO showed significantly ($p < 0.05$) lower weight losses than the untreated controls (Fig 3.15). Weight losses of veneers treated with cerium oxide nanoparticles (CNP) were lower than those of untreated veneers (UC) but the difference in weight loss is not statistically significant ($p > 0.05$).

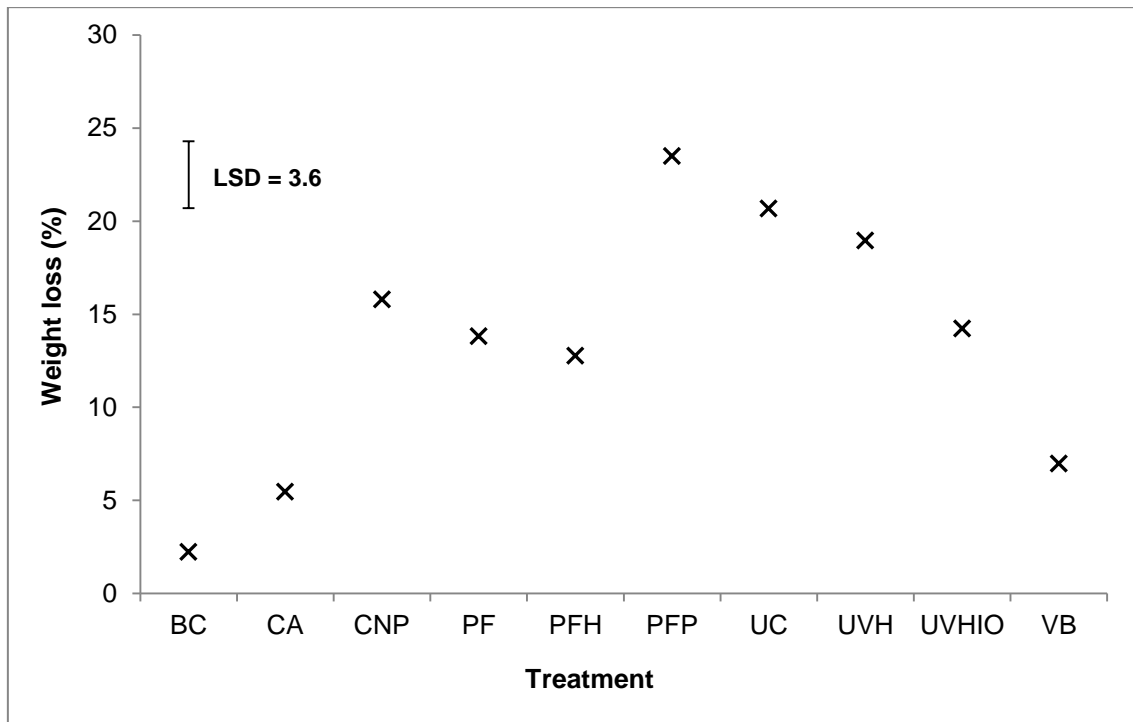


Figure 3.15: The effect of chemical treatments on weight losses of wood veneers exposed to 35 days of natural weathering

3.3.2 Effect of chemical modification on the tensile strength of veneers

Chemical treatment also had a highly significant ($p < 0.001$) effect on tensile strengths of wood veneers before and after weathering (Table 3.3). Figure 3.16 compares the tensile strength of modified and unmodified veneers after chemical modification (before weathering). Wood veneers treated with CA had the lowest tensile strength after modification followed by veneers treated with BC. Tensile

strengths of these veneers were significantly lower ($p < 0.05$) than the tensile strengths of all other treated veneers and untreated controls. Veneers treated with CNP, PF, PFH, UVH and UVHIO had significantly higher tensile strengths after modification than untreated veneers. There was no significant difference in the tensile strength ($p > 0.05$) of untreated veneers and veneers treated with PFP and VB.

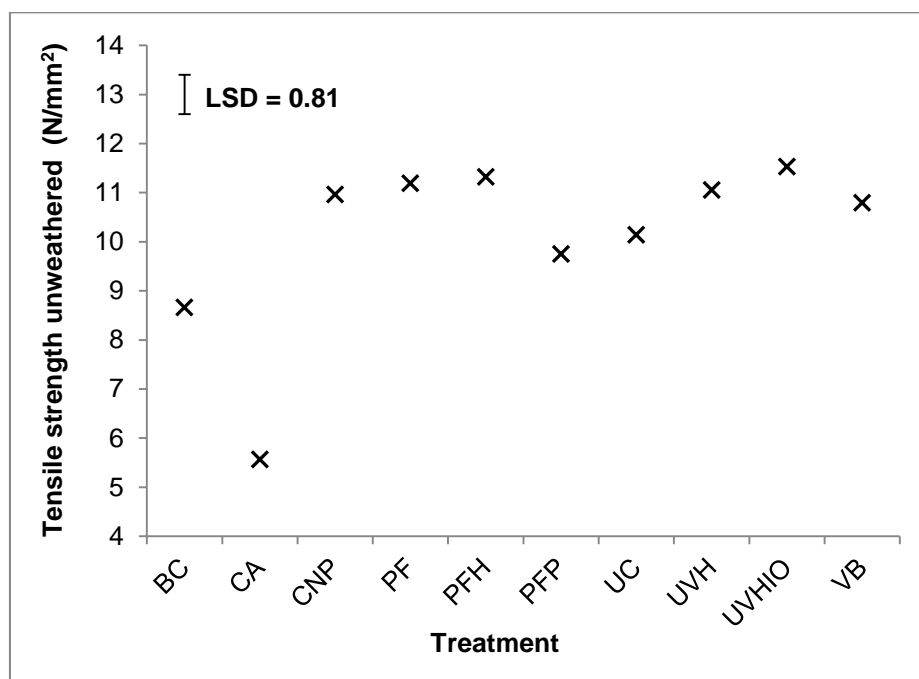


Figure 3.16: The effect of chemical treatments on the tensile strengths of wood veneers before weathering

The tensile strengths of treated and untreated veneers after weathering are shown in Figure 3.17. In comparison to the tensile strength results before weathering, all treated veneers had significantly higher ($p < 0.05$) tensile strengths after weathering than the untreated weathered veneers. An exception was veneers treated with chromic acid (CA), which showed significantly lower tensile strengths than the untreated weathered controls. Veneers treated with PFH, PFP and UVHIO

had significantly higher tensile strengths after weathering than all other treated veneers. There was no significant difference ($p>0.05$) between the tensile strengths of veneers treated with BC, CNP, PF, UVH and VB.

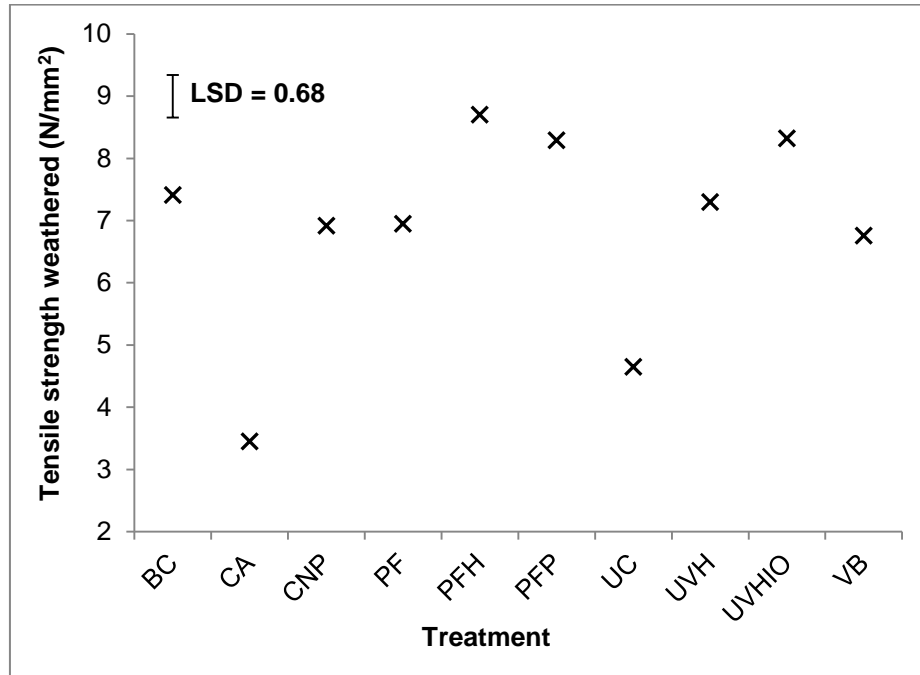


Figure 3.17: The effect of chemical treatments on the tensile strengths of wood veneers after weathering

Chemical treatment had a highly significant effect ($p<0.001$) on the tensile strength ratios of exposed wood veneers (Table 3.3). A tensile strength ratio² of 1 indicates that there was no significant difference ($p>0.05$) in tensile strengths of veneers before and after outdoor exposure. All of the treated and untreated veneers tested in this study showed significant ($p<0.05$) tensile strength losses during weathering, as indicated by their tensile strength ratios having values less than 1 (Fig. 3.18). All of the treated veneers were effective at restricting tensile strength losses during weathering because their tensile strength ratios were significantly

² see page 63 for definition of tensile strength ratio

($p < 0.05$) higher than that of untreated veneers. The lowest tensile strength losses were observed for veneers treated with BC and PFP. These veneers had significantly lower tensile strength losses than all other treated veneers except for those treated with PFH. Veneers treated with PFH and UVHIO had significantly lower tensile strength losses than veneers treated with CNP, PF and VB. Veneers treated with CA and UVH showed no significant difference ($p > 0.05$) in tensile strength losses compared to other treated veneers, except for BC and PFP treated veneers.

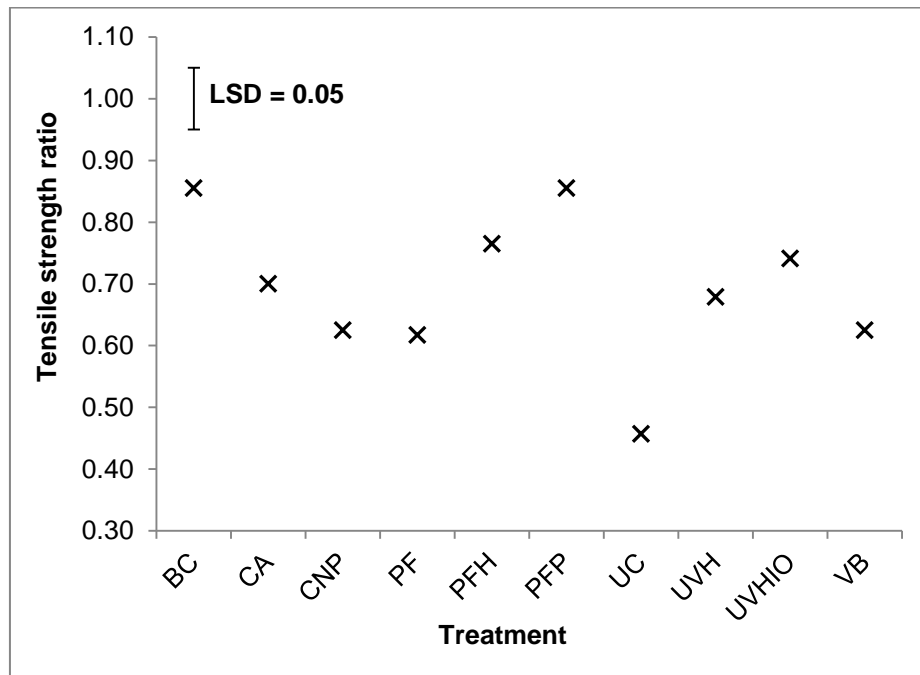


Figure 3.18: The effect of chemical treatments on the tensile strength ratios of wood veneers after weathering

3.3.3 Effect of chemical modification on the erosion of veneers

All of the chemically treated veneers eroded significantly less ($p < 0.05$) during weathering than untreated veneers (Fig. 3.19). The most outstanding result was the

very low erosion of veneers treated with benzoyl chloride (BC). BC treated veneers showed an average erosion of only 1.8 μm which was 21 times lower than the erosion of untreated veneers. Statistically significant ($p < 0.05$) differences in the erosion of veneers were found between BC v. CNP, BC v. PF as well as BC v. UVH. There were no significant differences ($p > 0.05$) between the erosion of the other chemically treated veneers.

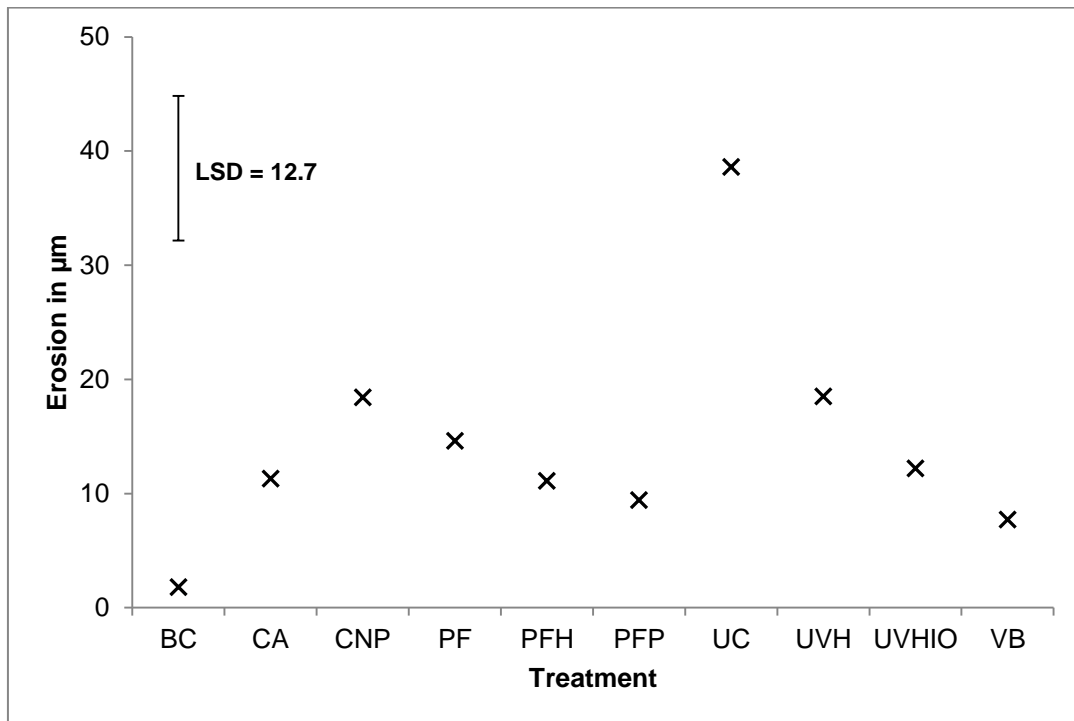


Figure 3.19: The effect of chemical treatments on the erosion of veneers exposed to 35 days of natural weathering

3.3.4 Effect of chemical modification on the wettability of coatings

Analysis of variance showed that there was a highly significant interaction ($p < 0.001$) between chemical treatment and coating type on wettability (Table 3.4). These interactions occurred because contact angles of the polyurethane coating (PUR) on treated wood surfaces were quite different to the contact angles of the

acrylic (AC) and alkyd (AL) coatings on the same surfaces (Fig. 3.20). PUR had significantly ($p < 0.05$) lower contact angles, and thus higher wettability, than AC and AL with the exception of contact angles on PFH treated wood and untreated controls (Fig. 3.20). The lowest contact angles for the PUR were found on wood treated with UVHIO, CA and UVH and such contact angles were all significantly lower than those on PFH and BC treated wood. Contact angles of the PUR on UVHIO and CA were also significantly lower than contact angles of the PUR on untreated controls. However, there was no significant difference ($p > 0.05$) between the contact angles of the PUR on UVHIO, CA and UVH treated wood as well as those on wood treated with PFH and BC. Furthermore, there was little difference in the contact angles of the PUR on wood treated with the remaining chemical treatments (CNP, PF, PFP and VB). There was no significant difference ($p > 0.05$) in the contact angles of the acrylic (AC) and alkyd (AL) coatings on different treated wood surfaces (Fig. 3.20). However, the contact angle of the AL coating was significantly ($p < 0.05$) higher on the untreated controls than that of the AC coating. Contact angles of both the AC and AL coatings were highest on wood treated with UVH and UVHIO. Contact angles of the AL and AC coatings on wood treated with UVH and UVHIO were significantly higher ($p < 0.05$) than those on wood treated with CNP, PF and PFH. In the case of the AL coating, contact angles on UVH and UVHIO treated wood were significantly higher than those on untreated wood. For the AC coating, contact angles on UVHIO treated wood were significantly higher than that on BC treated wood. There were no significant differences ($p > 0.05$) in contact angles of the AC and AL coatings on other treated wood surfaces.

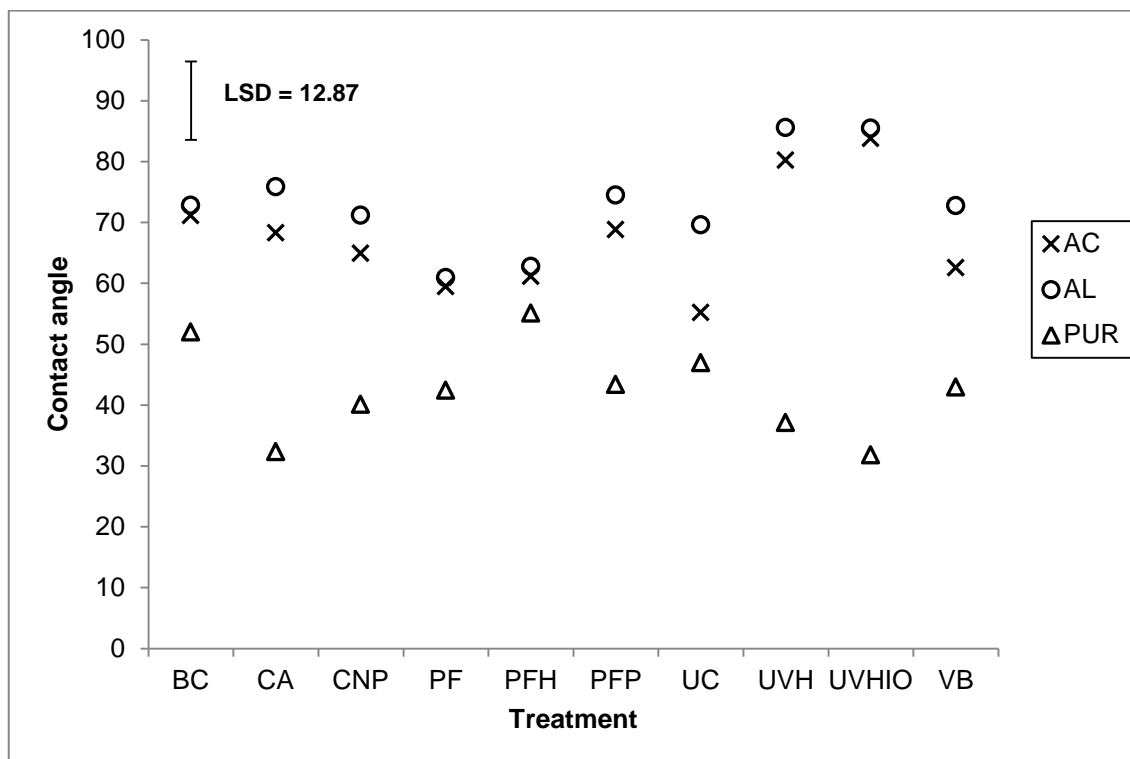


Figure 3.20: The effect of chemical treatments of wood surfaces on the wettability of acrylic (AC), alkyd (AL) and polyurethane (PUR) coatings

3.3.5 Effect of chemical modification of wood surfaces on coating adhesion

3.3.5.1 Tensile stress

Coating type had a highly significant effect ($p < 0.001$) on coating adhesion (Table 3.4). Adhesion was greatest for the PUR, followed by AC and AL (Fig. 3.21). There was no significant effect ($p > 0.05$) of wood treatment on coating adhesion and no significant interaction ($p > 0.05$) between treatment and coating type on coating adhesion.

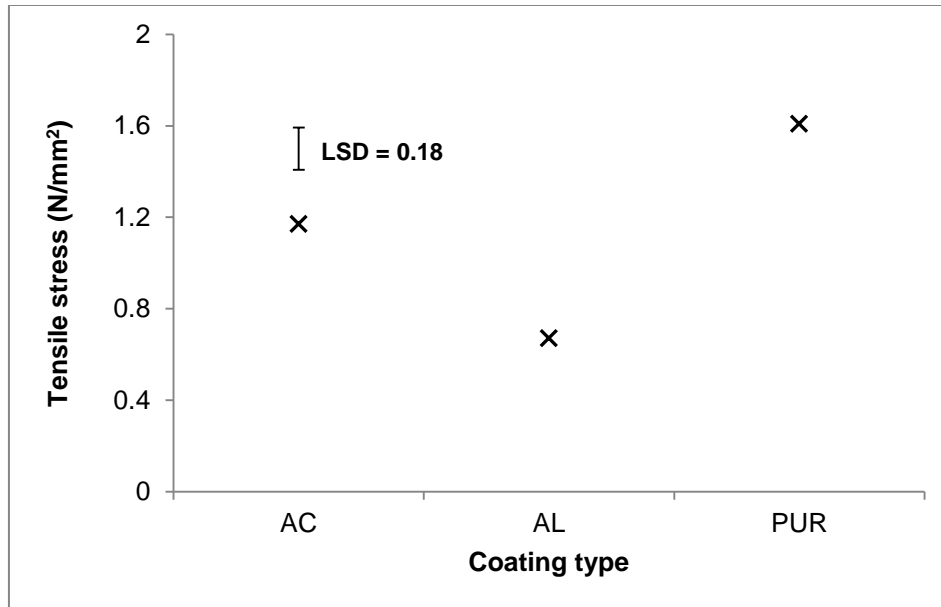


Figure 3.21: The effect of coating type on adhesion of the coatings to treated wood surfaces (results are averaged across the different chemical treatments)

3.3.5.2 Wood failure

Analysis of variance revealed that there was a significant interaction ($p < 0.05$) between chemical treatment and coating type on percentage wood failure (Table 3.4). These interactions occurred because percentage wood failures were generally, but not always higher for PUR, compared to those observed for the AC and AL coatings (Fig. 3.22). Significant differences ($p < 0.05$) in wood failure between the PUR and water-borne AC and AL coatings, were observed for wood treated with BC, PFP, UVH, UVHIO and VB treatments and also on untreated wood. Significant differences in percentage wood failure for the PUR and AL coatings were only observed on wood treated with CA, PF and PFH. There was no significant difference ($p > 0.05$) in wood failure between the three different coating types on wood treated with CNP. The highest percentage of wood failure for the PUR coating was found on

wood treated with UVHIO followed by BC. Wood failure levels for these treatments were higher than those on surfaces treated with CA, CNP, PF and the untreated control. In contrast, the highest percentage wood failure for the acrylic coating (AC) was found on CA treated wood. Failure of the AC coating on CA treated wood was significantly higher ($p < 0.05$) than that observed on wood treated with CNP, UVH and all PF treatments, and also on untreated controls. There was no significant difference ($p > 0.05$) in percentage wood failure for the other treatment and coating combinations. No significant difference ($p > 0.05$) in wood failure was found between most of the treated samples coated with AL. The only exception was on samples treated with UVHIO, where wood failure was significantly greater than that found on PF treated wood.

