Abstract

Wood is susceptible to photodegradation, particularly by ultraviolet (UV) light which triggers photochemical reactions in wood up to 100 µm from the surface. Painting may protect the wood from sunlight, however, consumers prefer clear-coatings because they reveal wood’s grain. Unfortunately, clear finishes on wood used outdoors fail within 1-2 years because sunlight transmitted through the clear-coating degrades the underlying wood. I hypothesized that the performance of clear-coatings on wood used outdoors would be improved if the clear-coating could penetrate deeply into the wood and bond with sub-surface layers of wood that are less affected by UV light. Glow discharge plasma derived from water was used to etch and open up flow paths at the surface of the refractory wood species, black spruce. Image analysis was used to assess the penetration of two polyurethane clear-coatings into wood, and the adhesion (pull-off) of clear-coatings to unweathered wood was measured. A second experiment examined the changes in color, gloss and integrity of clear-coats on plasma treated and coated specimens subjected to artificial accelerated weathering. Plasma treatment of black spruce for 20 min significantly increased the penetration of clear coatings into sub-surface layers of wood (50-75 µm). However, the adhesion of the polyurethane clear coatings on wood depended much more on coating type (adhesion of the water-borne was better than that of the oil-borne coating). Plasma pre-treatments decreased film failure of coatings on flat-sawn specimens exposed to artificial weathering, but increased the surface yellowing of coated wood specimens. The oil-borne polyurethane performed better in terms of three performance criteria (redness, yellowness and gloss), while the water-borne was superior in terms of changes in lightness. I conclude that plasma treatment can increase the penetration of coatings into wood if the plasma can etch the wood and open up important flow-paths. However, plasma treatments have no positive effect on the adhesion of polyurethane coatings to black spruce wood and adhesion is influenced more by the type of coating. Finally, plasma treatments can have positive and negative effects on the exterior performance of coatings on wood depending on the criteria used to assess performance.
Preface

Some of the results in Chapter 3 were published in the Proceedings of the 5th European Conference on Wood Modification, Riga, Latvia (Haase and Evans 2010, See Appendix 5).

I prepared the first draft of the article which was extensively edited by Professor Evans to fit in four pages as specified by the conference organizers. Professor Evans prepared all the figures in the article from data I collected in my experiments. The light microscope pictures as well as the methodology for measuring clear coating penetration into wood are of my authorship. Professor Evans diagrammed the article and finally submitted it to the conference organizers.
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Figure 4.19: Yellowness (a*) of specimens coated on their radial surfaces and exposed to artificial weathering. Changes in yellowness defined as the ratio of b* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time ........................................................................................................................................ 109

Figure 4.20: Yellowness (a*) of specimens coated on their tangential surfaces and exposed to artificial weathering. Changes in yellowness defined as the ratio of b* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time ........................................................................................................................................ 109

Figure 4.21: Gloss (G*) of specimens coated on their (a) radial and (b) tangential surfaces and exposed to artificial weathering for 1500 h (radial) or 500 h to 1500 h (tangential). Gloss changes defined as the ratio of G* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time ........................................................................................................................................ 110
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Yesterday, today and tomorrow I will keep on being grateful to my family and friends and the values they have taught and continue to teach to me.
Dedication

I should like to dedicate this thesis to my dad, who reminded me every morning:

“macho parado no gana flete hijo”
1. General introduction

1.1 Introductory remarks

Wood continues to be used in outdoors because of its pleasant appearance, favourable properties and low cost (Hon and Chang 1984). Wood is easy to process into a wide variety of products such as siding, windows and doors (Walker 2006). In British Columbia (BC), legislation has been enacted that favours the use of wood in all provincially funded building projects. This legislation, the Wood First Act (2009), supports communities in BC that rely on the wood processing industry (BC Ministry of Forests, Mines and Lands 2010). Wood is a sustainable and unique material with a favourable suite of properties, but its continued use will require higher levels of performance (Kozak and Gaston 2001). Otherwise, less sustainable materials such as concrete, metals and plastics will continue to displace wood from the market (Damery and Fisette 2001, Clemons 2002, Ganguly and Eastin 2009).