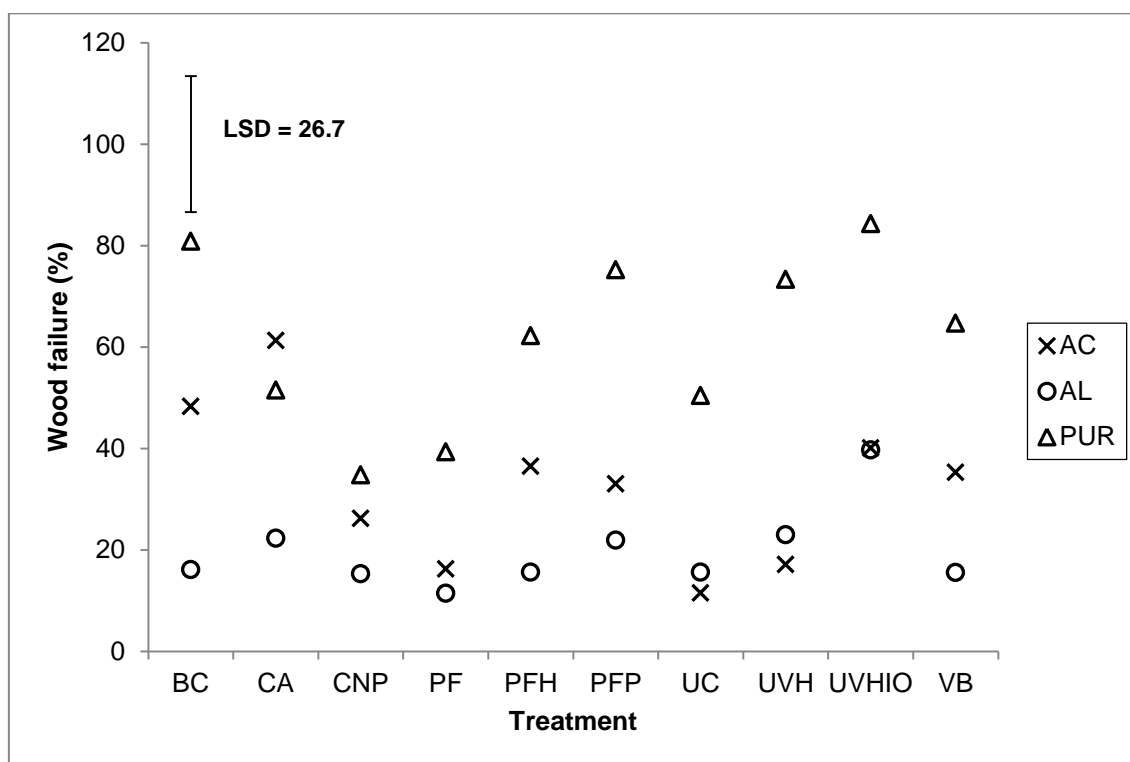


Figure 3.22: The effect of chemical treatment and coating type on wood failure during adhesion testing

The data for wood failure and tensile stress (adhesion) were subjected to a regression analysis to determine if there was any relationship between coating adhesion and percentage wood failure (Fig. 3.23). The regression analyses showed that there was the expected positive relationship between higher tensile stress and wood failure. However, the relationship was not strong ($r^2 = 0.25$) and there were many outliers. These outliers are labelled on the regression (Fig. 3.23).

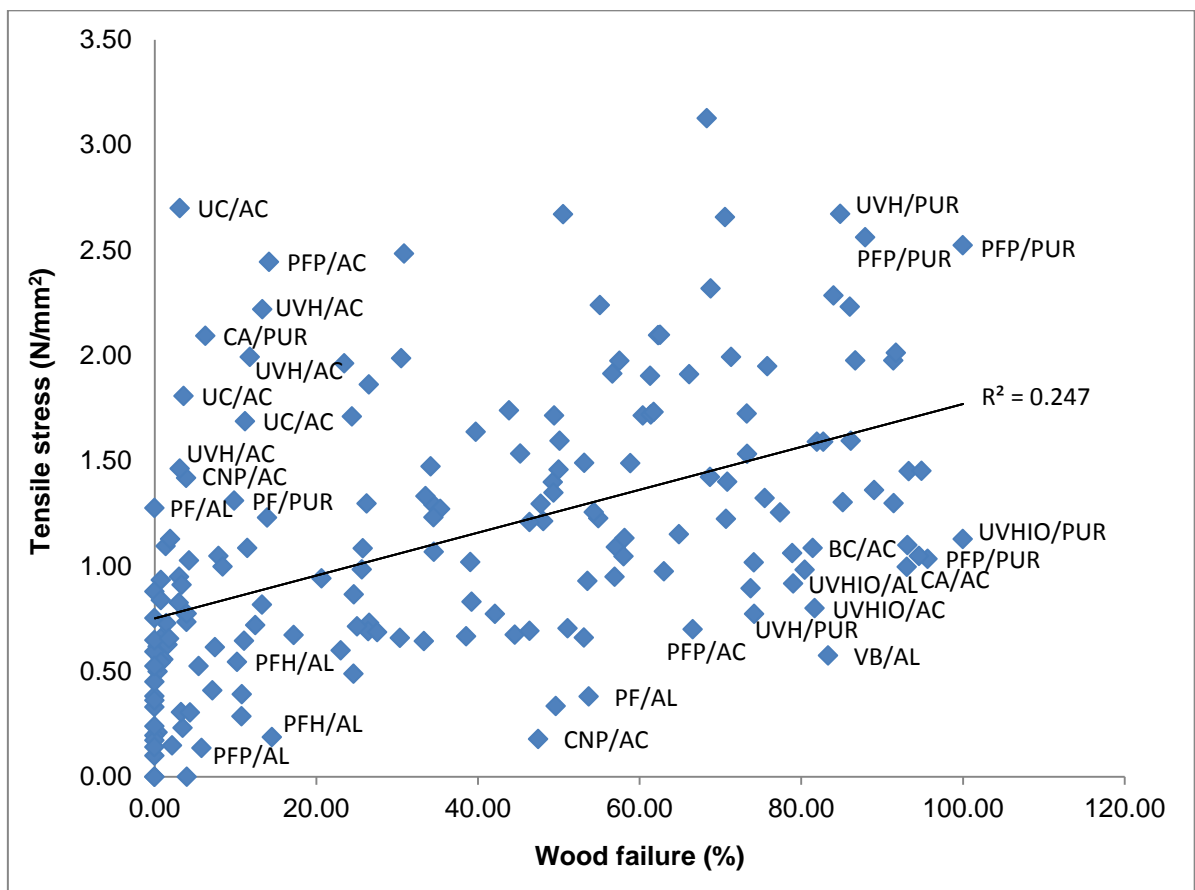


Figure 3.23: Regression of coating adhesion (tensile stress) versus percentage wood failure

All coatings that showed dolly failures of more than 70% were analyzed. Results showed only 9.5% of dolly failures occurred with the PUR and 16.5% with AC. However, 74% of dolly failures occurred with the AL coating. From these 74%,

well over half (61%) had tensile stresses lower than the average for the AL coating (0.67 N/mm^2) and 35% had tensile stresses less than half of the average value.

3.3.6 Coating permeability

There were significant differences ($p < 0.01$) in the permeability of the three different coatings (Table 3.4). The permeability of the PUR coating was significantly lower than that of the AC and AL coatings, as indicated by the longer time it took for a water droplet to penetrate the PUR coating (Fig. 3.24). There was no significant difference ($p > 0.05$), however, in the permeability of the acrylic and alkyd coatings.

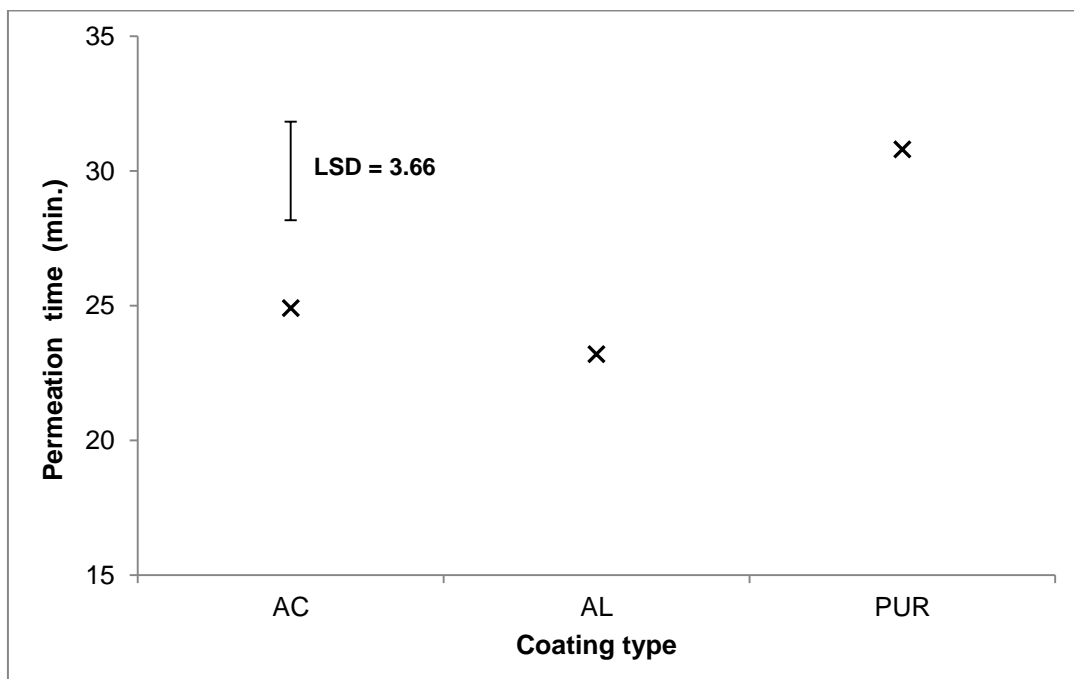


Figure 3.24: Differences in permeability of acrylic (AC), alkyd (AL) and polyurethane (PUR) coating. Permeability was assessed as the time taken for a water droplet ($5 \mu\text{l}$) to penetrate the coating

3.4 Discussion

Comparisons of the best available photostabilizing treatments for wood showed that there were significant differences in their ability to protect wood from photodegradation. I also observed that there were significant differences in the effects of the treatment on wettability of wood and coating adhesion.

Weight losses of wood veneers during natural weathering occur due to the photodegradation of lignin and the leaching of low molecular weight lignin fragments from wood surfaces (Evans & Schmalzl 1989). BC, CA and VB are able to photostabilize lignin and the veneers treated with these chemicals showed the lowest weight losses (Evans & Schmalzl 1989; Evans et al. 2002; Jebrane et al. 2009). The ratio of weight losses of veneers treated with CA or VB compared to those of the controls accord with results of previous studies (Evans & Schmalzl 1989; Jebrane et al. 2009). Surprisingly, the effectiveness of BC at reducing weight losses of wood veneers during weathering was even higher than that observed by Evans et al. (2002). They found that the weight losses of BC treated veneers were 3 to 3.5 times lower than those of untreated controls whereas results here indicate that weight losses of BC treated wood veneers were approximately 9 times lower than those of untreated veneers.

It has been suggested that the introduction of aromatic groups into wood as, for example, occurs with the BC and VB treatments, protects wood from photodegradation by absorbing UV radiation and/or the formation of free radicals (Evans et al. 2002; Jebrane et al. 2009). PF treatments introduce aromatic groups into the wood cell wall and the higher weight losses of PF treated wood veneers in

comparison to BC and VB treated veneers were unexpected (Smith & Côté 1971). However, the high weight losses of PFP treated veneers is probably due to the leaching of polyethylene glycol (PEG) from the wood as PEG is very water soluble (Ohkoshi 2002). One possible reason for the poorer performance of PF treatments compared to BC and VB is that low concentrations (12% (v/v)) of PF-resin were used to treat the veneers. Previous research has found an inverse relationship between weight gain due to modification with BC and VB and weight losses of veneers during weathering (Evans et al. 2002; Jebrane et al. 2009). It is possible that treatments that use higher concentrations of PF-resins and impart higher weight gains to veneers might be better at restricting weight losses of veneers during weathering.

Veneers treated with CNP had significantly lower ($p < 0.05$) weight losses than the untreated controls, whereas weight losses of UVH treated veneers were similar to those of the controls. These observations contrast with those of Liu et al. (2010). They found that veneers treated with UVH had significantly lower ($p < 0.05$) weight losses during 30 days of natural weathering than untreated controls, whereas weight losses of veneers treated with CNP were not significantly different ($p > 0.05$) from weight losses of untreated controls. Liu et al. (2010) used cerium oxide nanoparticles to treat veneers whereas in this study cerium oxide nanoparticles doped with TiO_2 were used.

It is possible that doping of cerium oxide nanoparticles with TiO_2 increased their ability to photostabilize wood resulting in lower weight losses for veneers treated with cerium oxide nanoparticles here, compared to those used by Liu et al.

(2010). On the other hand the finding that treatment of wood veneers with iron oxide is very effective at restricting weight losses during weathering accords with the findings of Liu et al. (2010). Furthermore, veneers treated with UVHIO had significantly lower ($p < 0.05$) weight losses than veneers treated with UVH alone. The hydrophobicity of iron oxide in addition to its ability to screen the wood from UV light may have reduced leaching of UVH from the wood, and could account for the finding that veneers treated with UVA/HALS in combination with iron oxide showed lower weight losses than veneers treated with UVA.

There is some evidence from previous studies that low weight losses of treated veneers during weathering are associated with low losses in tensile strength (Evans et al. 2002; Evans 2009; Jebrane et al. 2009). BC and CA treated veneers followed this trend. Veneers treated with BC or CA showed low weight losses and lower losses in tensile strength during natural weathering than untreated controls. Nevertheless, treatment of veneers with BC (before weathering) caused significant tensile strength losses. A possible reason for these tensile strength losses could be related to the formation of hydrochloric acid during the esterification of wood with BC. Hydrochloric acid might have caused hydrolysis of the cellulose, although the hydrochloric acid should have been neutralized by the alkaline pyridine catalyst. Tensile strength losses of BC treated wood prior to weathering were also observed by Evans et al. (2002). They suggested the introduction of benzoyl groups into the cell wall disrupted intermolecular bonding of cellulose leading to reduced tensile strengths. Tensile strength reductions of BC treated veneers were less pronounced in this study probably because the veneers used here had larger cross sectional

dimensions than those used by Evans et al. (2002). Treatment of veneers with CA led to even higher tensile strength losses prior to weathering than treatment with BC. A similar trend was also observed by Evans (2009). He found that CA treatment of wood veneers to higher weight gains resulted in significant tensile strength losses. However, tensile strength losses in this study were four times higher than those observed by Evans (2009) despite the fact that the weight gains of the veneers were similar.

Treatment of wood with PFP restricted tensile strength losses during weathering and the treatment was as effective as BC and more effective than CA at preventing tensile strength losses. This finding is interesting because veneers treated with PFP had significantly higher weight losses than BC and CA treated veneers during weathering. During the experiment, when handling veneers treated with PFP, it was noticed that these veneers were much more flexible than those treated with PF or PFH. The increased flexibility of these veneers might be related to the higher flexibility of the PEG molecule itself due to its low glass transition temperature (Miyata et al. 2005). The higher flexibility of veneers treated with PEG might also be associated with the lower tensile strength losses for weathered PFP treated veneers compared to the weathered PF and PFH treated veneers. Another possible explanation for the lower tensile strength losses of PFP treated veneers might be related to the ability of PEG to scavenge free radicals which could have led to additional photoprotection particularly in comparison to veneers treated with PF-resin only (Minemura 1978; Janson & Forsskåhl 1989).

Another interesting finding was that veneers treated only with PF showed significantly higher tensile strength losses than veneers treated with PF containing the hindered amine light stabilizer Lignostab 1198. The ability of Lignostab 1198 to improve the performance of the PF-resin is presumably linked to its ability to scavenge free radicals (Wicks et al. 1999; DebRoy 2006). According to Evans (2008), free radicals are formed in wood exposed to UV light due to the photodegradation of lignin. These aromatic radicals and other radicals are then involved in the degradation of cellulose and hemicellulose. Scavenging of these radicals by Lignostab 1198 probably protected cellulose from photo-oxidation and led to lower tensile strength losses of PFH treated veneers. The other treated veneers had significantly lower tensile strength losses during weathering than the untreated veneers. This finding indicates that all of the treatments were able to photostabilize cellulose to some extent.

The lack of precise measuring tools and the long times needed for wood to erode during natural weathering has led to a rejection of erosion measurements as a tool for assessing the weathering of wood during natural weathering (Evans & Schmalzl 1989). The introduction of confocal profilometry changed this view because it has been shown that this technique can accurately measure very small levels of erosion in metals, ceramics and wood (Wilken et al. 2003; Liu & Evans 2009). Erosion measurements here revealed that all of the pre-treatments significantly reduced the erosion of wood veneers exposed to weathering. BC was particularly effective in restricting erosion. This finding is noteworthy and together with results for weight and tensile strength losses during weathering, supports the

suggestion that BC is highly effective at photostabilizing wood exposed outdoors (Evans et al. 2002).

The addition of PEG or HALS to the PF-resin did not influence the effectiveness of the PF-resin to prevent the erosion of treated veneers during weathering in contrast to the results for weight and tensile strength losses. This finding suggests that the PF-resin was responsible for restricting erosion of wood veneers during weathering. UVA and HALS additives when combined, however, reduced the erosion of veneers. This observation accords with the findings of Williams (1983). He found that the grafting of the UV absorber 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone (HEPBP) to western red cedar wood significantly reduced the erosion rate of the treated wood exposed to artificial weathering. The specific type of additive applied to veneers did not greatly influence erosion of veneers because there was no significant difference ($p>0.05$) in the erosion of veneers treated with UVH, UVHIO or CNP.

Some of the chemical pre-treatments significantly altered the wettability of coatings applied to treated veneer surfaces. This was particularly noticeable for veneers treated with UVH and UVHIO. Both, UVH and UVHIO treatments reduced the wettability of wood surfaces, and high contact angles were recorded for the AC and AL coatings on veneers treated with UVH and UVHIO. A possible explanation for this effect is related to the polarity of the aromatic groups found in the UV absorber Tinuvin 384 and the HALS Tinuvin 292. Aromatic groups are non-polar and show hydrophobic characteristics towards polar molecules such as water. The AC and AL coating are both water-based, which possibly explains the high contact

angles that developed when the AC and AL coatings were applied to wood surfaces treated with UVH and UVHIO. Conversely, the PUR coating used here is solvent-borne and carrier solvents commonly used for PUR coatings are either aromatic or aliphatic and thus have non-polar characteristics (Stoye & Freitag 1998). Because non-polar molecules are attracted to other non-polar molecules this might explain why, in contrast to the water-based coatings, the solvent based PUR coating had significantly lower contact angles on wood surfaces treated with UVH and UVHIO than the water-based coatings.

All of the other treatments had no significant effect on the wettability of different coatings, except for CA which increased the wettability of the PUR coating. Nevertheless, there was a pronounced difference in the wettability of the water-based AC and AL coatings and the solvent-based PUR coating on chemically treated veneers. Most of the treatments including BC, VB, UVH, UVHIO and the PF treatments introduced aromatic groups to the wood surface and, as mentioned above, the polarity of these groups may have altered the wettability of the water-based and solvent-based coatings on treated veneers. An exception to this trend can be seen with PFH treated veneers. PFH contains aromatic groups, but there was no difference in the wettability of the three coating types on veneers treated with PFH. A possible explanation for this effect is that the addition of Lignostab 1198 to the PF-resin altered the polarity of the PF molecule. However, there is no information available on the structure of Lignostab 1198 and thus further research would be needed to confirm this suggestion.

CA and CNP did both not introduce aromatic groups into the wood, although CA alters the structure of lignin (Schmalzl et al. 2003). However, there was still a significant difference between the wettability of the water-based and solvent-based coatings on wood veneers treated with CA or CNP. CA treated veneers were hydrophobic to water-based coatings. This observation accords with that of Chauhan et al. (1997). They found that CA treatment of rubber (*Hevea brasiliensis* Müll.Arg.) and mango (*Mangifera indica* L.) wood led to significant reductions in water absorption.

According to Shiraishi et al. (2009), polar molecules such as water have a poor affinity with metal oxides such as TiO₂. The CNP used in this study is a metal oxide and also included 10% TiO₂. This observation may explain why water-based coatings had poor affinity to veneers treated with CNP, and it may also account for the lower wettability of CNP treated veneers to water-based coatings compared to the solvent-based PUR.

AC coatings had higher wettability on untreated veneers than the AL coatings. This finding is surprising for two reasons. Firstly, both AC and AL coatings are water based and their solid particle contents were similar. Secondly, there was no significant difference in the wettability of the AC and AL coatings on treated veneers. Further research would be needed to better understand this difference in the wetting properties of the water-based AC and AL coating on untreated veneers.

A pull-off test was used to determine the adhesion of different coatings on chemically treated wood surfaces. Results from this test showed that the chemical treatments had no effect on the maximum tensile stress needed to pull off coatings

from the substrate. However, there was a difference in the adhesion of the three coatings to the wood substrates. The PUR coating had the highest adhesion to the wood, followed by the AC coating. For the AL coating, a lower tensile stress was needed to pull the coating from the wood substrate. In fact, the adhesion (tensile stress) of the AL coating was less than half that of the PUR coating.

According to de Moura & Hernández (2005) coating adhesion is related to wettability of the coating on the wood substrate. They observed a positive relationship between the wettability of a UV-curable PUR coating on sugar maple (*Acer saccharum* Marsh.) and tensile stresses in adhesion pull-off tests. This relationship may explain why the PUR coating which had the highest wettability of the 3 coatings tested here, bonded more strongly to the different wood substrates (de Moura & Hernández 2005). However, the wettability of the AC and AL coatings was not significantly different although the adhesion (tensile stress) of the AC coating was greater than that of the AL coating. One possible explanation for this discrepancy is that the pull-off test did not accurately measure the adhesion of the AL coating to the wood veneers. In support of this suggestion, it was observed that there was poor adhesion between the AL coatings and the dollies. Failure often occurred between the coating and the dollies, and, hence, low tensile stresses were recorded.

In contrast to the tensile stress results, both chemical treatment and coating type influenced wood failure during adhesion testing. Wood failure was higher for the PUR coating than for the AC and AL coatings. This observation accords with the higher tensile strength and wettability of the PUR coating compared to the AC and

AL coatings. Regression analyses confirmed that there was a positive relationship between tensile stress and wood failure.

There was a significant interaction between coating type and treatment on wood failure, as mentioned above. The PUR coating had higher percentage wood failure on all treated veneers except those treated with CA. Also PUR was significantly different from the other coatings in terms of percentage wood failure except on wood treated with CNP and PF. These findings are contrary to the wettability results. A possible explanation for these discrepancies might be the poor adhesion of dollies to the AL coating, as mentioned above. It is also possible that poor adhesion between some of the treated veneers and solid wood blocks might have contributed to the discrepancies between results for coating failure and coating wettability.

There was no difference in the permeability of the AC and AL coatings. The PUR coating, however, was significantly less permeable than both the AC and AL coatings. This observation accords with Ahola (1991) who found that the permeability of PUR coatings applied to pine and Norway spruce (*Picea abies* L. H. Karst.) wood was very low. PUR films contain a network of highly cross-linked resin which prevents the ingress of water molecules and explains their relatively low permeability.

Based on the observations in this Chapter the most effective chemical treatments to reduce photodegradation of wood were BC, VB and CA followed by the PF treatments and UVHIO. The successful treatments, with the exception of UVHIO, achieved their protective effects either by modifying lignin or incorporating

aromatic groups into wood cells. The most pronounced differences in coating properties were observed between the water-based coatings and the solvent-based PUR coating. The PUR coating had lower contact angles and better adhesion properties than the AL and AC coatings on almost all of the effective photoprotective pre-treatments. The PUR coating was also less permeable than the AL and AC coatings. Therefore, it seems reasonable to assume that the combination of an effective photoprotective treatment such as BC or VB with a PUR clear coating would perform the best on wood used outdoors. Nevertheless, outdoor weathering involves many factors that are difficult to incorporate into service life predictions. Thus, a natural weathering trial of the chemical wood treatments tested here in combination with several clear coatings was carried out to test the hypothesis that a good photoprotective wood treatment and the PUR coating would perform well outdoors. The results of this trial are described in the next chapter.

3.5 Conclusions

The aim of the research in this chapter was to compare the ability of several different chemical treatments to photostabilize wood and to determine how these treatments alter the properties of three different types of clear coatings. The most effective photoprotective treatments were BC, VB and CA, followed by PF treatments and UVHIO. These treatments were all effective at reducing weight loss, tensile strength loss and erosion of wood veneers during natural weathering. Chemical pre-treatments of wood surfaces influenced the wettability of different coatings. The highest wettability occurred on CA, UVH and UVHIO treated veneers with the PUR coating. Coating wettability was lowest on UVH and UVHIO treated

veneers. The other treatments did not significantly alter wettability regardless of the type of coating used. However, there was a distinct difference in the wettability of the solvent-based PUR coating and the water-based AC and AL coatings on treated wood veneers, except for the PFH treatment. Chemical modification of veneers had no effect on coating adhesion. However, coating adhesion was highest for the PUR coating followed by the AC and AL coatings. Wood failure during adhesion testing, which is a measure of the effectiveness of bonding, however, was influenced by both chemical treatment and coating type. The highest levels of wood failure occurred on UVH, UVHIO and BC treated veneers coated with PUR. The lowest wood failure occurred with the water-based AC and AL coatings. For these coatings, chemical treatment did not influence wood failure except for BC and CA treatments. There was also no difference in the permeability of AC and AL coatings. However, the PUR coating was significantly less permeable than the AC and AL coatings.

4. Effect of pre-treatments on the durability of clear coatings (experiment 2)

4.1 Introduction

In Chapter 3, I compared the ability of different chemical treatments to photostabilize wood exposed outdoors. The most effective treatments were benzoyl chloride (BC), vinyl benzoate (VB), chromic acid (CA), UVA/HALS with yellow iron oxide (UVHIO) and PF-resin (PF). Chemical treatment of wood also altered some of the surface properties of wood that affect coating performance such as wettability and adhesion. The extent of changes to these surface properties appeared to depend on both wood treatment and the type of clear coating that was applied. In general, however, the PUR appeared to be the most compatible coating with modified wood surfaces.

As mentioned in Chapter 2 there has not been a lot of research on the influence of chemical modification on the performance of water-borne clear coats on wood used outdoors. However, it has been widely suggested that the key to longevity of clear coats on wood used outdoors is to photostabilize the wood prior to finishing (Black & Mraz 1974; Feist 1979; Derbyshire & Miller 1981). Williams & Feist (1985) found that pre-treatment of wood with chromic acid increased the longevity of clear coats on wood exposed outdoors from 2-3 years to 15 years. Kiguchi & Evans (1998) also reported that grafting of wood with the UV absorber HEPBP improved the performance of two types of clear coats (silicone-urethane and polybutadiene) on wood exposed to natural and artificial weathering.

Based on these observations and the earlier findings in Chapter 3, it seems reasonable to hypothesize that modification of wood with pre-treatments such as BC, and VB which can photostabilize lignin will enhance clear coat performance on wood used outdoors. Furthermore, based on findings in Chapter 3 it is hypothesized that clear coat performance will depend on the combination of chemical pre-treatment and coating type, and it appears likely that coating performance would be better when a PUR coating is used. The aim of this research was to test these hypotheses by examining the effect of nine different chemical pre-treatments and seven different clear coat types on color, coating failure and general appearance of coated modified wood samples exposed to one year of natural weathering in Australia. The results of this experiment are expected to show which treatment and clear coat combination performs best during outdoor exposure. The findings are expected to improve our understanding of the interactions of pre-treatment and clear coat type on coating performance and help manufacturers to design better (highly durable) clear coat systems (pre-treatment plus coating) for wood used outdoors.

4.2 Methods and materials

4.2.1 Experimental design and statistical analyses

A factorial experiment was designed to examine the effect of two fixed factors: (1) Treatment (nine chemical treatments and an untreated control); (2) Coating (seven different clear coat types). Veneer samples were cut from four different wood blocks which provided replication at the higher level. Within each experimental block (1-4), veneers were randomly assigned to the different pre-

treatments. Veneered and coated composite samples within each block (1-4) were then randomly assigned to four weathering racks (one block per weathering rack). An appropriate ANOVA was performed to assess the effect of fixed and random factors on the response variables: color and appearance of coated composite samples. Prior to statistical analysis, diagnostic checks were performed to determine whether data conformed to the underlying assumptions of ANOVA, i.e., normality and equal variance of residuals. To fulfill these assumptions, data for the color parameter 'a' (green to red) were transformed into natural logarithms. Statistical computation was performed using Genstat 12.1 (VSN International 2009) with the significance level α defined at 0.05. Significant results ($p < 0.05$) are plotted graphically and LSD bars or \pm SED bars can be used to compare differences between individual means. Appendix 3 contains a complete record of all statistical analyses that were performed.

Coating failure measurements such as cracking, blistering and delamination were also used to assess the coating performance. Results from these measurements, however, were not subjected to statistical analysis, but rather tabulated.

4.2.2 Sample preparation

A total of 280 yellow cedar veneers measuring 100 mm (length) x 35 mm (width) x 100 μ m (thickness) were cut from four different t-shaped wood blocks (70 veneers per block) using the methods described previously in Chapter 3. Veneers were conditioned (20°C; 65% r.h.) for 14 days, and then Soxhlet extracted with a mixture of toluene/ethanol/acetone (4:1:1 v:v:v; all industrial grade) for four hours.

Veneers were then oven-dried at $105\pm 5^{\circ}\text{C}$ for 2.5 hours and cooled for 10 minutes in a desiccator over silica gel before their weight was measured using a digital scale (A&D GR-200). The chemical treatments were the same as those described in Section 3.2.1.2.b. After chemical treatment, veneers were stored in a conditioning room for two days and then oven dried and re-weighed, as above. Weight gains of veneers due to chemical treatment are expressed as a percentage of their oven-dry, unreacted, veneer weight.

A total of 280 western red cedar blocks measuring 100 mm (length) x 35 mm (width) x 10 mm (height) were cut from four larger boards using an Altendorf F45 table saw. Wood blocks were first planed with a Martin T44 planer and then sanded with a wide belt sander (SCM Unisand K) using a feed speed of 5 m/min, a belt speed of 24 m/s and 150 grit sandpaper (3M with XODUST). These western red cedar blocks were used as the 'core' of a composite which contained modified yellow cedar face veneers. Red cedar was chosen as the core because it is dimensionally stable and decay resistant (Scheffer 1957). Modified yellow cedar veneers were glued onto the red cedar core as described above in Section 3.2.2.2.a. A phenol-resorcinol-formaldehyde adhesive (Arclin, Inc.) was used instead of polyvinyl acetate glue to create a durable water-resistant glue line. The clamping time used to bond yellow cedar veneers to the red cedar core was increased from one to two hours. After all veneers were glued to the wood blocks, the edges of the composite were rounded by hand with 150 grit sandpaper. Veneered wood blocks were then stored in a conditioning room for one week.

Each veneered block was coated with one of seven different types of clear coatings (Table 4.1). Clear coatings were applied to the upper veneered face of the composites with a HVLP (High Volume Low Pressure) spray gun (Graco, Air Pro) which was connected to a pressure pot, as described in Section 3.2.2.2.b. Each coating was applied twice (two films), according to manufacturer's recommendations, which can be found in Appendix 4. The acrylic and alkyd coatings were ready-to-use systems, whereas the PUR coating had to be prepared as described in Section 3.2.2.2.b. Coated wood composite blocks were then stored in a conditioning room for two days.

Table 4.1: Clear coat types applied to composite wood specimens

No.	Binder	Additives	Abbreviation	Company	Wet film thickness (per film)
1	Standard Acrylic*	UVA/HALS	SA	Akzo Nobel	130 µm
2	Standard Acrylic*	(UVA/HALS) x 2	SA+	Akzo Nobel	130 µm
3	Harder Acrylic*	UVA/HALS	SAH	Akzo Nobel	130 µm
4	Alkyd*	UVA/HALS	AL	Akzo Nobel	130 µm
5	Standard Acrylic*	UVA/HALS + 1.0 % cerium oxide nanoparticles	SAC+	Akzo Nobel	130 µm
6	Standard Acrylic*	UVA/HALS + 0.5 % cerium oxide nanoparticles	SAC	Akzo Nobel	130 µm
7	Polyurethane**	n.a.	PUR	ICA	100 µm

* = water based; ** = solvent based

The backside of each veneered wood composite block was coated with three layers of an exterior spar varnish (Behr, No. 31-12) using a medium-hard paint brush. All edges of the veneered wood composite blocks were sealed with two-part epoxy (Industrial Formulators, G2) to avoid water uptake on side and end grain. Edges containing end-grain, which is more permeable than side-grain, were sealed twice. Samples were conditioned for two days and a hole 4 mm deep with a diameter of 11.5 mm was drilled into the center of the back of each sample using a manual drill press (Delta type 16 ½). Holes were then filled with two-part epoxy glue, and stainless steel machine bolts (M6 x 30) were set into the holes in the back of samples as shown in Figure 4.1. Veneered wood blocks were conditioned again for one week, to allow the epoxy adhesive to harden and secure the bolts in place.

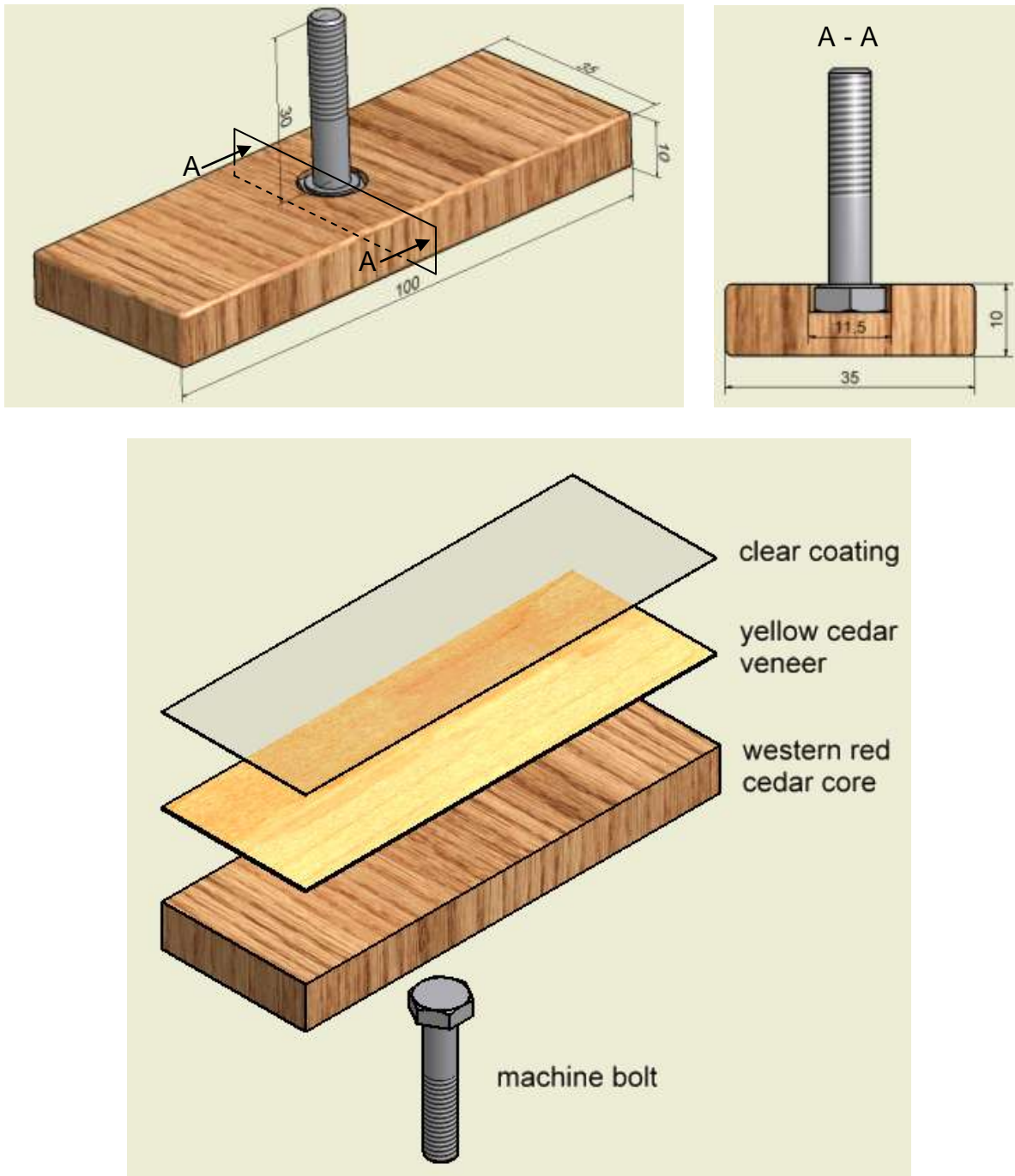


Figure 4.1: Top: Veneered wood composite block with attached stainless steel machine bolt (left) and detail A-A of drilled hole to accommodate machine bolt (right). Bottom: Exploded view of coated wood composite assembly. Note: grain direction of wood block shown above does not represent the actual grain direction

4.2.3 Weathering racks

Two pressure-treated (alkaline copper quarternary compound) plywood sheets measuring 2440 mm (length) x 1220 mm (width) x 18 mm (thickness) were obtained from a 'Big Box' retailer (Home Depot). Plywood sheets were cut in half using an Altendorf F45 table saw, and then resawn to produce four sheets with the following dimensions: 887mm (length) x 560 mm (width). These sheets were each mounted onto the pods of a SCM 'pod and rail' CNC router (Action Line) to produce the backing board for a weathering rack (Figure 4.2). Machined plywood sheets were then sanded with an orbital sander (Dynabride® Dynorbital®) equipped with 150 grit sandpaper (3M). Prior to any finishing, all edges were rounded by hand using 150 grit sandpaper.

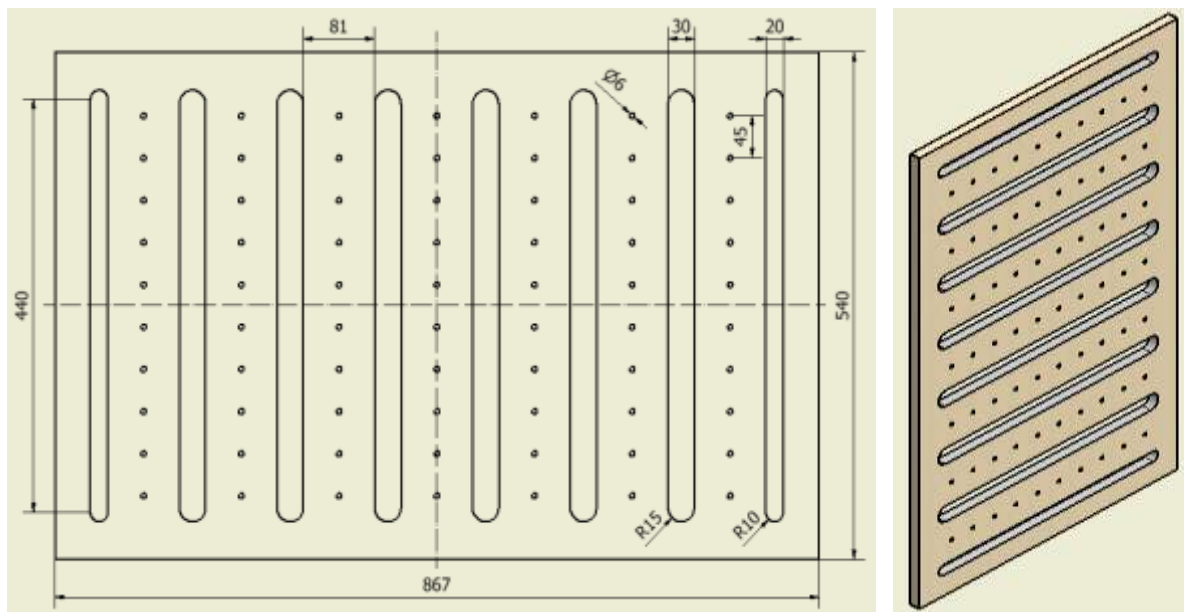


Figure 4.2: Machined backing board for the weathering rack used for outdoor exposure tests of veneered and coated composite wood blocks

Each of the four backing boards was coated with a white acrylic latex primer (Benjamin Moore, ultrawhite 10301) using a medium-hard paintbrush. Primed racks were dried at room temperature for four hours and then manually sanded with 220 grit sandpaper. Finally, two coats of brown acrylic latex paint (Benjamin Moore, Moorestyle HC-67) were brushed onto the boards with four hours drying between each coat. Boards were then air dried for 24 hours at room-temperature. Veneered wood composite blocks were mounted onto the backing boards. The blocks were fastened to the backing boards with M6 stainless steel nuts screwed onto the threads of the bolts that protruded from the backsides of the panels (Figure 4.3).



Figure 4.3: Detail of wood blocks fastened with M6 stainless steel nuts to weathering racks

The assembled weathering racks (backing boards and mounted finished wood composite blocks) were securely wrapped with bubble wrap and packed into a

large cardboard box filled with polystyrene foam (Styrofoam). Boards were air-freighted to Australia. Four tables (one for each weathering rack) each consisting of four CCA-treated legs (100 mm x 100 mm cross sectional area, 700 mm length) and a three ply plywood top (1200mm length x 600 mm width x 15mm thickness) reinforced with a 30 mm thick CCA treated wood frame (70 mm frame width) were constructed at the test site in Australia. Plywood tops including the reinforced frame were painted with two coats of a brown acrylic paint (Wattyl solar guard opaque Mission Brown). The plywood tops and CCA treated legs were then attached to each other using screws that were screwed through the plywood top into the end-grain of the legs. Steel strips were used to connect and brace the legs and the plywood tops. The assembled tables were secured to the ground with iron stakes (pickets) that were attached to the legs with screws. Plywood wedges with a 10° slope were fastened with screws onto each table top. These plywood wedges (600 mm length x 106 mm width x 36 mm thickness) were made from the same material as the backing boards and were primed and painted with the same acrylic latex paint (as above). Assembled weathering racks were placed onto these wedges and fastened with screws.

4.2.4 Natural weathering

Veneered and coated wood blocks were exposed to the weather in Kioloa, New South Wales, Australia (-35° 32' 24.00", +150° 22' 12.00") for a total of 349 days from the 16th of December 2009 to the 30th of November 2010 (Fig. 4.4).



Figure 4.4: Exposed samples facing the equator (North) at the test side in Kioloa, New South Wales, Australia. Note the 10° inclination of the samples on the tables

The monthly average, lowest and highest temperatures as well as the monthly total rainfall during the exposure period are shown in Table 4.2.

Table 4.2: Monthly weathering data for the exposure period of test samples in Australia. Data obtained from a weather station in Ulladulla, NSW approximately 30km north of the test site at Kioloa

Month	Average temperature*	Lowest temperature*	Highest temperature*	Total amount of rainfall*
December 2009	20.3 °C	13.9 °C	26.9 °C	73.8 mm
January	21.3 °C	10.6 °C	36.9 °C	56.4 mm
February	22.1 °C	15.0 °C	35.2 °C	217.4 mm
March	20.1 °C	13.8 °C	32.1 °C	111.4 mm
April	18.4 °C	9.4 °C	29.4 °C	27.8 mm
May	15.5 °C	8.4 °C	24.0 °C	180.4 mm
June	12.9 °C	5.0 °C	19.6 °C	128.2 mm
July	12.3 °C	6.2 °C	20.0 °C	97.8 mm
August	12.8 °C	5.8 °C	20.5 °C	38.8 mm
September	14.3 °C	6.1 °C	24.5 °C	70.8 mm
October	16.3 °C	7.3 °C	27.5 °C	69.4 mm
November 2010	17.1 °C	9.8 °C	24.6 °C	197.8 mm
Average/Total	16.9 °C	5 °C	36.9 °C	1270 mm

*Source: <http://www.bom.gov.au/climate/dwo/IDCJDW2138.latest.shtml>.

A complete record of weather for each day of the exposure trial can be found in Appendix 5. Coated wood composite blocks were removed from the weathering racks at the end of the weathering trial.

4.2.5 Color measurements

A Minolta CM-2600d spectrophotometer was used to measure the color of each of the 280 samples before and after weathering (560 color measurements in total). Color is expressed using the CIE (Commission Internationale de l'Eclairage (HunterLab 2008)) LAB space system consisting of the following three parameters:

- L^* = Lightness (0 = black; 100 = white)
- a^* = greenness/redness (-60 = green; 60 = red)
- b^* = blueness/yellowness (-60 = blue; 60 = yellow)

An SCI (specular component included) setting was used for the measurements. This setting includes gloss measurements and, hence, results account for color changes due to gloss differences as perceived by the human eye. To ensure color measurements were made at exactly same position before and after weathering, 280 paper overlays with the same dimensions as the samples (100 mm x 35 mm) were cut from ordinary office paper (80 g/m²) and a hole 6 mm in diameter was punched at a random location in each paper overlay. The paper overlays assigned to the different samples were placed onto the specimens. The color of the coated samples was measured at the center of the holes in each paper mask.

The chemical treatments altered the color of the yellow cedar veneers. Therefore, the changes in color of samples were calculated and are presented in preference to absolute color measurements. Color changes are expressed as the ratio of color parameters after weathering to the initial color parameters of unweathered treated samples. These ratios were analyzed statistically as described in Section 4.2.1. The total color change delta E occurring as a result of weathering was also calculated according to ASTM standard D2244 (ASTM 2010) as follows:

$$\text{delta } E = ((L_{\text{before}} - L_{\text{after}})^2 + (a_{\text{before}} - a_{\text{after}})^2 + (b_{\text{before}} - b_{\text{after}})^2)^{0.5}$$

4.2.6 Coating failure

Each of the 280 coated wood blocks was assessed for three different types of coating failures: cracking, delamination and blistering using the method described by

Kiguchi et al. (2005). Each specimen was overlaid with a transparent rectangular grid measuring 100 mm (length) x 35 mm (width). The transparent grid was divided into 140 squares, each with a side length of 5 mm. The mode of coating failure in each of the 140 areas (squares) in each grid was recorded after the transparent grids were overlaid on specimens. The total numbers of each type of defect (delamination, blistering or cracking) in each specimen was summed and expressed as percentages by dividing the totals by 140.

4.2.7 Appearance ranking

Each of the 280 coated wood composite samples was scanned using a desktop scanner (Canon CanoScan LiDE 200) attached to a lap-top computer (scanning resolution 300 dpi, File format: Tagged Image File Format (TIFF)). The resulting scans were compared to scans of unweathered samples and an appearance ranking from 1-4 was assigned as follows:

- | | |
|----------------------|---|
| 1 – Perfect | → no coating defects and/or delta E \leq 8 |
| 2 – Minor defects | → minor coating defects and/or delta E \leq 12 |
| 3 – Moderate defects | → moderate coating defects and/or delta E \leq 15 |
| 4 – Severe defects | → severe coating defects and/or delta E $>$ 15 |

Images of every sample before and after weathering can be found in Appendix 6.