One area where higher levels of performance are needed is in the resistance of wood to the weather (Tarkow et al. 1966, Black and Mraz 1974). Unprotected wood left outdoors weathers and grays, which ruins its appearance (one of wood’s positive characteristics) and upsets consumers (Evans 2008). The main factor that induces weathering is sunlight, particularly the ultraviolet (UV) component that degrades wood’s constituents, particularly lignin (Leary 1968, Fergus et al. 1969). Lignin makes up about 26-32% by weight of softwoods (Sjöström 1981), and its degradation by UV affects the structural integrity of wood surfaces (Miniutti 1964, 1967). UV degradation of lignin accelerates the checking of wood (Evans et al. 2008), triggers color changes (Leary 1968) and encourages the growth of staining fungi that cause the graying of wood (Dickinson 1971).

Blocking UV light from reaching wood is a trivial task that can be accomplished by finishing the wood with an opaque paint (Bravery and Miller 1980). For example, a white paint can restrict the deleterious effects of sunlight on wood, and painted wooden objects can remain in service for over 10 years with little maintenance (Cassens and Feist 1991). A far more difficult task is to maintain the natural appearance of wood for extended periods of time using clear finishes (Harris et al. 1964). Clear finishes
include high build film forming clear coatings and non-filming transparent stains/water repellents, which give wood a ‘natural’ appearance (Bulian and Graystone 2009). Unfortunately, most of the film forming coatings do not maintain the natural appearance of wood for more than 2 years because sunlight photodegrades the wood beneath the coating (Estrada 1958, 1967, Ashton 1967, Miniutti 1967). Furthermore, clear coatings often fail by delamination of the film which is considered “highly objectionable due to the difficulty in recoating” (Estrada 1967). Because of the poor performance of such finishes, the California Redwood Association in the late 60’s, no longer qualified or listed clear finishes for redwood used outdoors (Estrada 1967).

However, photodegradation of wood is only a surface phenomenon extending approximately 500 microns into the wood and, furthermore, degradation caused by UV-radiation only affects approximately the first 100 microns of ‘surface’ (Kataoka et al. 2004, 2007). Lignin readily absorbs UV at the ‘surface’ and the highly energetic UV wavelengths, which can cleave molecular bonds and cause discoloration, do not penetrate deeper than 100 microns into wood (Leary 1968, Fergus et al. 1969, Kataoka et al. 2004). However, other less energetic wavelengths in the visible spectrum (e.g. violet light) can cause photodegradation of wood beyond the latter zone, but with less impact (Derbyshire and Miller 1981, Kataoka et al. 2007). Therefore, the depth of penetration of light into wood is directly proportional to the wavelength, and the degree of photodegradation is inversely proportional to the wavelength (Kataoka et al. 2004, 2007). The photoprotection of wood needs to take into account these relationships between ‘wavelength’, the penetration of light into wood and photodegradation.

The approach that has mainly been used to restrict photodegradation of clear coated wood surfaces, without altering the wood’s color, has been to add UV absorbers and light-stabilizers to the clear coating or to the wood itself (Hon et al. 1985, Chang et al. 1998, Hayoz et al. 2003, Aloui et al. 2007, Chou et al. 2008, Forsthuber and Grülll 2010). This approach improves coating performance, but still such systems do not match the longevity of opaque finishes, because after 3-4 years the finishes fail by loss of interfacial adhesion due to wood’s degradation at the clear coat/wood interface (MacLeod et al.
1995, Singh and Dawson 2003). Quite clearly, alternative approaches to improving the performance (longevity) of clear coatings on wood exposed outdoors are needed.

1.2 General hypothesis

Light is transmitted through clear coatings, and light penetrates into uncoated wood to depths of approximately 500 microns, depending on wood density (Horn et al. 1994, Kataoka et al. 2005). The transmission of highly energetic UV light through the clear coating results in the photodegradation of the clear coat/wood interface (at 25-50 microns depth) causing loss of interfacial adhesion between the coating and wood (Miniutti 1967, Vasishth et al. 1974, Derbyshire and Miller 1981). Normally, clear coatings do not penetrate beyond 25-50 microns, and rarely beyond 500 microns. Hence their performance is affected by the photodegradation of wood in the upper-most layer of wood cells (MacLeod et al. 1995, de Meijer et al. 1998, Singh and Dawson 2003). However, the performance of clear coatings might be improved if they could penetrate into wood and adhere with subsurface layers of wood that are not damaged by light (Fig. 1.1). Thus, an increase in penetration could increase the bonding sites between undamaged wood and the coating leading to higher performance (Vasisht et al. 1974, Bardage and Bjurman 1998).

The effect of penetration of clear coatings into wood on their performance has received little attention compared to other coating performance indicators such as coating adhesion on wood, gloss, film failure and color stability (Rijckaert et al. 2001b, Van den Bulcke et al. 2008). The penetration of finishes into wood is influenced amongst other factors by the wood’s permeability and the presence of open flow paths (Schneider 1972, de Meijer et al. 1998). Bordered pits and rays play a key role in connecting tracheids in softwoods, but many bordered pits are aspirated in dry wood (Liese and Bauch 1967a). The removal of pit membranes by bacteria increases penetration of finishes into *Pinus radiata* D. Don wood (Singh et al. 1998). Singh et al. 1998 hypothesized that this effect might improve the performance of clear finishes on radiata pine wood.
The membranes in bordered pits and in the pits connecting rays can be removed by glow-discharge plasma creating open flow paths (Jamali and Evans 2011). Furthermore, plasma treatments can increase the permeability of wood (Chen and Zavarin 1990). I hypothesize that plasma treatment will improve the performance of clear coatings on wood because the coating will penetrate wood to depths that are less affected by UV light. Therefore, the clear coatings will be less prone to failure when exposed to the weather.

Figure 1.1: Diagrammatic representation of UV and visible light transmitted through a clear coating and penetrating into wood to different depths: (i) < 50 µm depth where coating is present, note that UV light transmitted through the coating and reached unprotected wood; (ii) increased coating penetration at 75-100 µm, note that UV light does not transmit through this zone; (iii) zone where photodegradation by visible light still occurs; (iv) beyond ~ 500 µm where photodegradation of wood by UV and visible light has not been reported (Developed following Horn et al. 1994, de Meijer et al. 1998, Kataoka et al. 2004, 2007)

1.3 Aim, scope and importance

The overall aim of this thesis is to examine whether glow discharge plasma treatment has an effect on the penetration of clear coatings into black spruce (Picea mariana (Mill.) B.S.P.) wood, leading to higher weathering performance of clear-coated wood. Adhesion of the coating to plasma-modified black spruce wood as well as other indicators of coating performance were examined during an extended artificial weathering trial, which tested whether plasma treatment improved clear coating performance. If this aim is achieved then plasma treatment of wood (before finishing) could be used to enhance the
performance of clear coatings, which as mentioned above, usually perform poorly when used on wood exposed outdoors.

1.4 Study outline

This chapter (Chapter 1) presents introductory material and develops the hypothesis for the study. Chapter 2 reviews the literature on the performance of clear coatings on wood exposed outdoors including the mechanisms of coating failure. A focus is given to the effect of solar radiation on the failure of clear coatings and the mechanisms responsible for the photodegradation of wood that result in the yellowing and graying of wood exposed outdoors. Chapter 2 also reviews information on the treatments that have been tested to enhance clear coating performance on wood exposed outdoors. This section of the literature review is sub-divided into 3: (1) treatments designed to improve the photostability of the clear coating formulations; (2) treatments seeking to photostabilize clear coat-wood interface and; (3) other less conventional approaches to improving the performance of clear coatings. The relevant literature that links coating penetration to coating adhesion on wood is also examined. The final section in Chapter 2 reviews the literature on the plasma modification of wood, emphasizing research that has examined the effects of plasma treatments on the microscopic structure of wood and its permeability.

Chapter 3 is an experimental chapter that examines the effect of plasma treatment on the penetration and adhesion of clear coatings in black spruce wood. This chapter also develops novel methodology to quantify clear coating penetration into the microstructure of wood.

Chapter 4 is a second experimental chapter that examines whether plasma treatment improves the performance of two types of clear coatings on black spruce wood exposed to artificial accelerated weathering. Both quarter- and flat-sawn panels were exposed to artificial weathering and a range of different indicators were used to evaluate the performance of the clear coatings on plasma-treated wood and untreated controls. Lastly, Chapter 5 discusses the results of both experimental chapters, draws conclusions and makes suggestions for further research.
2. Literature review

2.1 Clear coating performance

2.1.1 Definitions

Coatings are organic materials that provide surface protection to materials and share the properties of “wetting substrates, transforming into a closed film, flowing, and then solidifying so that the desired mechanical and chemical protection of the object is achieved” (Goldschmidt and Streitberger 2007). Feist (2007) suggests judging coating performance upon the coat’s ability to “execute a set of actions or primary functions during its expected service life.” Generally, three primary functions are common to any wood finish: (1) protecting the wood surface; (2) helping to maintain its appearance; (3) ease of cleaning (Feist 2007). Additionally, the idea of coatings providing sustainable protection for timber has recently been postulated (Dawson et al. 2005). Testing of clear coating performance mainly addresses durability and appearance, but rarely addresses ease of cleaning (Estrada 1958, Ashton 1967). Therefore, throughout this review, clear coating performance refers to the ability of the coating to protect the wood surface and maintain its appearance.