4.3 Results

There were statistically significant effects of treatment (T) and coating type (C) and interactions between treatments and clear coat types on 'L* ratio' (lightness), 'a* ratio' (greenness/redness), 'b* ratio' (blueness/yellowness), 'delta E' and the overall appearance of exposed test samples, which are summarized in Table 4.3.

Table 4.3: Significant effects of and interactions between chemical treatments and coating types on color parameters and overall appearance of test samples exposed for 349 days of natural weathering in Kioloa, New South Wales, Australia

Experimental Factors	Response variables				
	Color				Appearance
	L* ratio	a* ratio	b* ratio	delta E	
Treatment (T)	***	***	***	***	***
Coating (C)	***	***	***	***	***
T x C	NS (0.287)	***	***	***	*

* = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$; NS = not significant ($p > 0.05$)

4.3.1 Effect of chemical modification and clear coat type on the color of exposed test samples

There were significant changes in the color of treated and coated wood samples during exterior exposure. The color changes that were observed are summarized below (Table 4.4):

Table 4.4: Initial color and color changes of different wood pre-treatments after outdoor exposure

Treatment	Color prior to exposure	Color changes after outdoor exposure		
		Lighter/ Darker	Greening/ Reddening	Blueing/ Yellowing
BC	Yellow	Slightly darker	Slight reddening	---
CA	Dark brown	Lighter	Greening	---
CNP	Yellow with slight brown tint	Darker	Reddening	---
PF	Yellow with slight brown and red tint	Darker	Reddening	Slight yellowing
PFH	Light brown with strong red tint	---	Slight reddening	Yellowing
PFP	Yellow with slight brown and slight red tint	Darker	Reddening	Slight yellowing
UC	Yellow with slight brown tint	Darker	Reddening	---
UVH	Yellow with slight brown tint	Slightly darker	Slight reddening	---
UVHIO	Slightly darker yellow with slight brown tint	Darker	Slight reddening	Slight blueing
VB	Yellow with slight brown tint	---	Slight reddening	Blueing

--- = no changes; BC = Benzoyl chloride; CA = Chromic acid; CNP = Cerium oxide nanoparticles; PF = PF-resin; PFH = PF-resin + HALS; PFP = PF-resin + PEG; UC = Untreated control; UVH = UV absorber + HALS; UVHIO = UV absorber + HALS + yellow iron oxide; VB = Vinyl benzoate.

The intensity of the color changes for pre-treated wood samples during outdoor exposure also varied between the different coatings. The effect of chemical treatment, coating type and the interaction of treatment and coating type on color parameters during outdoor exposure is described in the following sections.

4.3.1.1 Effect on lightness

4.3.1.1.a Treatment effects

Chemical treatment had a highly significant effect on the L^* ratios of exposed wood samples (Table 4.3). An L^* ratio of close to 1 in Figure 4.5, for example for wood samples pre-treated with PFH and VB, indicates that there were no significant ($p>0.05$) differences in lightness of samples before and after outdoor exposure. L^* ratios less than 1 indicate a darkening of samples.

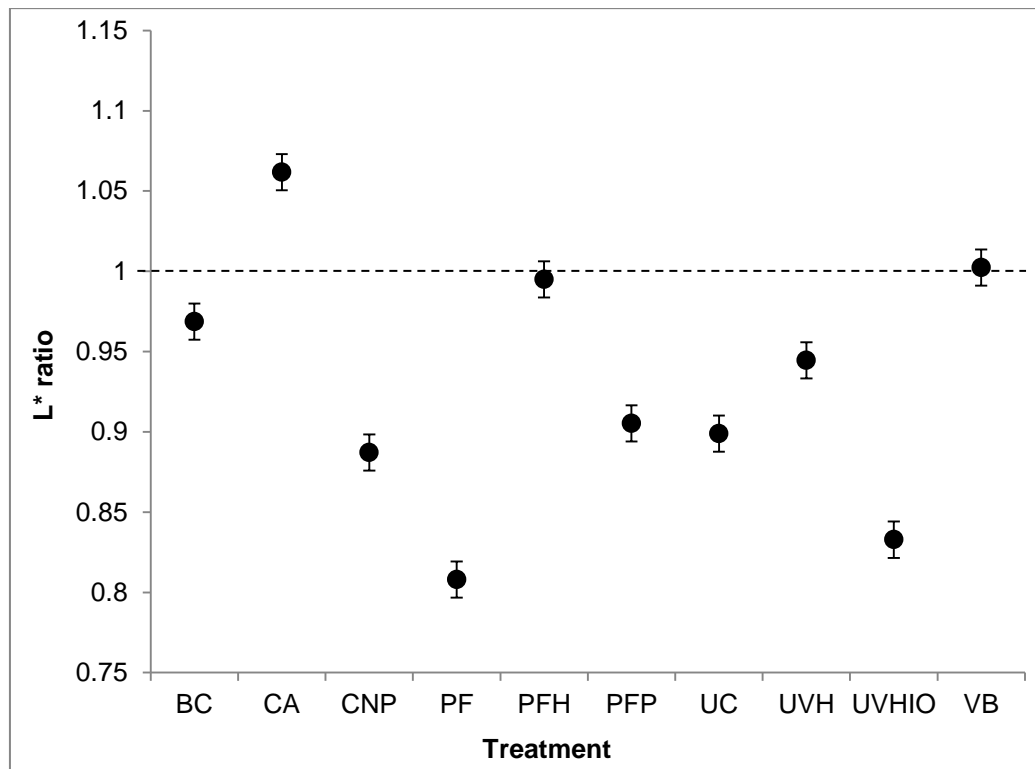


Figure 4.5: Effect of chemical treatment on the lightness ratio (L^* ratio) of coated wood samples exposed to natural weathering. Results are averaged across samples with the different coatings

There was little overall change in the lightness of samples pre-treated with BC, PFH and VB after they were exposed to natural weathering (Fig. 4.6). Samples

pre-treated with these chemicals or UVH were significantly lighter than untreated controls, even though samples treated with UVH darkened significantly more than those treated with BC, PFH or BC.

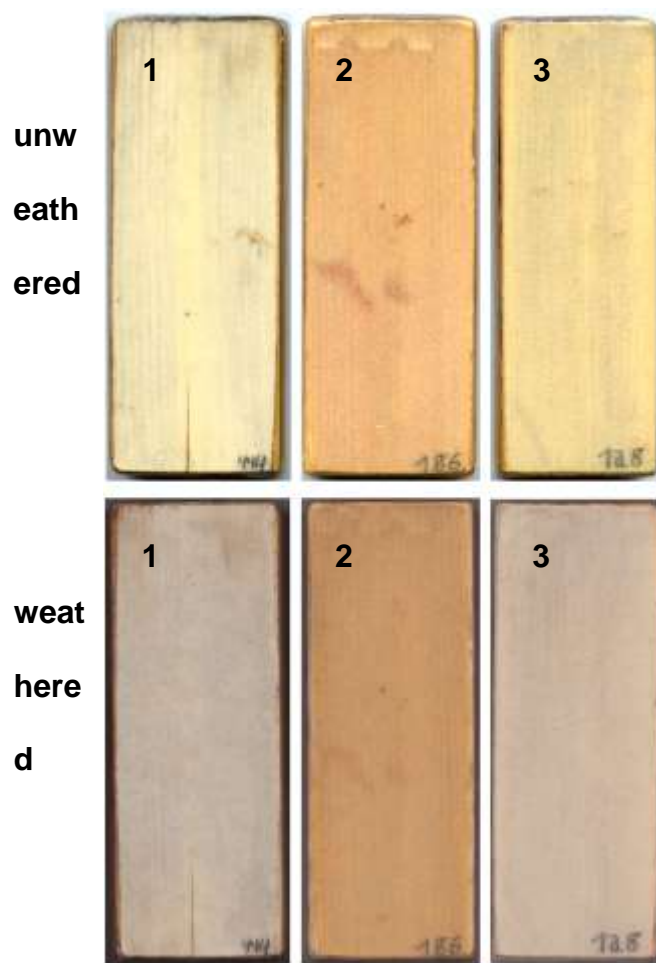


Figure 4.6: Pre-treated wood samples with lowest lightness changes during outdoor exposure: before exposure (top row) and after outdoor exposure (bottom row). From left to right: Benzoyl chloride treated samples (1); PF/HALS treated samples (2); Vinyl benzoate treated samples (3)

Wood samples pre-treated with CNP and PFP darkened significantly more ($p < 0.05$) during outdoor exposure than BC, PFH and VB treated samples. The darkening of samples treated with CNP and PFP was similar to that of untreated

controls because there was no significant difference ($p>0.05$) in their L^* ratios. In contrast, wood samples pre-treated with UVHIO and phenol resin darkened significantly more ($p<0.05$) during outdoor exposure than untreated controls and any of the other pre-treated samples (Fig. 4.5). Furthermore, phenol resin treated samples darkened significantly more than samples treated with UVHIO (Figs. 4.5 and 4.7).

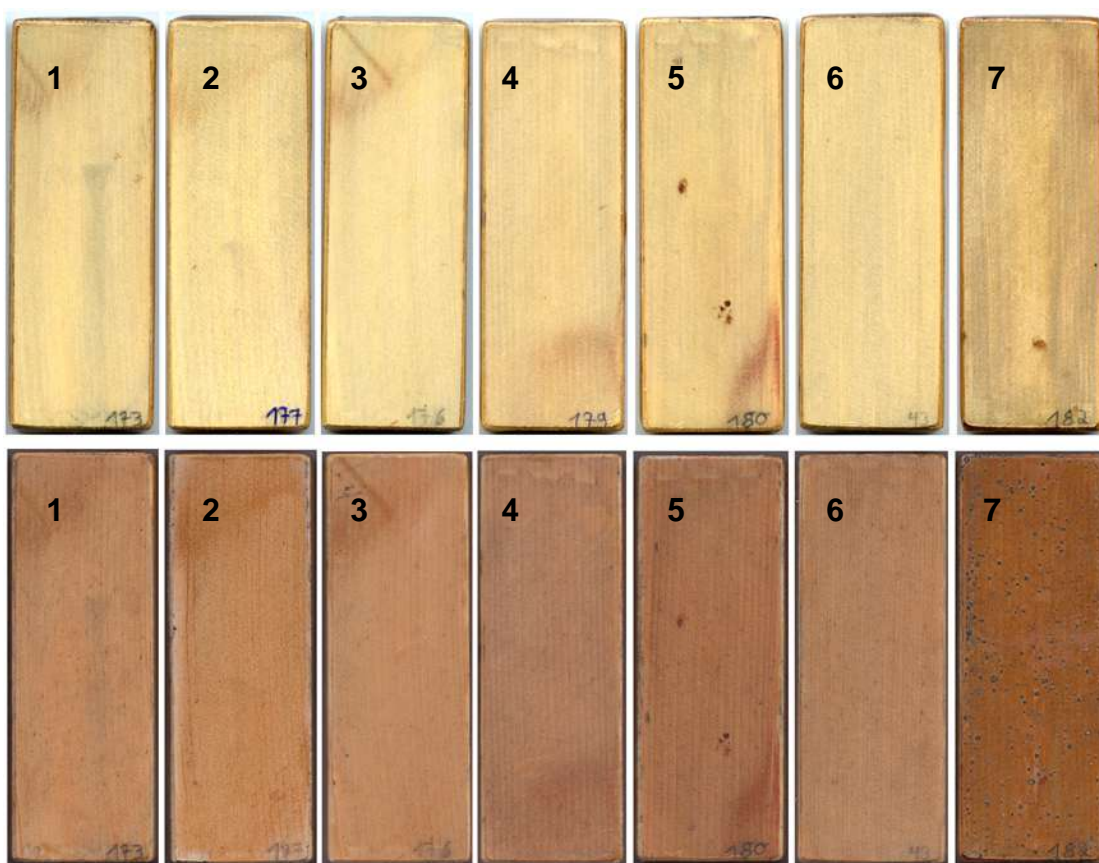


Figure 4.7: Wood samples pre-treated with PF-resin before outdoor exposure (top row) and after outdoor exposure (bottom row). Note the pronounced darkening of the samples. From left to right: PF with standard acrylic coating (1); PF with harder acrylic coating (2); PF with acrylic coating containing double the amount of UVA/HALS (3); PF with alkyd coating (4); PF with acrylic coating containing 1% cerium oxide nanoparticles (5); PF with acrylic coating containing 0.5% cerium oxide nanoparticles (6); PF with polyurethane (7)

Darkening was not observed for wood samples pre-treated with CA. Instead these samples became much lighter during outdoor exposure than any of the other pre-treated samples and also the untreated control.

4.3.1.1.b Coating effects

Coating type also had a highly significant effect ($p < 0.001$) on the L^* ratios of wood samples exposed outdoors. The results below are averaged across samples with the different chemical treatments. Therefore, they indicate that coated samples became darker during outdoor exposure (L^* ratio less than 1), in accord with results described above. Nevertheless, it is still possible to discern the effects of coating type on changes in lightness of samples during outdoor exposure (Fig. 4.8).

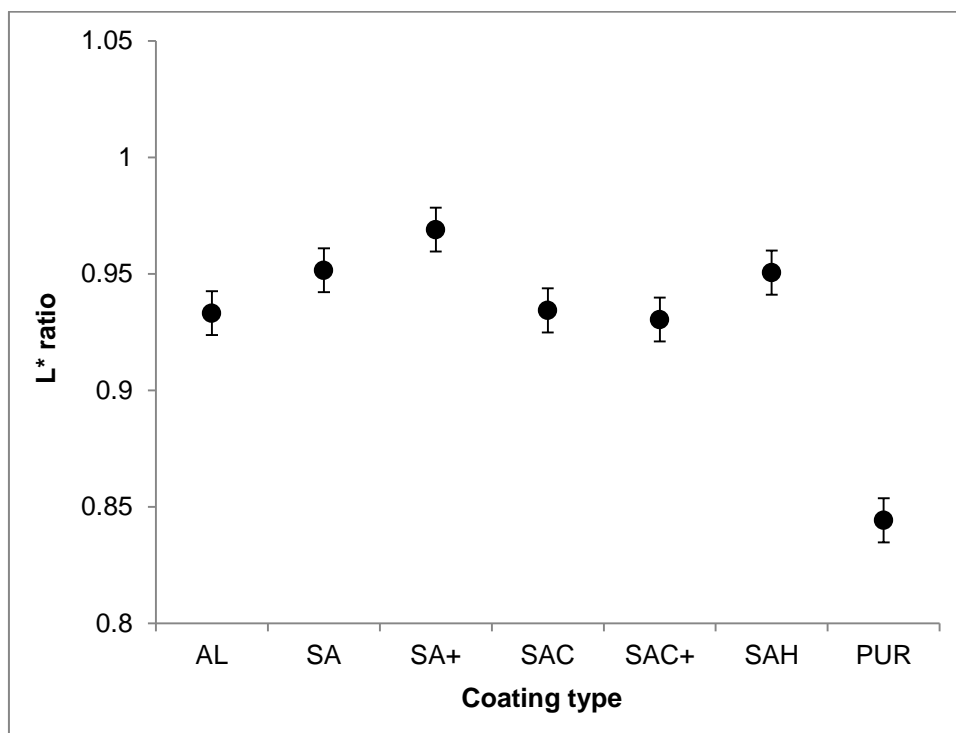


Figure 4.8: Effect of coating type on the lightness ratio (L^* ratio) of coated wood samples exposed to natural weathering. Results are averaged across samples with the different pre-treatments

Results show that samples coated with the acrylic coating containing double the amount of UVA/HALS (SA+) did not darken as much ($p < 0.05$) during outdoor exposure than the other coated samples, except those coated with the standard acrylic coating (SA) or the acrylic coating with the harder binder (SAH). The addition of cerium oxide nanoparticles did not reduce the darkening of the standard acrylic coating (SA) because there is no significant difference ($p > 0.05$) between the lightness ratio of the samples coated with the standard acrylic and the samples coated with the acrylics containing cerium oxide nanoparticles (SAC and SAC+) (Fig. 4.8). The alkyd coating (AL) was generally less effective at restricting the darkening of samples than the acrylic coatings except the acrylics that contained cerium oxide nanoparticles. The PUR coating was much less effective at restricting the darkening of samples. PUR coated samples darkened significantly ($p < 0.05$) more during outdoor exposure than all other coated samples (Figs. 4.8 and 4.9).

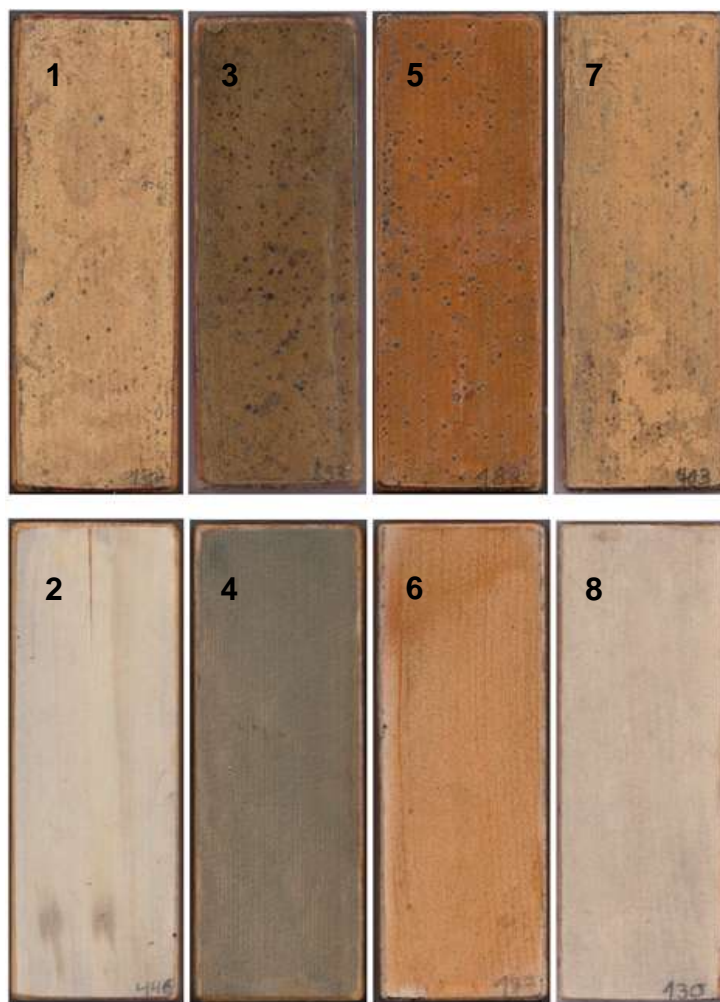


Figure 4.9: Darkening of samples finished with the polyurethane (PUR) coating (top row) in comparison to samples finished with acrylic and alkyd coatings (bottom row) after outdoor exposure. Comparing from left to right: Benzoyl chloride treated samples finished with PUR (1) vs. benzoyl chloride treated samples finished with the standard acrylic coating containing double the amount of UVA/HALS (2); Chromic acid treated samples finished with PUR (3) vs. chromic acid treated samples finished with the standard acrylic coating containing cerium oxide nanoparticles (4); PF-resin treated samples finished with PUR (5) vs. PF-resin treated samples finished with the acrylic coating containing the harder binder (6); Vinyl benzoate treated samples finished with PUR (7) vs. vinyl benzoate treated samples finished with the alkyd coating (8)

4.3.1.2 Effect on greenness/redness

4.3.1.2.a Treatment effects

Analysis of variance showed that 'treatment' had a highly significant effect ($p < 0.001$) on a^* ratios (reddening and greening) of exposed wood samples (Table 4.3). Samples treated with BC, CA, PFH, UVH, UVHIO and VB showed significantly less ($p < 0.05$) reddening during outdoor exposure than untreated controls (Fig 4.10). Of these samples, PFH, UVH and UVHIO in particular were the most effective at restricting the reddening of samples during outdoor exposure, which is indicated by their a^* ratios which are close to 1 (Figs. 4.10 and 4.11). BC and VB treated samples exhibited slightly more reddening and greening, respectively, than PFH, UVH and UVHIO during outdoor exposure. Chromic acid treated samples showed a significantly lower a^* ratio than all other treated samples because their color changed from brown to greyish-green during weathering.

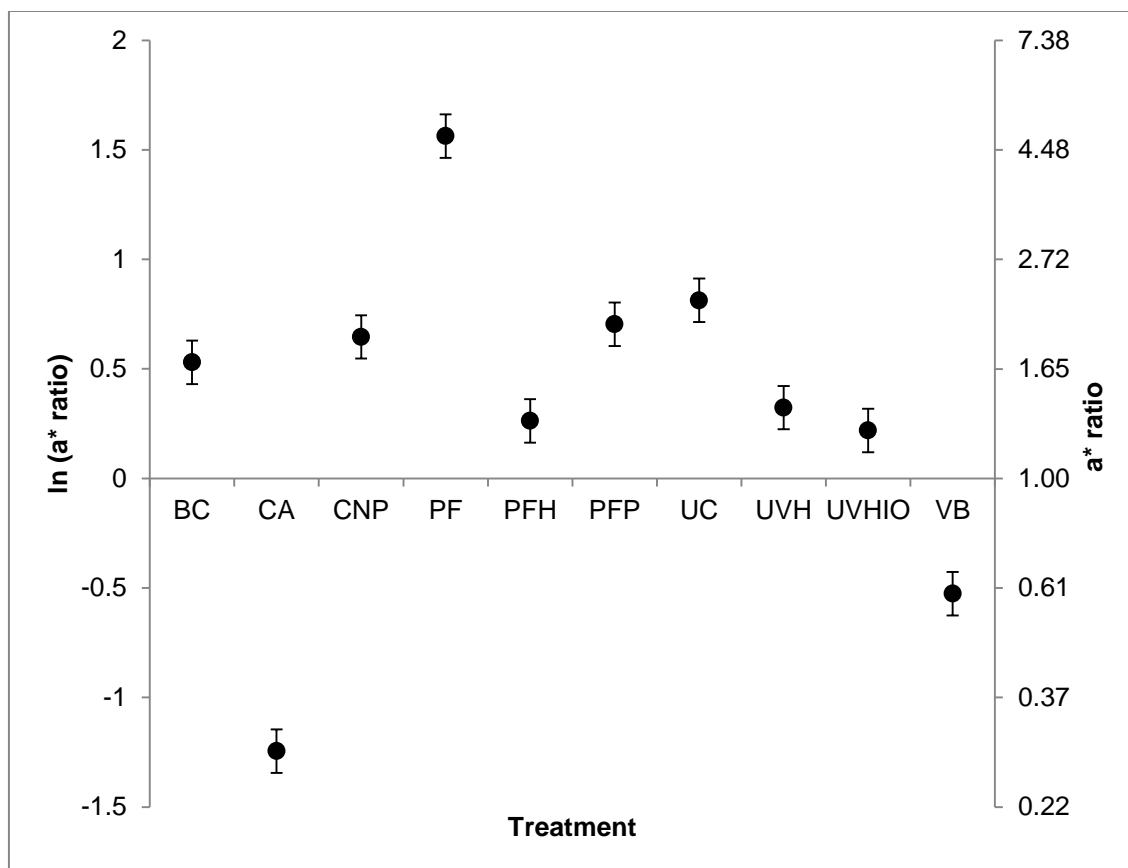


Figure 4.10: Effect of chemical treatment on the a^* ratio (redness/greenness) of coated wood samples exposed to natural weathering. Note the left y-axis displays the transformed data and the right y-axis the untransformed data. Results are averaged across samples with the different coatings

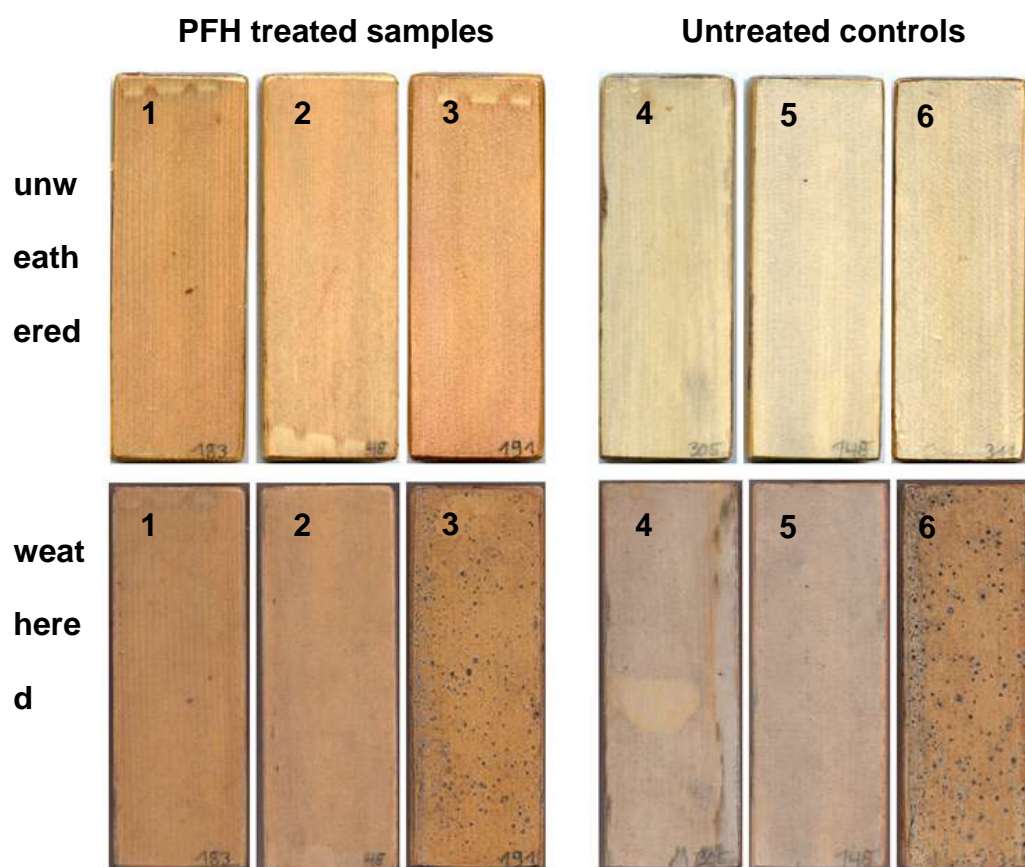


Figure 4.11: Comparison of the redness of PF-resin treated wood samples containing HALS (left) and untreated controls (right) before weathering (top row) and after weathering (bottom row). From left to right within left column: PFH finished with standard acrylic coating (1); PFH finished with alkyd coating (2); PFH finished with PUR (3). From left to right within right column: Untreated controls finished with standard acrylic coating (4); Untreated control finished with alkyd coating (5); Untreated control finished with PUR (6)

CNP and PFP treatments were ineffective at restricting changes in redness of samples during outdoor exposure as both showed no significant difference ($p>0.05$) in a-ratio compared to untreated controls. A particularly large change in a* ratio occurred on samples treated with PF. These samples became much redder during outdoor exposure than any of the other treated samples or the untreated controls (Fig 4.12).

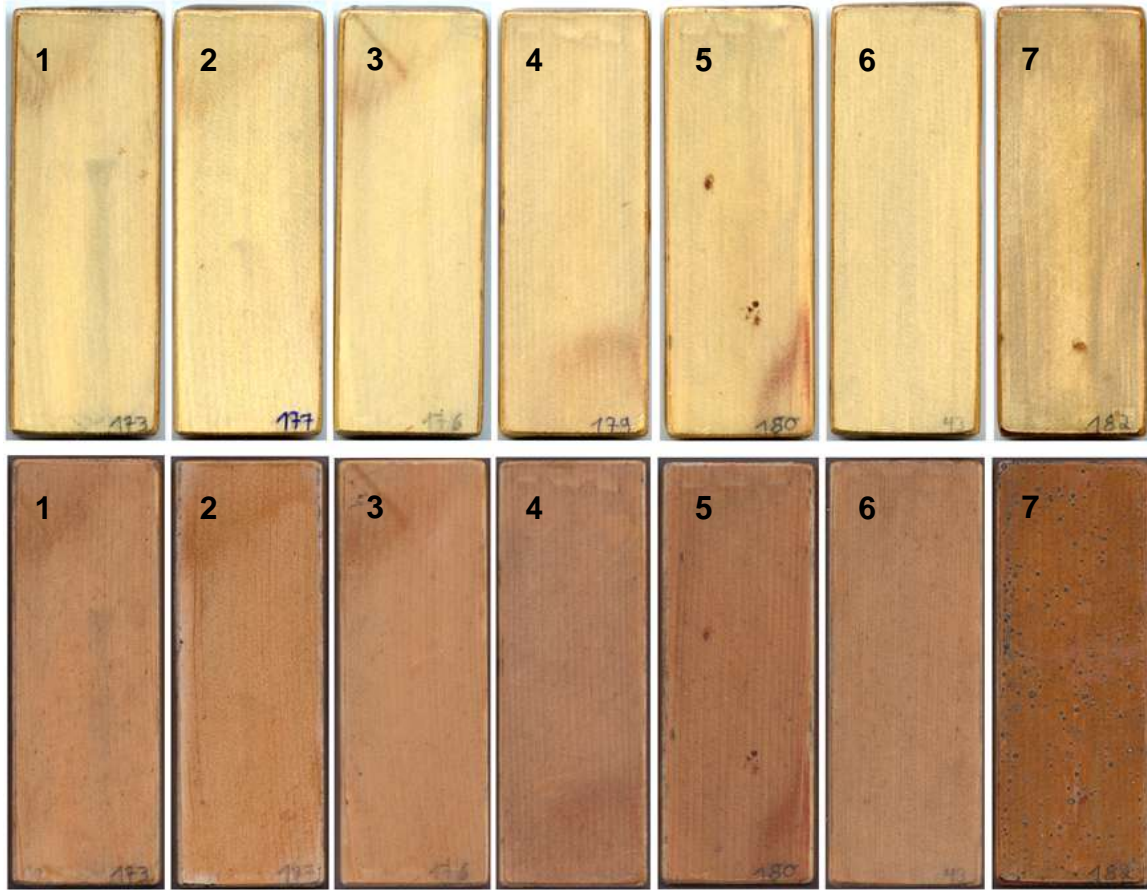


Figure 4.12: Wood samples pre-treated with PF-resin before outdoor exposure (top row) and after outdoor exposure (bottom row). Note the pronounced reddening of the samples. From left to right: PF with standard acrylic coating (1); PF with harder acrylic coating (2); PF with acrylic coating containing double the amount of UVA/HALS (3); PF with alkyd coating (4); PF with acrylic coating containing 1% cerium oxide nanoparticles (5); PF with acrylic coating containing 0.5% cerium oxide nanoparticles (6); PF with polyurethane (7)

4.3.1.2.b Coating effects

Analysis of variance showed that there was a highly significant effect ($p < 0.001$) of coating type on a^* ratios of wood samples exposed outdoors. Wood samples finished with the alkyd coating (AL) and the standard acrylic coating (SA) showed the least reddening during outdoor exposure as indicated by a^* ratios which are close to 1. All of the other acrylic coatings were significantly less ($p < 0.05$) effective than AL and SA and there was no significant difference ($p > 0.05$) in their a^*

ratios (Fig. 4.13). PUR coated samples reddened significantly ($p<0.05$) more than any of the other coated samples.

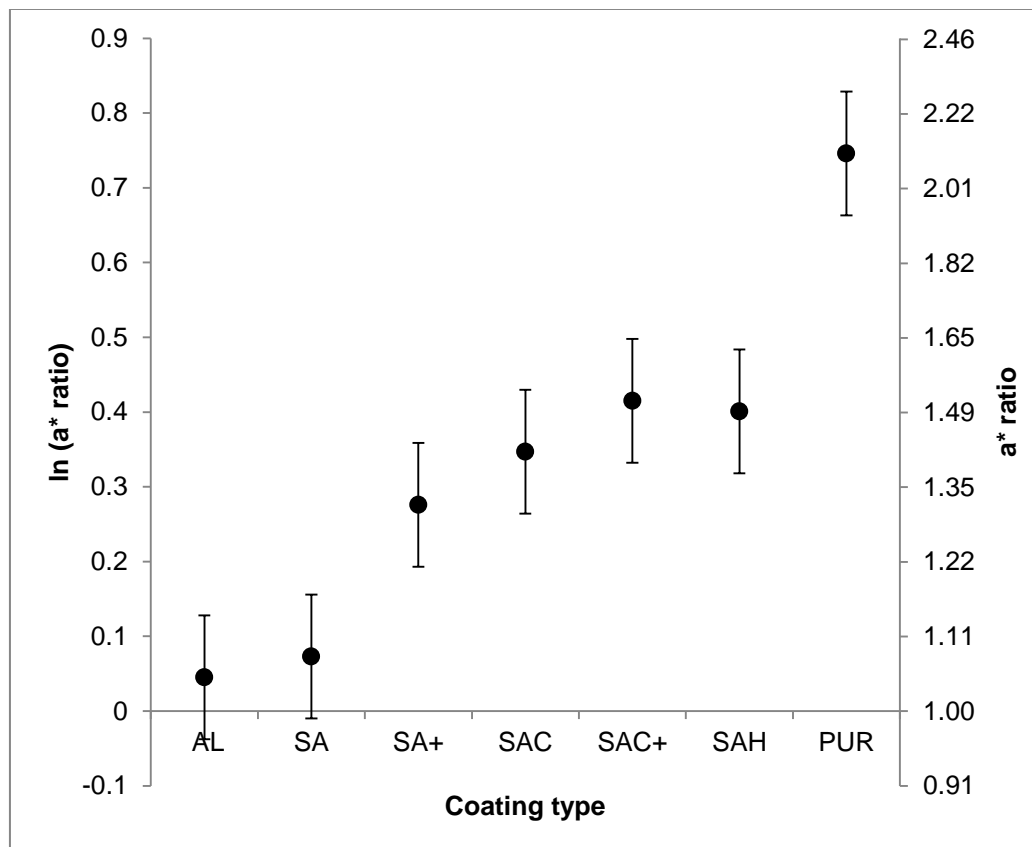


Figure 4.13: Effect of coating type on the a* ratio (redness/greenness) of coated wood samples exposed to natural weathering. Results are averaged across samples with the different pre-treatments

4.3.1.2.c Interactions

There was also a highly significant interaction ($p<0.001$) between treatment and coating type on a* ratios of exposed wood samples (Table 4.3). These interactions occurred because a* ratios of the standard acrylic coating containing 0.5% cerium oxide nanoparticles (SAC), the standard acrylic coating with the harder binder (SAH) and the PUR coating varied between different pre-treated wood samples (Fig 4.14). For example, the a* ratio of the SAC coating was similar to

those of the other water-based coatings on most treatments during outdoor exposure (except those of the alkyd coating [AL]) and the standard acrylic coating [SA], see previous section). However, the SAC reddened more than the other coatings on PF-resin treated samples (circled in Fig. 4.14). Similarly, the SAH coating showed little differences in a^* ratios compared to the other water-based coatings, but on the untreated samples it showed significantly more reddening than all other coatings, except that of the polyurethane (circled in Fig 4.14).

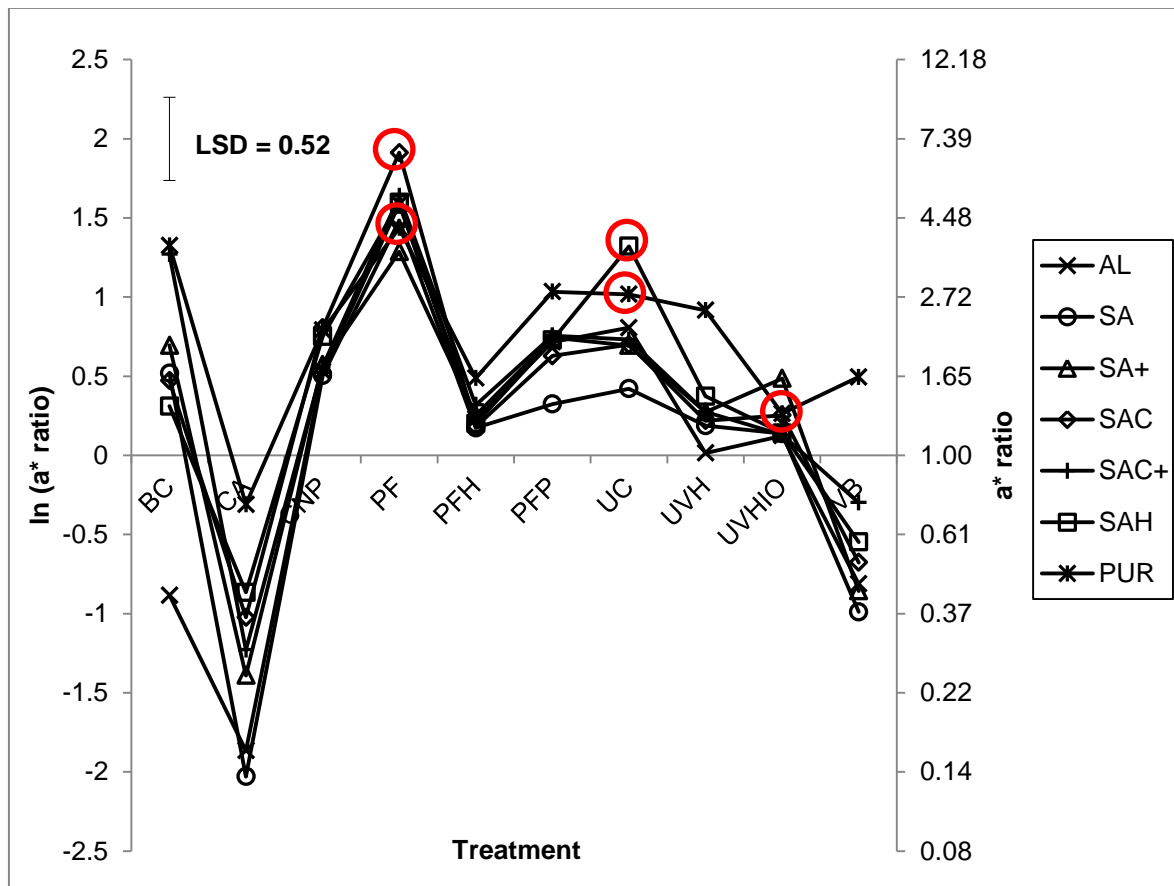


Figure 4.14: Interactions of chemical treatment and coating type on the a^* ratio of coated wood samples exposed to natural weathering. Note the left y-axis displays the transformed data and the right y-axis the untransformed data. Data points are connected by lines to show interactions. Interactions are highlighted with a red circle

The PUR coating reddened more than the water-based coatings during outdoor exposure (see previous section). On PF treated samples, however, the PUR coating reddened less during outdoor exposure than the SAC coating. Furthermore, on untreated controls the PUR coating showed less reddening than the SAH coating and on samples treated with UVHIO the PUR coating reddened less than the standard acrylic coating containing double the amount of UVA/HALS (SA+).

4.3.1.3 Effect on blueness/yellowness

4.3.1.3.a Treatment effects

Chemical treatment had a highly significant effect on the b^* ratios (yellowing and blueing) of exposed wood samples (Table. 4.3). All PF-resin treated samples showed significantly more yellowing during outdoor exposure than the untreated control, whereas samples treated with CA, UVH and UVHIO showed significantly less yellowing (Fig. 4.15).

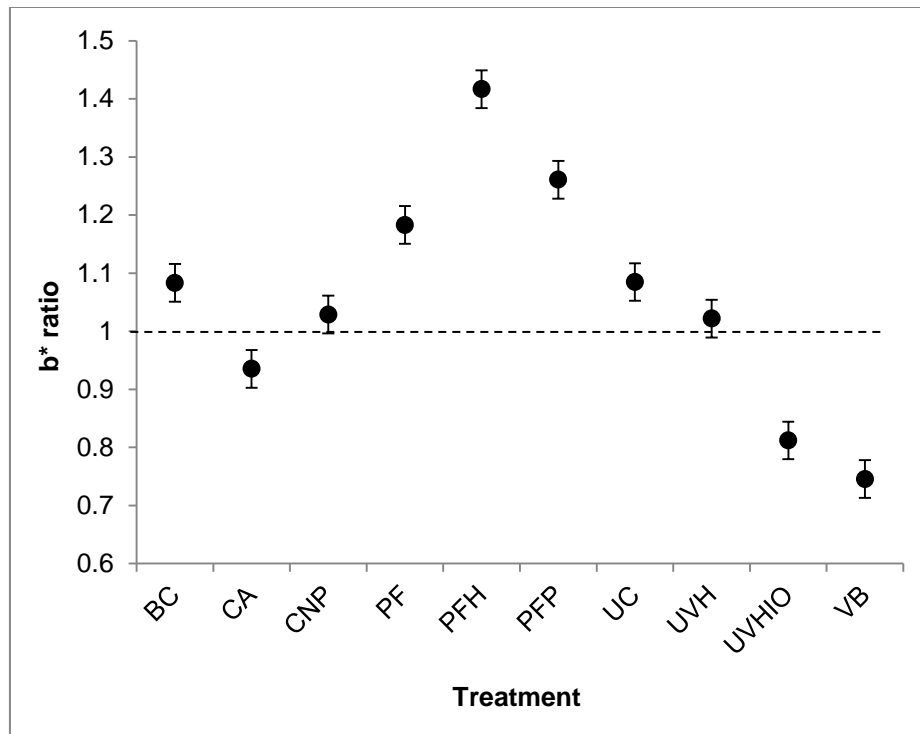


Figure 4.15: Effect of chemical treatment on the b* ratio (yellowness/blueness) of coated wood samples exposed to natural weathering

Within the PF-resin treatments, samples treated with PFH yellowed significantly more than those treated with PFP, and the latter yellowed significantly more than PF. In other words, samples treated with PFH showed the highest degree of yellowing of all treated samples during outdoor exposure (Fig. 4.16). In contrast, UVHIO and VB treated samples showed the highest amount of 'blueing' during outdoor exposure.

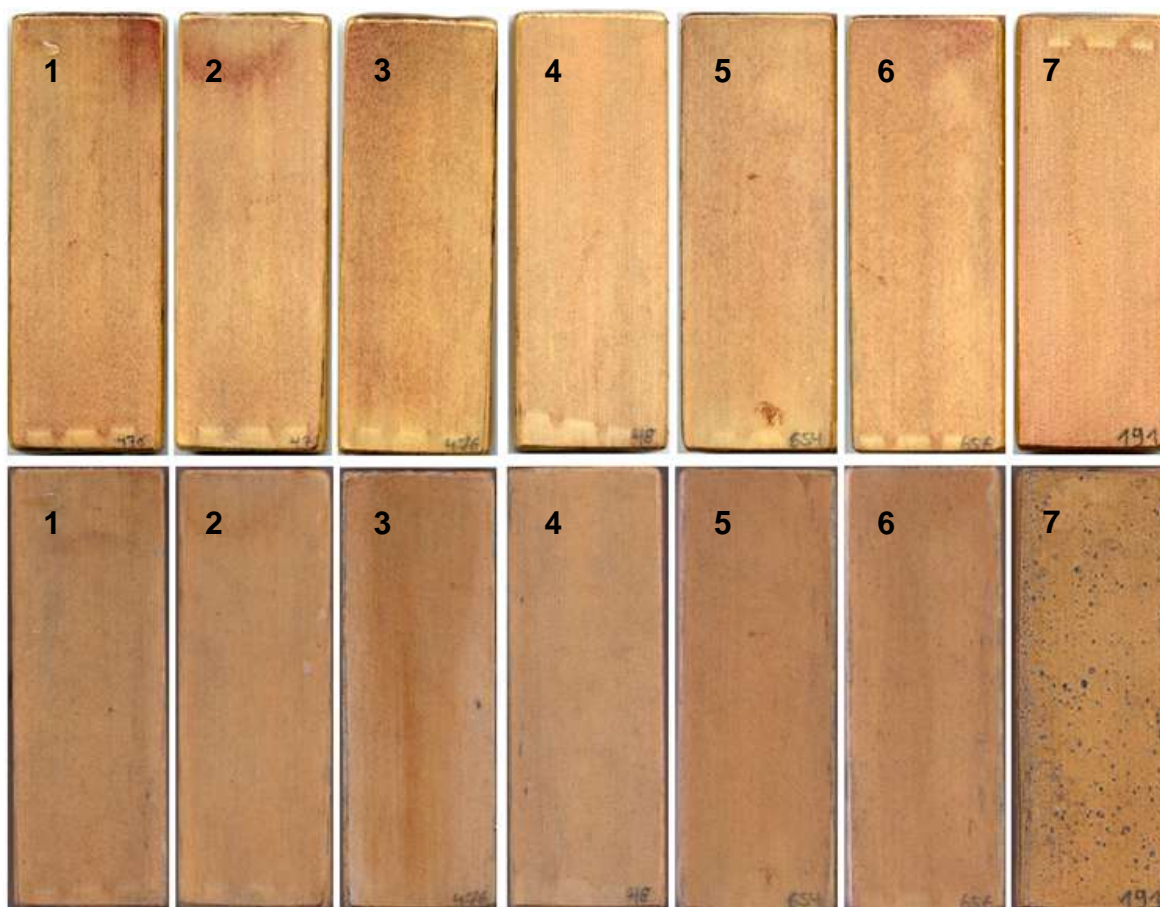


Figure 4.16: Wood samples pre-treated with PF-resin containing HALS (PFH) before outdoor exposure (top row) and after outdoor exposure (bottom row). Note the red hue of unexposed samples has changed to a darker yellowish tint after exposure. From left to right: PFH with standard acrylic coating (1); PFH with acrylic coating containing double the amount of UVA/HALS (2); PFH with harder acrylic coating (3); PFH with alkyd coating (4); PFH with acrylic coating containing 1% cerium oxide nanoparticles (5); PFH with acrylic coating containing 0.5% cerium oxide nanoparticles (6); PFH with polyurethane (7)

Yellowing of samples treated with BC, CNP and UVH was lower than that of the untreated control after outdoor exposure. However, there was no statistically significant difference ($p>0.05$) in the b^* ratios of these samples and that of the untreated control. Nevertheless, samples treated with BC, CNP and UVH still had the lowest yellowing overall, which is indicated by the fact that the b^* ratios of these samples are close to 1 (Fig. 4.15).

4.3.1.3.b Coating effects

Coating type also had a highly significant effect ($p < 0.001$) on b^* ratios of wood samples exposed outdoors (Table 4.3). Samples coated with PUR yellowed the most during outdoor exposure. All other coated samples showed significantly less ($p < 0.05$) yellowing (Fig. 4.17). The lowest amount of yellowing was found on samples coated with the standard acrylic coating containing the harder binder (SAH). This coating yellowed significantly less than all other acrylic coatings, except the standard acrylic coating (SA).