Clear coatings are a sub-set of coatings in general (Goldschmidt and Streitberger 2007). The European standard EN 971-1 1996 states that a clear coating is one which “when applied to a substrate forms a solid transparent film having protective, decorative or specific technical properties.” Transparency is “the property of transmitting light without appreciable scattering so that bodies lying beyond are seen clearly” (Miriam Webster 2010). The transparency of clear coatings is a major factor affecting their performance on wood (Kiefer 1967). The wavelengths of light reaching the wood surface through a clear film can be measured using a spectrophotometer to obtain transmission spectra (Cohen et al. 1971), and wavelength of light is positively correlated with the depth of the penetration of light into wood, as mentioned above (Kataoka et al. 2007).

Before stressing the importance of transparency in determining the performance of clear coatings, it is important to describe some of the different types of exterior clear coatings that are used to protect wood outdoors. Due to the extensive amount of literature available on the topic of coating technology,
most of the information presented in the following section is based on the *BASF Handbook of Coating Technology* (Goldschmidt and Streitberger 2007), unless otherwise stated.

### 2.1.2 Clear coating types

Clear coatings are composed of a film forming agent (*i.e.* resin), a solvent and additives. Binders are the pigment free and extender free parts of the dried or cured coating (DIN EN 971-1). The historical development of resin types in clear coatings shares similarities with that of paints. In Germany, for example, access to the more popular hardened natural resins (used in varnishes) such as copal, colophony, dammar and shellac, could not be guaranteed during the early 20th century due to political instability in some of the countries producing natural resins. This led to a search for ways of producing synthetic resins. However, this was not the only reason for a shift from natural resins to synthetic resins. The latter are highly reproducible, have “unlimited” availability and can be customized for different applications. Natural resins also tend to yellow more than synthetic resins, furthermore, they often constitute “food” for other organisms.

Film forming agents can be divided into physically curing (*i.e.* set by giving off solvents) and chemically reactive (*i.e.* set by crosslinking) types. Clear coatings contain additives and solvents besides the film forming agent. Additives, such as ultraviolet absorbers (UVA’s), will be detailed below (*Section 2.3.1.2*). Solvents might be either synthetic (*e.g.* naptha, mineral spirits, alcohols) or natural (*e.g.* water). Traditionally, clear coatings have been formulated with organic solvents (termed solvent-borne or oil-borne coatings), which are classified as volatile organic compounds (VOC’s). Recently, environmental legislation has been enacted in some countries to favor the use of water as a solvent and thus, not only solutions (particle size ~ 0.001 µm), but also colloids (0.001-0.1 µm) and dispersions (> 0.1 µm) in water are being formulated (Dören *et al.* 1994). With appropriate technology, most of the existing synthetic resin types can be formulated into water or organic solvent-borne clear coatings.

Today, natural film forming agents such as drying fatty oils are still used as raw materials in clear coating formulations (Fig. 2.1). Because of their polyunsaturated nature, these inexpensive raw materials are able to transform from a low viscosity liquid and dry to a solid by the interaction of the binder with
oxygen. In the wood finishing field, fatty oils are often used in the formulation of varnishes: an “oil-and-resin liquid preparation which, when spread on a surface, dries, forming a hard, lustrous, transparent coating” (Montague 1972). According to Montague (1972), varnishes are classified based on the amount of imperial gallons per 100 lb of resin as follows: (i) long-oiled, 28- >50 gal; (ii) medium-oiled, 12-28 gal and; (iii) short oiled (<15 gal). In terms of the International System of Units, 100 lb is roughly 45 kg, and one imperial gallon is 4.5 L. A commercial synthetic varnish used for wood finishing generally contains an oil-modified synthetic resin, for example a product label could read: long linseed oil polyurethane solvent-borne varnish.