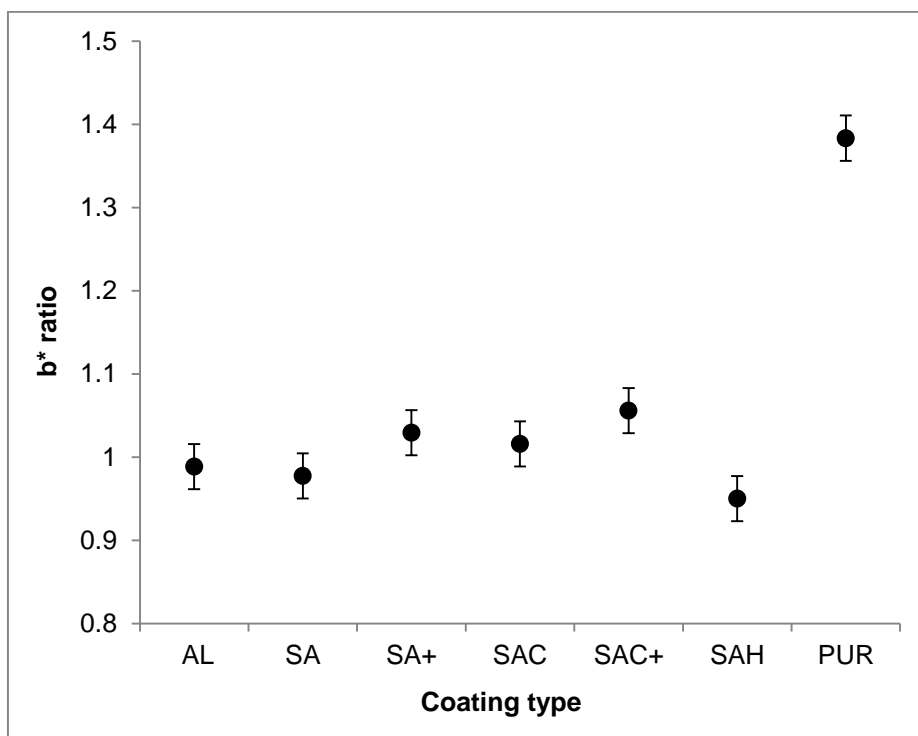


Figure 4.17: Effect of coating type on the b^* ratio (yellowness/blueness) of coated wood samples exposed to natural weathering. Results are averaged across samples with the different pre-treatments

4.3.1.3.c Interactions

There was a highly significant interaction ($p < 0.001$) between treatment and coating types on b^* ratios of exposed wood samples (Table 4.3). This interaction occurred because the coating with the harder binder (SAH) yellowed less than other water-based coatings, but on PF treated samples it showed the most yellowing (Fig. 4.18).

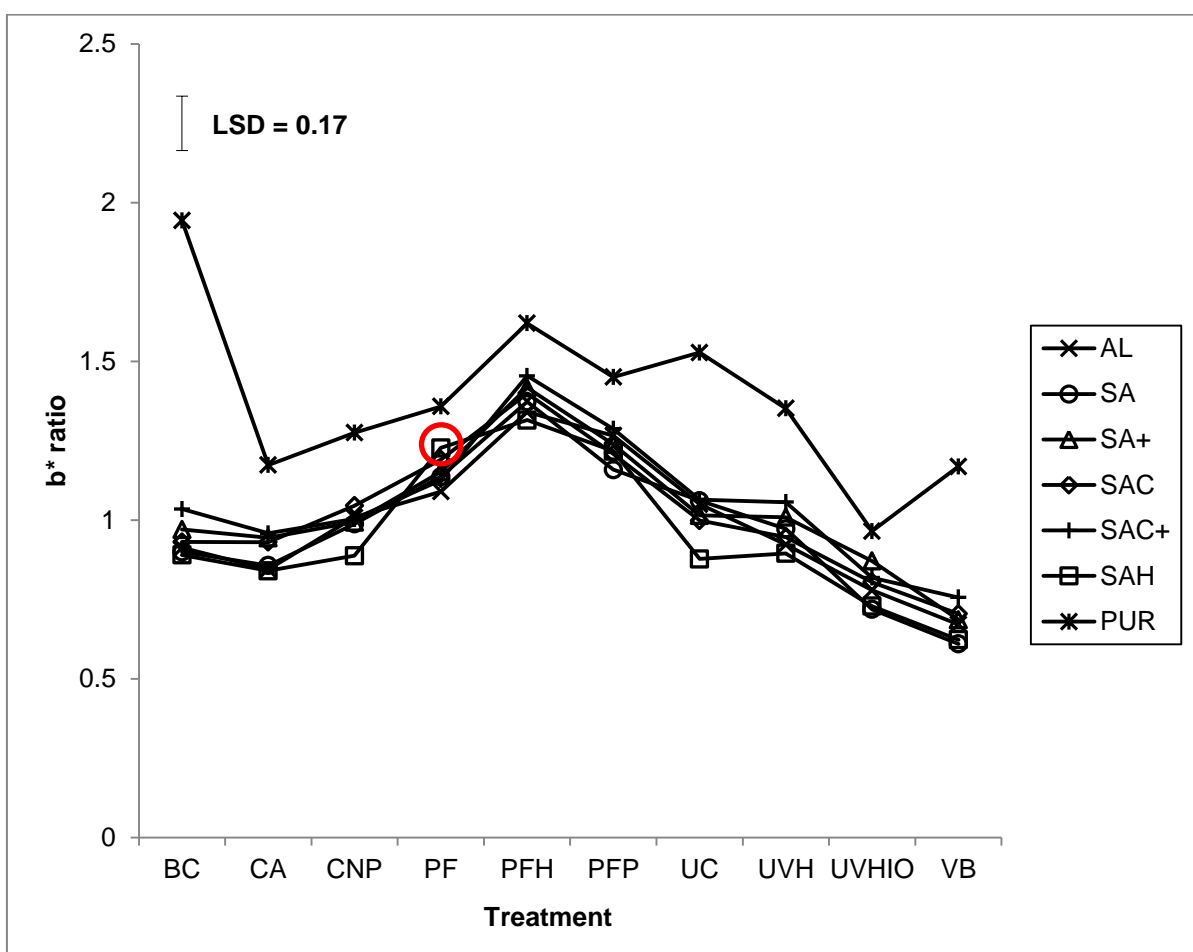


Figure 4.18: Interaction of chemical treatment and coating type on the b^* ratio of coated wood samples exposed to natural weathering. Data points are connected by lines to show interactions. The interaction is highlighted with a red circle

4.3.1.4 Effect on delta E

4.3.1.4.a Treatment effects

As expected 'treatment' had a highly significant effect ($p < 0.001$) on delta E (total color change) of exposed wood samples (Table. 4.3). The smallest changes in delta E were observed in samples treated with BC, CA and UVH. These samples had significantly lower ($p < 0.05$) total color change after outdoor exposure than all other treated samples, including the untreated controls (Fig. 4.19).

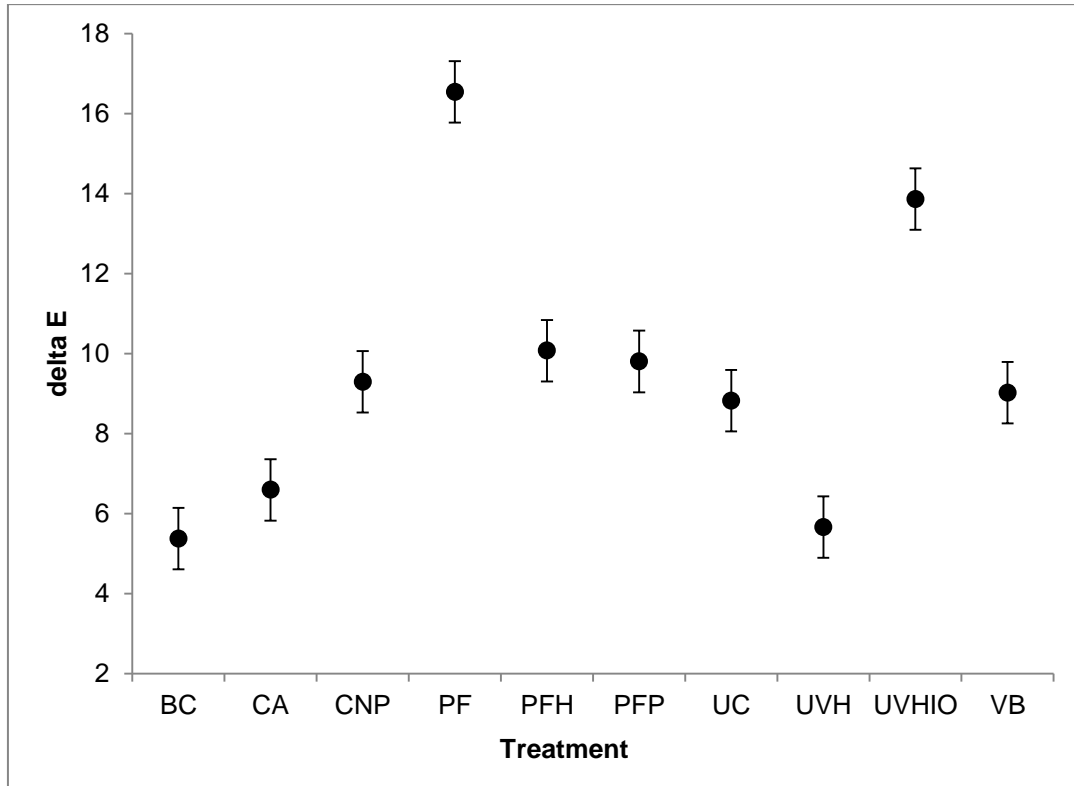


Figure 4.19: Effect of chemical treatment on delta E (total color change) of coated wood samples exposed to natural weathering. Results are averaged across samples with the different coatings

The CNP, PFH, PFP and VB treatments were ineffective at restricting the total color change after exposure because their delta E values are not significantly different ($p>0.05$) from that of the untreated controls (Fig. 4.19). For the PFH treatment the total color change is mainly due to the higher degree of yellowing as described in Section 4.3.1.3.a. The highest overall color change was observed on samples treated with PF and UVHIO. Samples treated with these chemicals showed significantly greater changes in color during weathering than all of the other treated and untreated samples (Fig. 4.19). Samples treated with PF-resin alone showed significantly higher total color change than those treated with UVHIO.

4.3.1.4.b Coating effects

Coating type also had a highly significant effect ($p<0.001$) on delta E of exposed wood samples (Table 4.3). The highest degree of total color change was observed on samples finished with the PUR coating. All other coated samples showed significantly less ($p<0.05$) change in delta E during outdoor exposure (Fig. 4.20). Conversely, the lowest total color change was observed on samples finished with the standard acrylic coating containing double the amount of UVA/HALS (SA+). These samples showed significantly lower total color change than all other coated samples after outdoor exposure (Fig. 4.20). There were no significant differences ($p>0.05$) in total color changes of the other coated samples during outdoor exposure.

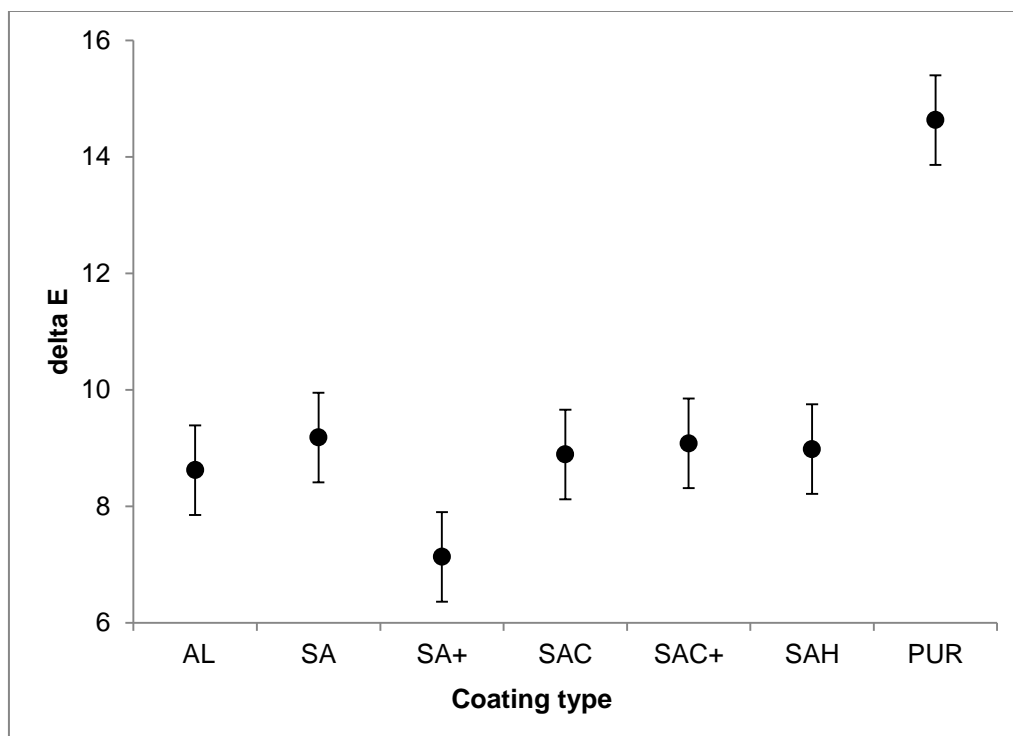


Figure 4.20: Effect of coating type on delta E (total color change) of coated wood samples exposed to natural weathering. Results are averaged across samples with the different pre-treatments

4.3.1.4.c Interactions

There was also a highly significant interaction ($p < 0.001$) of treatment and coating type on delta E values of exposed wood samples (Table 4.3). These interactions occurred because delta E values of the PUR coating, the standard acrylic (SA) coating and the alkyd coating (AL) varied on different pre-treated wood samples (Fig. 4.21). For example, treated samples and untreated controls finished with the PUR coating generally exhibited significantly higher ($p < 0.05$) total color changes after outdoor exposure than the same samples finished with water-based coatings. However, on samples treated with UVHIO and VB there was no significant difference ($p > 0.05$) in delta E values of samples coated with the PUR coating and

samples coated with the water-based coatings. Furthermore, the delta E value of CA treated samples finished with PUR was significantly lower after outdoor exposure than that of CA treated samples finished with the standard acrylic coating which does not conform to the findings in Section 4.3.1.4.b. Similarly, samples coated with SA usually exhibited relatively large color changes after outdoor exposure. On PFH treated samples, however, the SA coating performed significantly better than the alkyd coating and the standard acrylic coating containing 1% cerium oxide nanoparticles (SAC+) (Fig. 4.21). Samples finished with the AL coating usually performed quite well on the different pre-treated samples. Nevertheless, on untreated controls AL coatings performed much poorer and showed significantly higher overall color changes than any of the other water-based coating, except the standard acrylic finish (Fig. 4.21).

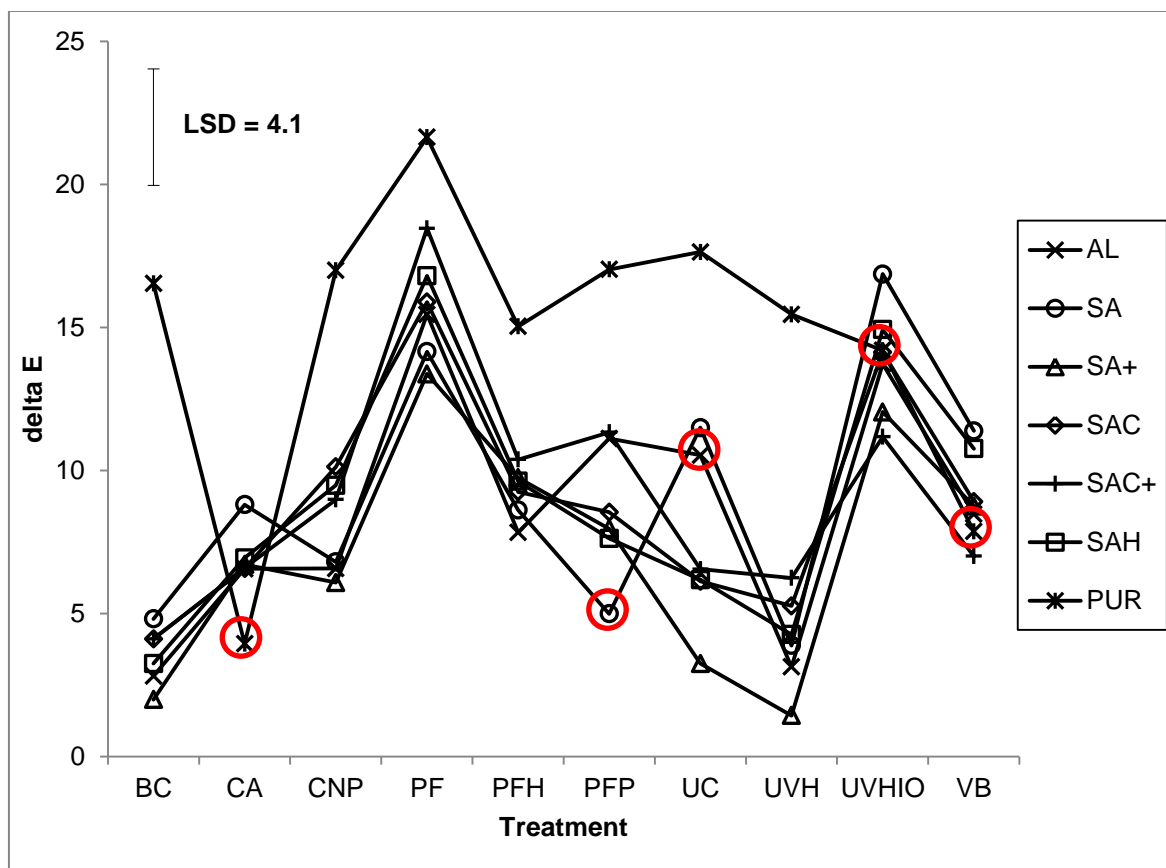


Figure 4.21: Interactions of chemical treatment and coating type on delta E values of coated wood samples exposed to natural weathering. Data points are connected by lines to show interactions. The interactions are highlighted with a red circle

4.3.2 Effect of chemical modification and clear coat type on coating failure

There was a relatively small amount of coating failure (delamination, blistering and cracking) on samples exposed to weathering, and differences in the levels of failure on samples with the different treatment and coated with the various water-based coatings were small. Therefore, coating failure results were not analyzed statistically, but rather they are tabulated. In contrast, all of the solvent-borne PUR coatings failed prematurely and exhibited large degrees of coating failure regardless of the type of pre-treatment that was used. These coating failures appear to be related to the large amounts of pinholes that were observed in the PUR coating prior

to outdoor exposure (Fig. 4.22). Because the PUR coating failed prematurely due to problems with film formation, measurements of the failure of PUR coatings were not made.



Figure 4.22: Example of pinholes on wood samples coated with PUR

4.3.2.1 Delamination

Overall there was little delamination of clear coatings on pre-treated samples and untreated controls because average failure levels were lower than 2% (Table 4.5). An exception to this was coatings on wood treated with cerium oxide nanoparticles (CNP), which had an average level of delamination of 6.25% (Fig. 4.23). Delamination of coatings occurred most often on untreated controls followed by samples treated with chromic acid. Delamination did not occur at all on samples treated with benzoyl chloride (BC), PF-resin/HALS and UVA/HALS.

Table 4.5: Delamination (%) of clear coats on pre-treated wood samples exposed to natural weathering in Australia for 349 days

Treatment	Coating type						Average
	AL	SA	SA+	SAC	SAC+	SAH	
BC	0	0	0	0	0	0	0
CA	0	0	0.54	0	1.07	0.54	0.72
CNP	0	0	0	0	0	6.25	6.25
PF	0	0	0	0	0	1.07	1.07
PFH	0	0	0	0	0	0	0.0
PFP	0	0	0	0	0	1.61	1.61
UC	0.89	0	0	0.36	0.71	1.25	0.80
UVH	0	0	0	0	0	0	0.0
UVHIO	0	1.61	0	0	0	0	1.61
VB	0	0	0	0	0	0.36	0.36
Average	0.89	1.61	0.54	0.36	0.89	1.85	

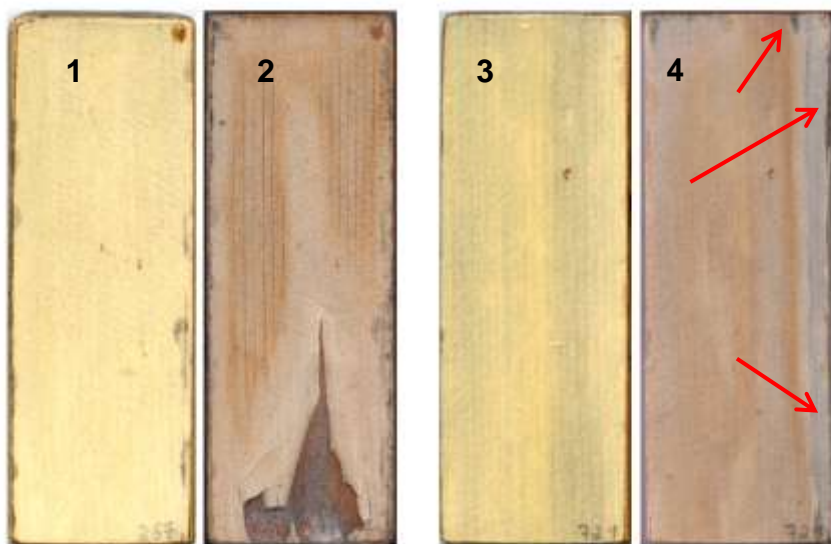


Figure 4.23: Left: Wood sample treated with cerium oxide nanoparticles finished with the harder acrylic coating before weathering (1) and with a strongly delaminated coating after weathering (2). Right: Untreated control finished with the harder acrylic coating before weathering (3) and with a slightly delaminated coating (arrows) after weathering (4). Note the grey discoloration underneath the delaminated parts of the coating

The harder acrylic finish delaminated more often than the other coatings and also had the highest average level of failure. Very low levels of delamination were found on samples coated with the standard acrylic coatings containing cerium oxide nanoparticles (SAC and SAC+), the standard acrylic coating containing double the amount of UVA/HALS (SA+) and the alkyd coating (Table 4.5).

4.3.2.2 Blistering

The average levels of blistering of coatings on treated samples were higher than the average levels of coating delamination (Table 4.6). The highest average level of blistering after outdoor exposure occurred on samples treated with cerium oxide nanoparticles (CNP), followed by samples treated with UVHIO (Fig. 4.24). The highest single level of blistering (16.8%) occurred in the alkyd coating on wood treated with UVHIO. Furthermore, blistering occurred more often on UVHIO treated samples than on samples treated with cerium oxide nanoparticles (Table 4.6). The second highest frequency of blistering occurred on untreated controls even though their average level of blistering was the lowest out of all samples with blistered coatings. Coatings on PF-resin (PF) and vinyl benzoate (VB) treated samples showed no blistering during outdoor exposure.

Table 4.6: Blistering (%) of clear coats on pre-treated wood samples exposed to natural weathering in Australia for 349 days

Treatment	Coating type						Average
	AL	SA	SA+	SAC	SAC+	SAH	
BC	0	0	0	0	0	1.43	1.43
CA	0	0	0	0	0	3.93	3.93
CNP	9.11	0	0	0	0	3.39	6.25
PF	0	0	0	0	0	0	0.0
PFH	0	0	0	0	0	0	0.0
PFP	0	0	0	3.21	0	0	3.21
UC	0	1.61	0	1.07	0	1.43	1.37
UVH	0	0	0	0	0	1.96	1.96
UVHIO	16.8	1.43	0	4.46	1.79	1.61	5.22
VB	0	0	0	0	0	0	0.0
Average	12.96	1.52	0	2.91	1.79	2.29	

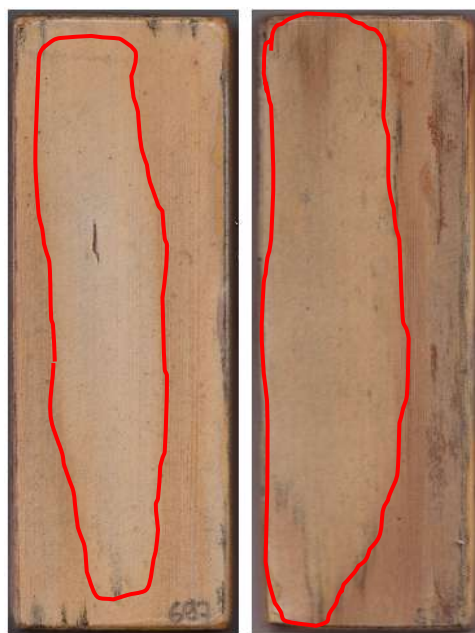


Figure 4.24: Large blisters formed during outdoor exposure on CNP treated wood coated with AL (left) and UVHIO treated wood coated with AL (right). Note the areas within the red borders represent the size of the coating blister on each sample

Blistering occurred most often on wood samples coated with the acrylic finish containing the harder binder (SAH) followed by wood samples coated with the standard acrylic finish containing cerium oxide nanoparticles (SAC) (Table 4.6). These findings accord with the results for delamination of coatings (described above). The highest average level and single level of blistering, however, was observed on samples finished with the alkyd coating (AL). There was no blistering observed on samples finished with the standard acrylic coating containing double the amount of UVA/HALS (SA+).

4.3.2.3 Cracking

The average levels of cracking of coatings on treated samples were smaller than the average levels of coating delamination and blistering (Table 4.7). The highest average level of blistering of coatings during outdoor exposure was found on UVHIO treated samples (3.84%) followed by samples treated with vinyl benzoate (2.5%), and the untreated controls (1.61%). Coatings on UVHIO treated samples had the highest single level of cracking (5%) followed by samples treated with vinyl benzoate (Fig 4.25). The highest frequency of clear coat cracking was found on samples treated with cerium oxide nanoparticles and samples treated with UVA/HALS, followed by PF/PEG, UVHIO and vinyl benzoate treated samples (Table 4.7). There was little cracking of coatings on samples treated with chromic acid or PF-resin. There was no cracking of coatings on samples treated with benzoyl chloride or PF-resin/HALS (Table 4.7).

Table 4.7: Cracking (%) of clear coats on pre-treated wood samples exposed to natural weathering in Australia for 349 days

Treatment	Coating type						Average
	AL	SA	SA+	SAC	SAC+	SAH	
BC	0	0	0	0	0	0	0.0
CA	0	0	0	0	0	0.89	0.89
CNP	0	0.36	0	0.36	0.36	0.54	0.41
PF	0	0	0	0	0	0.18	0.18
PFH	0	0	0	0	0	0	0.0
PFP	0	0	0.54	0.18	0	0	0.36
UC	0	0	0	0	0	1.61	1.61
UVH	0	0.36	0	0.54	0.54	2.32	0.94
UVHIO	0	0	0	0	2.68	5	3.84
VB	0	0	0	0	1.25	3.75	2.50
Average	0	0.36	0.54	0.36	1.21	2.04	

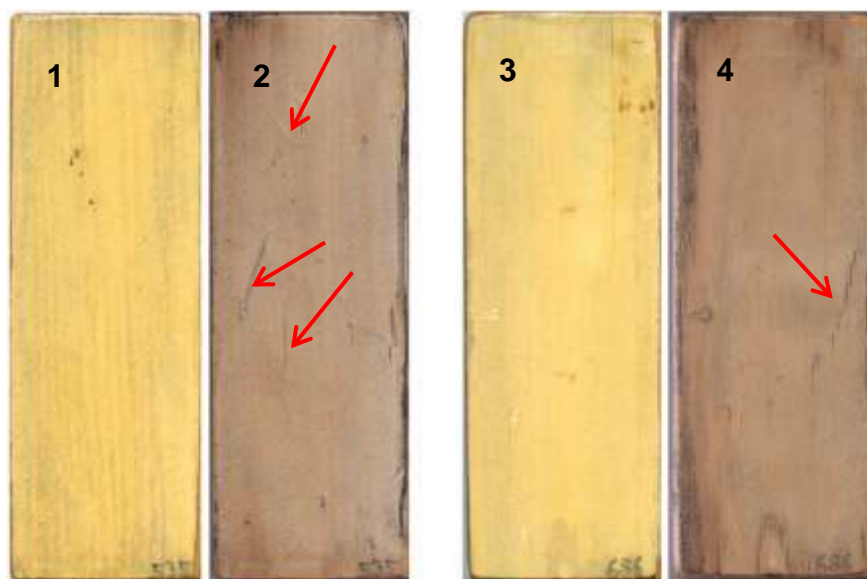


Figure 4.25: Cracking of coatings. Left: UVHIO pre-treated wood sample finished with the harder acrylic coating (SAH) before outdoor exposure (1) and after outdoor exposure (2). Right: UVHIO pre-treated wood sample finished with the acrylic coating containing 1% cerium oxide nanoparticles (SAC+) before outdoor exposure (3) and after outdoor exposure (4). Note: the arrows indicate cracks in the coating

The degree of cracking of coatings during outdoor exposure was greatest on samples finished with the harder standard acrylic coating (SAH) followed by samples finished with the standard acrylic coating containing 1% cerium oxide nanoparticles (SAC+). The frequency of cracking was also greatest on SAH coated samples followed by samples coated with SAC+. Furthermore, samples coated with SAH had the highest single level of coating failure (3.75 % for VB treated samples), which was again followed by SAC+ coated samples. All other finished samples showed less cracking of coatings during outdoor exposure. Samples coated with the alkyd coating (AL) exhibited no coating cracks after weathering.

4.3.2.4 Fungi colonization on PUR coatings

Measurements of the failure of PUR coatings were not made because the PUR coating failed due to colonization by fungi, as mentioned above. The levels of colonization of the PUR coating by fungi varied depending on the underlying wood pre-treatment (Table. 4.8). The lowest level of colonization was found on wood samples pre-treated with benzoyl chloride followed by PF-resin/PEG and vinyl benzoate treated samples. The highest levels of fungal colonization were found on untreated controls and chromic acid treated wood samples (Fig 4.26).

Table 4.8: Fungal colonization of the PUR coating on pre-treated wood samples exposed to natural weathering in Australia for 349 days

Treatment	Area covered with fungi (%)
Benzoyl chloride	34.82
Chromic acid	50.89
Cerium oxide nanoparticles	46.79
Phenol resin	48.21
Phenol resin with water soluble HALS	49.64
Phenol resin with PEG	39.82
Untreated control	54.11
UV absorber and solvent soluble HALS	47.50
UV absorber and HALS (as above) and yellow iron oxide	45.00
Vinyl benzoate	44.29

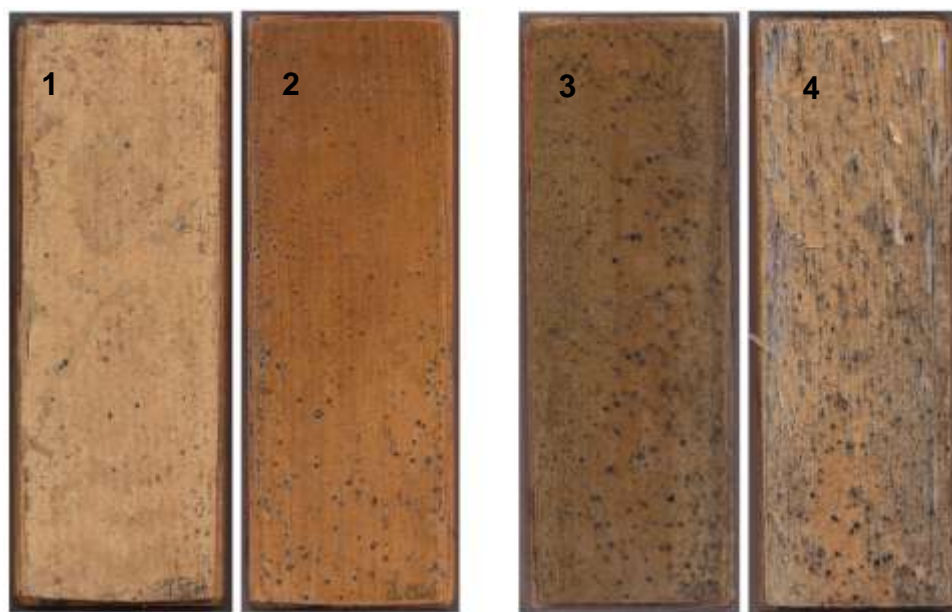


Figure 4.26: Lower amount of fungal colonization on BC treated wood samples coated with PUR (1) and PFP treated wood samples coated with PUR (2) (left). Larger amount of fungal colonization on CA treated wood samples coated with PUR (3) and untreated controls coated with PUR (4) (right)

4.3.3 Effect of chemical modification and clear coat type on the appearance ranking of exposed test samples

4.3.3.1 Treatment effects

Analysis of variance showed that there was a highly significant effect ($p < 0.001$) of treatment type on the appearance ranking of wood samples exposed to natural weathering. The appearance of all treated samples, except for those treated with UVA/HALS (UVH) was significantly better ($p < 0.05$) than that of the untreated controls (Fig. 4.27).

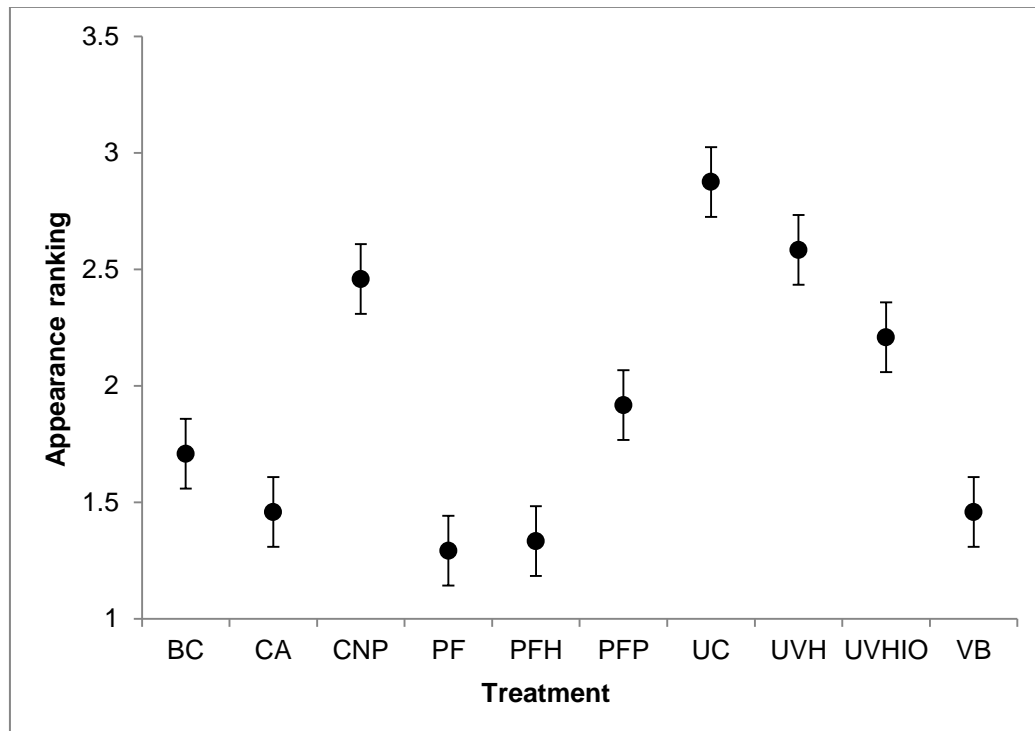


Figure 4.27: Effect of chemical treatment on the appearance ranking of coated wood samples exposed to natural weathering. Results are averaged across samples with the different coatings

Coated samples treated with PF-resin (PF) and the PF-resin/HALS (PFH) combination looked good and their appearance rankings were significantly better

than those of all other samples, except those treated with chromic acid (CA) and vinyl benzoate (VB). The least effective treatments at maintaining the appearance of the coated samples during weathering were the cerium oxide nanoparticles (CNP) and UVHIO treatments (Fig. 4.27).

4.3.3.2 Coating effects

Analysis of variance showed that coating type also had a highly significant effect ($p < 0.001$) on the appearance ranking of exposed wood samples (Table 4.3). The appearance ranking of samples finished with the standard acrylic coating containing double the normal amount of UVA/HALS was significantly better ($p < 0.05$) than that of all other coatings (Fig 4.28). In contrast, the appearance of samples finished with the acrylic coating containing the harder binder (SAH) was significantly worse than that of all other finished samples except for samples coated with the acrylic finishes containing cerium oxide nanoparticles (SAC and SAC+) (Fig. 4.28).

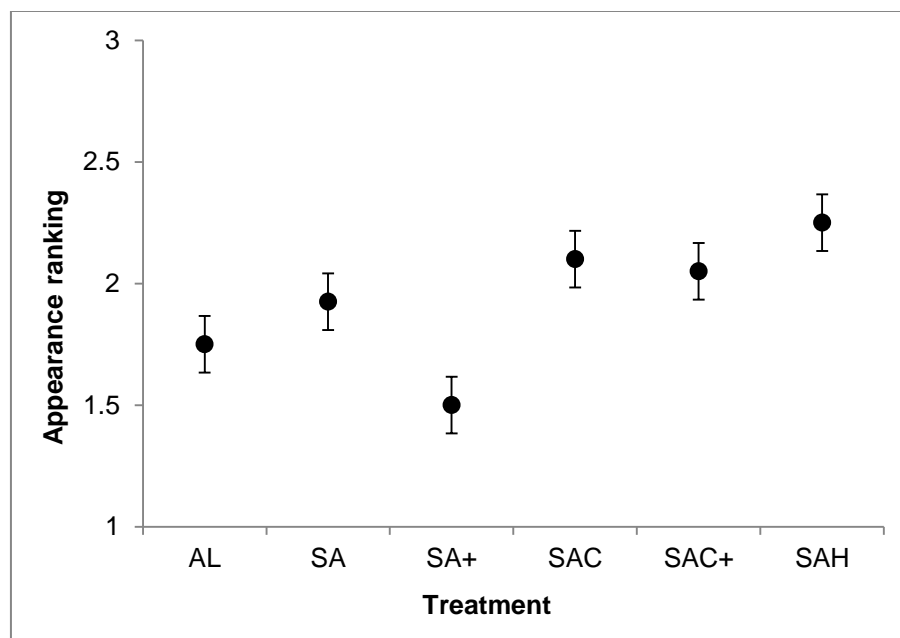


Figure 4.28: Effect of coating type on the appearance ranking of coated wood samples exposed to natural weathering. Results are averaged across samples with the different pre-treatments

4.3.3.3 Interactions

There was also a significant interaction ($p < 0.05$) between chemical treatments and coating type on the appearance ranking of exposed wood samples. This interaction occurred because the appearance rankings of the standard acrylic coating with the harder binder (SAH) and the acrylic coating containing double the normal amount of UVA/HALS (SA+) varied between wood samples with the different pre-treatments (Fig. 4.29). For example, the SAH coating which, overall performed badly (see previous section), performed quite well on wood treated with PFH. Conversely, the SA+ coating which was the best performer overall (see previous section), did not perform very well on wood treated with CNP.

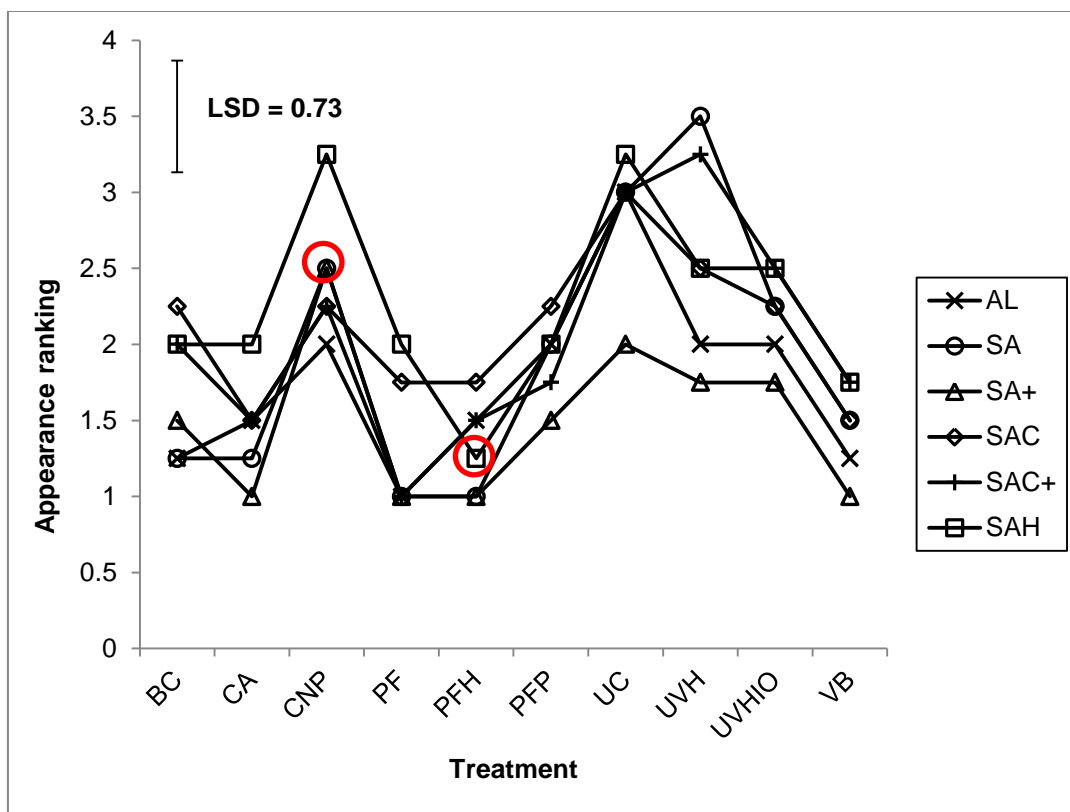


Figure 4.29: Interactions of chemical treatment and coating type on the appearance ranking of coated wood samples exposed to natural weathering. Data points are connected by lines to show interactions. The main interactions are highlighted with a red circle

4.4 Discussion

I hypothesized in the introduction to this chapter that modification of wood with pre-treatments that can photostabilize lignin such as benzoyl chloride and vinyl benzoate would enhance the performance of clear coatings on wood exposed outdoors, as has already been shown for chromic acid (Williams & Feist 1985; Ohtani 1987). It was anticipated that coatings would also perform well on wood treated with PF-resin because this treatment deposits low molecular weight aromatic compounds in wood cell walls like benzoyl chloride and vinyl benzoate. It was further anticipated that the ability of the PF-resin to enhance the performance of clear

coatings would be increased by combining the PF-resin with additives that have a proven ability to photostabilize wood (Minemura 1978; Janson & Forsskåhl 1989; Schaller & Rogez 2007). Finally it was hypothesized that clear coat performance would depend on the combination of pre-treatment and coating type as has been suggested by Evans et al. (2002) and Evans (2003). It was assumed that the performance of the PUR coating would be good because a previous study had showed that this coating performed well on wood samples exposed to natural weathering (Evans et al. 2007). The extent to which results in this chapter met expectations (hypotheses above) will be discussed in turn. The extent to which results accord with findings in the literature will also be discussed and general conclusions from the work will be drawn.

4.4.1 Comparison of the performance of coatings on wood modified with benzoyl chloride, vinyl benzoate and chromic acid

Previous research has shown that treatment of wood with benzoyl chloride (BC) and vinyl benzoate (VB) photostabilized lignin (Evans et al. 2002; Jebrane et al. 2009). Treatment of wood with BC was as effective at photostabilizing wood as treatment with chromic acid (Evans et al. 2002; Pandey & Chandrashekar 2006). Because chromium treatments improve the performance of clear coats on wood used outdoors I hypothesized that treatment of wood with BC and VB would also enhance the performance of clear coats on wood used outdoors (Black & Mraz 1974; Williams & Feist 1985). Results here showed that there was little photo-discoloration of clear coated wood samples pre-treated with BC. In contrast, clear coated wood samples pre-treated with CA and VB discoloured more during outdoor

exposure than wood pre-treated with BC. The explanation for these color differences between BC, CA and VB pre-treated wood samples is that during outdoor exposure samples treated with CA and VB became brighter and bluer, respectively. Furthermore, CA treated wood samples turned green during outdoor exposure, which accords with previous observations of the discoloration of chromic acid treated wood during exterior exposure (Evans et al. 1992). Pre-treatment of wood with BC, VB and CA prevented clear coat failure during outdoor exposure, because there was no delamination or cracking of the treated and clear coated samples and only a small amount of blistering. There was little delamination and no blistering of clear coatings on wood samples pre-treated with VB, but there was cracking of coatings on the edges of samples. The integrity of coatings on chromic acid treated samples was similar to that of coatings on samples treated with vinyl benzoate, except there was much more delamination of the coatings and less cracking. These coating failures at the edges of samples appeared to be associated with damaged edge seals. These damaged edge seals could have allowed rain water to penetrate into the side of the wood samples causing loss of coating adhesion. However, loss of coating integrity on treated samples during natural weathering was small. To get a better idea of the effect of treatments on coating performance, the appearance of the samples after weathering was ranked from 1 (good) to 4 (poor). Wood samples pre-treated with BC, VB and CA ranked highly after outdoor exposure. Not surprisingly this finding accords with observations of discoloration and integrity of coatings on samples treated with BC and VB. Samples treated with CA discolored more than those treated with BC or VB, but despite this difference, the appearance rankings of

samples treated with BC, VB and CA were similar. Therefore, preliminary results here suggest that treatment of wood with benzoyl chloride and vinyl benzoate will enhance the performance of clear coats on wood samples exposed outdoors. Treated and coated samples need to be exposed to the weather for longer to confirm this suggestion.

4.4.2 Performance of coatings on wood modified with PF-resin treatments

It was anticipated that treatment of wood with low molecular PF-resin would enhance the performance of clear coats on wood used outdoors as the PF-resin treatments deposit aromatic compounds into the cell walls of wood, like the BC and VB treatments. In accord with this hypothesis, results in Chapter 3 showed that PF-resin was able to photostabilize wood veneers, although not as effectively as BC or VB.

However, clear coated samples pre-treated with PF-resin showed more discoloration than the untreated controls during outdoor exposure. For example, PF-resin treated samples darkened and became redder to a greater extent than all other samples and they also became yellower during outdoor exposure. As a result the total color change (ΔE) of PF-resin treated samples was higher than that of all other treated samples and the untreated controls. The greater discoloration of PF-resin treated samples might be related to oxidation of the PF-resin. According to Devlin & Harris (1984), oxidation of phenol leads initially to the formation of dihydroxylated aromatic rings such as catechol or hydroquinone. These intermediates then form highly colored compounds such as para-benzoquinone (yellow) and ortho-benzoquinone (red), which may explain why clear coated

specimens pre-treated with PF-resin became much darker, redder and yellower during exterior exposure (Devlin & Harris 1984; Mijangos et al. 2006). Coatings on samples treated with PF-resin showed little delamination and cracking and no blistering during outdoor exposure. The excellent integrity of coatings on PF-resin treated samples may explain why their appearance rankings exceeded that of untreated controls, even though PF-resin treated samples discolored during outdoor exposure.