![Figure 2.1: Main fatty acids in linseed oil, which is a common oil used in the manufacture of varnishes (Goldschmidt and Streitberger 2007)](image)

2.1.2.1 Alkyd resins

The synthesis of alkyd resins was the result of the failure in performance of glyptal resins tested in the 1920’s. Instead of merely esterifying glycerine with phthalic anhydride, which resulted in premature gelling, Roy Kienle (General Electric Co.) successfully synthesized oil-modified polyesters known today as alkyds. Alkyds are film forming agents synthesized by polycondensation via two paths: the fatty acid process or the transesterification process (Fig. 2.2). Both paths are used industrially, but the fatty acid process is favored due to the greater flexibility in selecting the raw materials for customized film forming agents. The most common raw materials in alkyds are the fatty acid, a polyol (e.g. glycerine) and a carboxilic acid (e.g. phthalic anhydridide). In the fatty acid method, the three materials are added separately and then reacted together. However, in the transesterification method, the polyol is previously reacted with the fatty acid to yield a hydroxyl-functional intermediate and afterwards the intermediate is reacted with phthalic anhydride.
In clear coatings for wood, alkyds usually receive a classification based on the percentage of oil to resin weight as follows: (i) long-oil, 60% or more; (ii) medium-oil, 40-60% and; (iii) short oil, less than 40%. Due to their relatively simple synthetic paths, alkyds may be chemically modified to better adapt them to practical requirements. One such chemical modification of alkyds occurs when the phthalic acid is replaced by a diisocyanate resulting in a urethane alkyd group (Fig. 2.3). Complete substitution of the phthalic acid by urethane alkyd groups lead to urethane oils, which have better resistance to acids and alkalis, and are also more wear-resistant.
2.1.2.2 Urethane resins

The basic chemical reaction that yields a urethane linkage is that of an isocyanate group with a hydroxyl group (Fig. 2.4). The latter reaction had been described by Charles-Adolphe Wurtz in 1849, but in 1947, Bayer transferred the reaction to the polyfunctional structural elements known today as polyurethanes (Bayer 1947). As reported by McGinnis (1960), the use of polyurethanes as clear coatings for wood has advantages and disadvantages. Properly formulated polyurethanes give a clear finish that is hard to mar and they wear 2 to 20 times better than conventional finishes (McGinnis 1960). In exterior applications over wood, polyurethanes are often favored due to their higher vapor transmission rate when compared to conventional clears, toughness, excellent adhesion to untreated wood and flexibility (McGinnis 1960, Damusis and Frisch 1967).

Polyurethane coatings sourced from aromatic diisocyanates such as toluene diisocyanate (TDI) are toxic and yellow more than those formulated with aliphatic diisocyanates such as hexamethylene diisocyanate (HDI) (Fig. 2.5). Polyurethanes are grouped by ASTM into five types (Table 3.1). However, the wood finisher might find it easier to apply polyurethanes as one-package systems (ASTM Type 1), which are commonly sold as varnishes (McGinnis 1960).
Figure 2.4: Basic reaction of polyaddition resins: urethanes in the top reaction and epoxies generated from the reaction of an oxiranring (Goldschmidt and Streitberger 2007)

Figure 2.5: Common aromatic (TDI) and aliphatic (HDI) diisocyanates as basic compounds for urethanes (Goldschmidt and Streitberger 2007)

Table 2.1: Five types of urethane coatings (Boylan 1972)

<table>
<thead>
<tr>
<th>Type</th>
<th>Oil-modified</th>
<th>Moisture-cured</th>
<th>Blocked adduct</th>
<th>Catalyzed</th>
<th>Polyl-cured</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Cure</td>
<td>+ O₂</td>
<td>NCO + H₂O</td>
<td>NCO + OH</td>
<td>NCO + H₂O + side reactions</td>
<td>NCO + OH</td>
</tr>
<tr>
<td>Pot life</td>
<td>Unlimited</td>
<td>Extended</td>
<td>Unlimited</td>
<td>Limited</td>
<td>Limited</td>
</tr>
</tbody>
</table>