The addition of polyethylene glycol to PF-resin treatments helped to reduce the discoloration of clear coated wood exposed outdoors. This observation may be explained by the ability of polyethylene glycol to scavenge free radicals and reduce the oxidation and discoloration of the phenol resin (Minemura 1978; Janson & Forsskåhl 1989). Clear coatings on wood samples pre-treated with PFP delaminated, blistered and cracked more during outdoor exposure than clear coats on wood samples pre-treated with PF, which probably explains the lower appearance ranking of PFP treated samples compared to PF treated samples.

The addition of a water soluble hindered amine light stabilizer (HALS) to PF-resin was more effective at reducing discoloration of clear coated wood samples during weathering than the addition of PEG to the PF-resin. The effectiveness of the PFH treatment at restricting the discoloration of clear coated samples exposed to natural weathering is probably related to the ability of the HALS to scavenge free radicals (Wicks et al. 1999; DebRoy 2006). Higher color stabilities of clear coated wood exposed outdoors due to the addition of HALS has been reported by Schaller & Rogez (2007). They found that pre-treatment of radiata pine wood with a 2%

aqueous solution of a HALS (4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl) prior to the application of a clear long oil alkyd finish reduced the discoloration of clear coated wood samples during 18 months of outdoor exposure in Switzerland. Clear coated wood samples pre-treated with PFH were the only samples here that exhibited no coating failure after outdoor exposure. De la Caba et al. (2007) also found that a clear coating performed well on a PF-resin impregnated composite. The appearance ranking of coated wood samples pre-treated with PFH were equivalent to those of clear coated samples pre-treated with BC, CA and VB.

4.4.3 Interactions of wood treatments and coating types

There were some noticeable examples of interactions between pre-treatments and clear coat types on the overall performance of clear coated wood samples during outdoor exposure. The polyurethane (PUR) coating performed much worse than the water-based coatings. For example, the high degree of yellowing of PUR coated samples during outdoor exposure compared to samples finished with water-based coatings was particularly noticeable. This finding probably indicates that the PUR coating contained aromatic rather than aliphatic isocyanates because the former are prone to yellowing when exposed outdoors (Nylen & Sunderland 1965). On samples treated with CA, UVHIO and VB, however, the PUR coating performed reasonably well and showed less total discoloration than the standard acrylic coating. It was very evident that surfaces of exposed samples finished with the PUR coating were colonized by dark colored fungi. The degree of coverage of the surface coating by fungi varied between the different treatments, but was generally lower on samples pre-treated with UVHIO and VB. This finding might

explain why the discoloration of PUR coatings was lower on UVHIO and VB treated samples than on any other samples, except those pre-treated with CA. PUR coatings cracked and delaminated during outdoor exposure. Coating failure was so high, that PUR coated samples were excluded from coating failure measurements and appearance rankings. This poor performance of the PUR coating was unexpected because the PUR coating had performed well during a previous natural weathering test (Evans et al. 2007). Furthermore, the PUR coating was compatible with treated wood surfaces as shown in Chapter 3. The poor performance of the PUR coating during outdoor exposure appeared to be associated with pinholes in the coating. According to Geurink et al. (2006) pinholes develop in PUR coatings because of the release of carbon dioxide. Carbon dioxide is released from water-based PUR coatings because of the reaction of isocyanates with the aqueous carrier solvent. The PUR used here was solvent-borne and therefore reaction of isocyanates with the carrier to form CO_2 could not have occurred. Instead it is possible that isocyanates in the PUR could have reacted with water in the wood to form CO_2 . Such CO_2 may have created the pinholes in the dried PUR coating film. Further research, however, would be required to determine why pinholes formed in the PUR that was tested here. Also it would be interesting to do research to see how the PUR coating used here would perform if pinholes were absent from dried coating films.

There were some interesting interactions between the harder acrylic coating (SAH) and some of the pre-treatments. The SAH coating had lower appearance rankings on most pre-treated samples, but particularly on samples treated with

cerium oxide nanoparticles (CNP) and the untreated controls. On samples treated with PFH, however, the appearance ranking of the SAH coating was much higher than on all other samples. Samples coated with SAH reddened to the same extent as samples finished with the other water-based coatings, except samples coated with the alkyd coating (AL) and the standard acrylic coating (SA). SAH coatings showed little or no coating failure on samples treated with vinyl benzoate (VB), benzoyl chloride (BC) and PFH but a high degree of coating failure was found in the SAH coating on untreated controls and samples treated with CNP. Differences in the ability of the various treatments to photostabilize wood may explain the variability in the performance of the SAH coating on treated samples. Both the untreated controls and wood treated with CNP were susceptible to photodegradation. Such degradation could have caused accumulation of degradation products underneath the SAH coating, leading to higher amounts of discoloration, and also reduced adhesion between the coating and wood. On the other hand, BC, VB and PFH were effective at photostabilizing wood, which would explain why the SAH coating performed much better over these pre-treatments.

There was evidence that the standard acrylic coating containing double the normal amount of UVA/HALS (SA+) performed better during outdoor exposure than most of the other coatings. For example, the SA+ coating discolored the least during exterior exposure, and developed fewer defects than all of the other coatings. As a result, the appearance ranking of samples coated with SA+ was better than those of samples coated with the other clear finishes. However, the SA+ coating performed poorly on wood pre-treated with CNP. The poor performance of the SA+ coating on

these samples cannot be explained by the inability of CNP to photostabilize wood because the SA+ coating performed well on untreated controls.

The AL coating performed well as its appearance was good on most pre-treated samples, due to the low levels of discoloration and coating failure (except blistering). However, discoloration of the AL coating on the untreated controls was relatively high, and there was a large amount of blistering on samples treated with CNP and UVHIO. The AL coatings contained normal levels of UVA/HALS and greater degradation of the coating and underlying wood may have occurred than with samples coated with SA+. The lower photostability of the AL coating may explain why it performed relatively poorly on substrates that lacked photostability such as untreated controls and samples treated with cerium nanoparticles. This deficiency might be rectified by increasing the quantity of additives such as UVA/HALS in the AL coating. Increasing the quantity of UVA/HALS in the alkyd coating might also improve its performance on photostable wood substrates such as those treated with benzoyl chloride, vinyl benzoate and PF-resin with HALS, however, further research would be needed to confirm this suggestion.

4.4.4 Comparison with previous findings

Previous research has shown that chromic acid treatment of wood greatly enhanced the outdoor performance of solvent-borne clear coatings such as acrylic urethane finishes and finishes based on linseed-oil (Black & Mraz 1974; Williams & Feist 1985; Ohtani 1987). Water-based coatings applied to chromic acid treated wood also performed very well here. Hence, my findings accord with previous findings of Black & Mraz (1974) and Williams & Feist (1985). All of the clear coated

chromic acid treated samples had high appearance ratings and low overall color changes after weathering, except they became green/grey during outdoor exposure. The change in color of chromic acid treated samples during exterior exposure was expected as this phenomenon has been noted previously (Evans et al. 1992).

Chromic acid was used in the 1980s in Japan to pre-treat wooden doors to enhance the exterior performance of acrylic-urethane finishes (Ohtani 1987). Solvent-borne PUR coatings used here, however, performed poorly on chromic acid treated samples, but this was related to problems with coating film formation. Nevertheless, the finding that the PUR coating performed poorly on chromic acid treated wood indicates that durable coating systems require durable defect-free clear coats as well as wood pre-treatments that can photostabilize the underlying wood.

Clear coated wood samples pre-treated with UVA/HALS retained their color well during outdoor exposure. For example, total color changes of UVH treated samples finished with water-based coatings were the lowest of all samples except those treated with BC and CA. This finding accords with results of Chang et al. (1998). They found that pre-treatment of *Taiwania* heartwood with UVA/HALS (Tinuvin1130/Tinuvin 292) significantly reduced the discoloration of the wood underneath a PUR clear coat during 96 hours of accelerated weathering. Nevertheless, the UVH treatment did not greatly reduce the discoloration of samples finished with the PUR, due to the poor performance of the PUR coating, as mentioned above. There is no published research available on the performance of clear coatings on wood pre-treated with combinations of UV absorbers and hindered

amine light stabilizers. However, it has been shown that grafting of wood surfaces with UV absorbers, for example, 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone can enhance the performance of various clear coats on wood exposed to artificial and natural weathering (Williams 1983; Kiguchi & Evans 1998; Kiguchi et al. 2001; Grelier et al. 2007). George et al. (2005) suggested that pre-treatment of wood with HALS would enhance the performance of clear coats on wood used outdoors. Clear coats on samples treated with UVH in this study developed more cracks during outdoor exposure than the untreated controls and samples treated with different chemicals (except CNP). Furthermore, there was no difference in the appearance rankings of clear coats on samples treated with UVH and clear coats on untreated wood. Hence, UVH treatment of wood does not appear to greatly enhance the performance of clear coats on wood exposed to natural weathering for a relatively short period of time. It is possible however, that differences in the appearance of clear coats on wood treated with UVH and those applied to untreated wood will emerge in due course as the samples are exposed to the weather for longer periods of time. Another possible explanation for the lower performance of clear coats on UVH treated wood might be related to the potential leaching of UVH additives. Grafting of the UVH additives to the coating binder, as described by Hon et al. (1985), might reduce the likelihood of leaching, and enhance the clear coat performance in comparison to direct application of the UVH additives to the wood.

Previous research has shown that additives can enhance the performance of clear coats on wood exposed outdoors. For example, DebRoy (2006) reported that the addition of the UV absorber hydroxyphenyltriazine to clear coatings helped to

increase their light stability on wood. Schaller & Rogez (2007) reported that a transparent long oil alkyd finish containing UVA and HALS and applied to wooden panels pre-treated with HALS did not show any coating defects after the panels were exposed outdoors in Switzerland for 18 months. Forsthuber & Gröll (2010) showed that acrylic based clear coats containing UVA/HALS combinations were protected from photodegradation during weathering. My findings accord with these findings, as follows. As mentioned above, the standard acrylic coating containing double the normal amount of UVA/HALS (SA+) had the lowest level of discoloration and coating failure, and the best appearance ranking of all samples except on samples pre-treated with cerium oxide nanoparticles (see above). On the other hand previous research has shown that inorganic UV absorbers such as titanium dioxide (TiO_2) can prevent the degradation of clear coatings on wood during weathering. According to Allen et al. (2002) clear coated wood containing TiO_2 performed well during artificial weathering. A similar finding was reported by Forsthuber & Gröll (2010). They observed that TiO_2 reduced the discoloration of clear coated wood exposed in a xenon arc weatherometer for 280 hours. My results do not accord with these findings because cerium oxide nanoparticles doped with TiO_2 when added to the acrylic coating were not able to enhance the performance of the clear coats on wood samples exposed to natural weathering. This discrepancy may have occurred because the cerium oxide nanoparticles were an experimental preparation and relatively little work had been done to fine-tune their performance in clear coatings.

The flexibility of wood coatings has an effect on their performance during weathering as noted by Podgorski et al. (1996). For example, they showed that

wood coatings with a high glass transition temperature (T_g) failed due to cracking during natural and accelerated weathering. Conversely, more flexible coatings with a lower T_g developed less cracking (Podgorski et al. 1996). Schmid (1988) suggested that coatings used outdoors should maintain their flexibility and should have lower T_g 's. One of the standard acrylic coatings tested here contained a harder less flexible binder (SAH). This coating cracked, delaminated and blistered more than any of the other coatings that were tested. Furthermore, the appearance rankings of samples finished with this coating were poor. Hence, our finding that an inflexible coating performed poorly on wood exposed outdoors accords with the findings of Podgorski et al. (1996) and the suggestion of Schmid (1988), but it does not accord with the findings of Ashton (1979) who showed that a less flexible short oil phenolic coating performed better than a flexible alkyd coating when the coatings were exposed to natural weathering.

4.5 Conclusions

The performance of clear coats on wood samples treated with BC, VB and CA and exposed to 349 days of natural weathering were similar. Therefore I conclude that benzoyl chloride and vinyl benzoate, which can both photostabilize lignin, can enhance the performance of clear coatings on wood exposed to natural weathering. Coatings applied to wood pre-treated with a PF-resin containing a HALS performed equally well. This treatment was also able to photostabilize wood, but it is not known if it can photostabilize lignin. Nevertheless, I conclude that significant improvements to the performance of clear coatings on wood exposed to the weather

can be obtained by photostabilizing wood surfaces prior to the application of clear coats.

The performance of clear coats on modified wood also varied depending on the properties of the coating. Samples coated with PUR performed badly during natural weathering, because the coating contained defects (pin holes). The SAH coating, which contained a harder inflexible binder, also performed poorly except on samples treated with BC, VB and PFH. Conversely, the standard acrylic coating containing double the normal amount of UVA/HALS (SA+) performed well on many of the pre-treated wood samples. Therefore, I conclude that the performance of clear coats on wood can be further enhanced by increasing the photostability and flexibility of the coating and ensuring that defects are absent from the final coating. Finally, I conclude that the performance of clear coatings on pre-treated wood depends on both the pre-treatment and coating type, and both need to be optimized to achieve high levels of performance from clear coats on wood exposed outdoors.

5. General discussion, suggestions for further research and conclusions

5.1 Discussion

In this thesis I hypothesized that pre-treatments that can photostabilize wood (without adversely affecting coating performance), when combined with state-of-the-art clear coatings, will create coating systems (pre-treatment plus coating) that are a significant improvement on those that are currently available. In this chapter the results from both experimental chapters are synthesized and the extent to which they accord with the general hypothesis (above) will be discussed. Chromic acid is the benchmark by which other treatments will be judged because it is very effective at photostabilizing wood and can significantly enhance the performance of clear coats on wood used outdoors (Black & Mraz 1974; Williams & Feist 1985; Ohtani 1987).

Chromic acid (CA) was able to photostabilize wood veneers as expected. Additionally, CA treated wood was more wettable by the polyurethane (PUR) coating, and there were relatively high levels of wood failure when the PUR and the acrylic (AC) coatings were pulled from CA treated wood during adhesion tests. As expected, the CA treatment enhanced the performance of clear coats on samples exposed to 349 days of natural weathering in Australia, particularly the performance of the water-based acrylic (AC) and alkyd (AL) coatings.

Benzoyl chloride (BC), vinyl benzoate (VB) and PF-resin/HALS (PFH) treatments were as effective at photostabilizing wood as CA. Treatment of wood with BC, VB, and PFH did not affect the wettability of coatings in comparison to untreated

controls. However, the treatments enhanced the adhesion of the AC and PUR coatings to wood. The BC, VB and PFH treatments were all able to enhance the performance of clear coats on wood exposed to natural weathering. Indeed, the BC, VB and PFH treatments were as effective as chromic acid at improving the performance of the various clear coats. Therefore, these findings support my hypothesis that pre-treatments that can photostabilize wood without adversely affecting coating performance will enhance clear coat performance.

In Chapter 3, I showed that the UVHIO treatment was able to photostabilize wood almost as effectively as CA, BC, VB and PFH. However, the UVHIO treatment decreased the wettability of wood surfaces to water-based AC and AL coatings. Clear coated wood samples pre-treated with UVHIO developed higher levels of coating failure than the clear coated untreated controls. Hence, their appearance ratings were worse than those of clear coated wood samples pre-treated with CA, BC, PFH and VB. The poorer performance of clear coated UVHIO treated wood samples during outdoor exposure might be related to the adverse effect of the treatment on the wettability of the coatings, as mentioned above.

The other wood pre-treatments examined in this study (cerium oxide nanoparticles [CNP], PF-resin [PF], PF-resin with PEG [PFP] and UVA/HALS [UVH]) were not able to photostabilize wood to the same extent as chromic acid. Not surprisingly, the outdoor performance of coatings on wood treated with CNP, PF, PFP and UVH was poorer than that of coatings on CA, BC, VB and PFH treated wood. This is mainly related to the inability of the former treatments to photostabilize the wood to the same extent as CA, BC, VB and PFH, because with the exception of

UVH, the CNP, PF and PFP treatments did not adversely affect coating properties such as wettability and adhesion. In case of the UVH treatment, poor clear coat performance may also be related to the adverse effect of this treatment on coating wettability.

There was clear evidence that the type of clear coating applied to samples influenced the outdoor performance of clear coated samples. In Chapter 3, the PUR coating performed well on all pre-treated wood surfaces in terms of wettability and coating adhesion. The permeability of the PUR coating was also significantly lower than those of the water-based AC and AL coatings. Based on these results and findings from previous research the PUR coating was expected to perform well during the natural weathering trial (Evans et al. 2007). Therefore, the poor performance of the PUR coating was unexpected. The PUR contained pinholes and the poor performance of the PUR coating is probably related to moisture ingress through these pinholes and colonization of the coating and underlying wood by fungi, as discussed in Chapter 4.

The properties of the different water-based coatings also influenced the performance of the coatings on treated and untreated wood samples during outdoor exposure in Australia. For example, the harder acrylic coating (SAH) performed poorly on untreated controls and on most pre-treated samples. Such poor performance is probably related to the lower flexibility of the binder in this coating because coating performance is correlated with the flexibility of the binder (Schmid 1988; Podgorski et al. 1996). Nevertheless, the SAH coating performed better on samples treated with BC, VB and PFH, which may be related to the higher

photostability conferred by these treatments, which in turn might reduce the level of stresses in the coating and make the coating less susceptible to failure.

Previous research has shown that clear wood coatings containing UVA/HALS additives performed well during outdoor exposure (Schaller & Rogez 2007; Forsthuber & Gröll 2010). Findings here accord with these observations because doubling the level of UVA/HALS additives in the acrylic coatings (SA+) improved the performance of the acrylic coating on treated wood samples, including the photostable substrates treated with BC, CA, VB and PFH. However, on wood samples pre-treated with CNP the SA+ coating performed poorly. Hence, it appears that increasing the level of UVA/HALS in clear coatings generally enhances the outdoor performance of coatings on untreated and pre-treated wood, but there may be exceptions to this rule.

Results in Chapter 3 and 4 demonstrate that wood treatments such as BC, CA and VB that can photostabilize wood are very effective at enhancing the performance of clear coats on wood used outdoors. The finding that a PF resin containing a HALS is able to photostabilize wood and enhances clear coat performance to levels achieved with BC, CA and VB treatments is noteworthy. Furthermore, increasing the level of UVA/HALS additives in the acrylic coatings enhanced their outdoor performance even on these photostable substrates. Thus the overall performance of the clear coated wood depends on the combination of pre-treatment and coating type and hence it should be possible to combine a wood treatment that photostabilizes wood and a highly durable (and flexible) clear coat to produce a high performance transparent coating system which will satisfy the

growing demand for finished wood products that look nice and have low maintenance requirements.

5.2 Suggestions for further research

BC, CA and VB increased the outdoor performance of the clear coats tested here. However, there are limitations to the use of all of these treatments. The reaction of BC with wood generates hydrochloric acid, whereas the reaction of VB generates acetaldehyde. Solvents and/or catalysts and high temperatures are required for BC and VB to react with wood. Chromic acid is very toxic. In contrast, the PFH is a water-based treatment that reacts with wood at room temperature. It is less toxic and expensive than BC and VB and it is equally effective as these chemicals and also CA at photostabilizing wood and improving the performance of clear finishes. It may be possible to further improve the performance of the PFH pre-treatment. It would be interesting to examine if increases in the concentrations of PF-resin and HALS in treatment solutions could increase the ability of this treatment to photostabilize wood. Once the treatment system has been optimized it would be necessary to test the performance of clear coatings on bigger composite panels laminated with thicker PFH pre-treated overlays. Such panels would allow for comparisons of color differences between masked and unmasked areas. Another suggestion for further research is to test the ability of the PFH treatments to improve the performance of clear coatings on other commercial wood species such as southern pine, radiata pine and red oak (*Quercus rubra* L.) during outdoor exposure.

The addition of HALS to PF-resin helped to reduce the discoloration of the resin during weathering which may be associated with the ability of HALS to

scavenge free radicals (Wicks et al. 1999; DebRoy 2006). HALS and UV absorbers act synergistically to photostabilize different polymers (Toda et al. 1985). Accordingly, it would be interesting to conduct further research to examine the ability of combinations of HALS with different organic and inorganic UV absorbers to photostabilize PF-resin treated wood samples and improve the performance of clear coats on the treated wood. It should be noted, however, that most UVA/HALS are not soluble in water and hence they would have to be dispersed in the PF resin using surfactants, which might influence the performance of coatings (Geurink et al. 2006).

The PFH treatment was almost as effective at photostabilizing wood as BC, CA and VB. All of the latter treatments are able to photostabilize lignin. No research has been carried out to examine whether the PF-resin or PFH treatment can photostabilize lignin. Hence, it would be interesting to determine whether the treatment can photostabilize lignin as well as the other structural constituents of wood.

The alkyd coating used in this study performed well on untreated controls and pre-treated wood samples during weathering. The alkyd coating contained the normal level of UVA/HALS additives. The acrylic coating containing double the normal level of UVA/HALS performed better than any of the other coating during the natural weathering trial. Hence, it would be interesting to conduct an experiment that includes alkyd coatings with double the normal level of UVA/HALS and to determine if the additional additives significantly improve the performance of the coating on modified wood.

The PUR coating used here performed unexpectedly badly possibly because of the presence of pinholes in the coating film. It would be interesting to test the performance of this coating in the absence of such coating defects. It would also be interesting to compare the effectiveness of water-based PUR coatings on pre-treated wood samples with that of the solvent-based PUR coating tested here, because water-based coatings are in greater demand compared to solvent-borne coatings and water-based PUR coatings are more comparable to the water-based acrylic and alkyd coatings used in this study.

5.3 Conclusions

The research performed in this thesis showed that pre-treatment of wood can significantly improve the performance of clear coatings on wood used outdoors as long as the treatments are able to photostabilize wood without adversely affecting the properties of the coating. Three treatments were as effective as chromic acid at improving clear coat performance. These treatments were benzoyl chloride, vinyl benzoate and PF-resin with HALS. It is noteworthy that the PF-resin with HALS improved the performance of the clear coats to the same degree as BC, CA and VB because the PFH treatment has the potential to be used as an industrial pre-treatment: PF-resin treatment of wood has been used in the past and there are also commercial treatment processes being used today for the treatment of knife handles and decking timber (Jay Fisher Company 1996; Kyushu Mokuzai Kougyou Co., Ltd. 2011).

The performance of clear coats can be enhanced further, even if they are applied to very photostable wood substrates. This can be achieved by using

coatings with larger than normal quantities of UVA/HALS additives, ensuring that the selected coating has a binder with adequate flexibility and the cured coating is free of defects.

Based on my findings I conclude that the performance of clear coatings on wood during outdoor exposure depends on the combination of wood pre-treatment and coating type, and, accordingly, the best performance can be obtained by combining very effective photostabilizing wood pre-treatments with state-of-the-art photostable clear coatings.

The development of more effective pre-treatment and clear coat combinations would pave the way for the increased use of wood in applications such as cladding, windows, and doors where consumers increasingly tend to favour wood because of its appearance and environmental friendliness.

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Appendices

Appendix 1 - statistical analysis, chapter 3

Effects of chemical treatment on weight loss, tensile strength loss and erosion (see CD).

Appendix 2 - statistical analysis, chapter 3

- a) Effect of chemical treatment, coating type and treatment coating interaction on contact angle, tensile stress and wood failure (see CD).
- b) Effect of coating type on permeability (see CD).

Appendix 3 - statistical analysis, chapter 4

Effects of chemical treatment, coating type and treatment coating interaction on color (L, a, b, delta E) and appearance (see CD).

Appendix 4 - manufacturers' recommendations

Manufacturers' recommendations for the application of clear coatings (see CD).

Appendix 5 - weathering data

Weathering data from Ulladulla, New South Wales, Australia for the 349 day outdoor exposure test (see CD).

Appendix 6 - images of pre-treated and clear-coated specimens

Images of clear coated veneered wood composite blocks before and after outdoor exposure (see CD).