2.1.2.3 Epoxy resins

Epoxies, like urethanes, are resins synthesized via polyaddition thus releasing no low molecular fragments (Fig. 2.4). These resins have been known for more than 100 years and are popular as two-package adhesive systems for wood. As clear coatings for wood, epoxies were introduced to the market several years before the urethanes, but they are not as old as phenolics or alkyds (Harris et al. 1964). The epoxide or oxirane group consists of a three-membered ring containing oxygen with a high ring strain.
This class of compounds may be divided into three broad categories: (1) glycidated resins; (2) cycloaliphatic epoxy resins; and (3) epoxidized oils (Somerville 1967). As observed with urethanes, chemical modification of alkyds is also possible with epoxy resins to improve adhesion, hardness, alkali-resistance and water-resistance of heavy-duty clear coatings used as floor and trim varnishes (Fig. 2.6) (Somerville 1967, Montague 1972). Epoxy resins, for use as clear coatings on wood, are usually esterified with oil acids, and drying occurs through the oil portion (Harris et al. 1964).

![Figure 2.6: Synthesis of epoxy modified alkyd resin. The epoxy groups and hydroxyl groups act as the polyol component for the mono- and dicarboxylic acids (FS = Fatty acid) (Goldschmidt and Streitberger 2007)](image1)

2.1.2.4 Phenolic resins

The synthesis of phenolic resins is attributed to Meier, while trying to manufacture shellac (i.e. a resin derived from the lac bugs secretion). He successfully produced phenolic resins by mixing phenol with low volume of formaldehyde by mistake and named the resulting resin, Novolak (Fig. 2.7).

![Figure 2.7: Synthesis of Novolak from phenol and formaldehyde (Goldschmidt and Streitberger 2007)](image2)

Phenol resins are important crosslinking agents in polycondensation reactions and are used to obtain desired coating properties. Within the various types of phenol resins (Fig. 2.8), some of the most
durable clear coatings for wood can be made from Bakelite resins (\(p\)-\textit{tert}-butyl-phenols or \(p\)-phenylphenol instead of phenol) in combination with tung oil and mineral spirits as solvent (Richardson and Wertz 1972). The latter non-heat reactive varnishes are known as “spar” varnishes, which have the following properties: oil lengths of 25-50, quick drying, glossy and resistance to both boiling water and strong alkalies at a 50-gal oil length (Montague 1972, Richardson and Wertz 1972). However, phenol resins have poor elasticity but this can be overcome to some extent by etherifying the resin with aliphatic alcohols and then reacting it with polyesters.

Figure 2.8 has been removed due to copyright restrictions. It contained the chemical structures of the types of phenols used in the manufacture of phenolic resins used in clear coatings. Original source: Richardson, S. H. & Wertz, W. L., 1972. Phenolic resins for coatings. In: Treatise on coatings (eds Myers, R. R. & Long, J. S.) Film-forming compositions Part III, pp. 129-170, Marcel Dekker, New York.

2.1.2.5 Acrylic resins

Acrylics, acrylates, polyacrylates and poyacrylics refer to the pure acrylic acid derivatives and the copolymers of the esters of acrylic and methacrylic acids and styrene. Acrylic resins are available as thermosetting (\textit{i.e.} cure by heat) and thermoplastic (\textit{i.e.} liquefy by heat) types depending on their basic components (Fig. 2.9). Aqueous thermoplastic acrylic resin dispersions are popular as wood coatings because the evaporation of water occurs relatively fast.

![Chemical structures](https://example.com/chemical structures.png)

Figure 2.9: Basic components for thermoplastic acrylic resins (Goldschmidt and Streitberger 2007)
As observed with other resins, acrylics may also show enhanced properties when used in combination with other resins (Fig. 2.10). For example, polyester acrylates are favored as clear coating for wood because they are extremely lightfast or fade resistant to UV, while urethane acrylates show good toughness, adhesion and wear resistance.

![Diagram of acrylic modified resins]

Figure 2.10: Examples of acrylic acid modified film forming agents (Goldschmidt and Streitberger 2007)

2.1.2.6 Other resins

Experimental work has examined the use of other resins for clear coatings on wood. For example, transparent silicone resins and fluorocarbon resins were tested in clear-coats by the Forest Products Laboratory in the USA and the New Zealand Forest Research Institute (Miniutti 1967, Black and Mraz 1974, Preston and Chittenden 1978). In the case of silicones, the skeleton-forming elements of these resins are silicon and oxygen, with hydrocarbon groups found only as substituents in the side-chains (Fig. 2.11). This skeleton results in greater UV stability because the bond energy in Si-O bonds is 375 KJ/mol compared to 340 KJ/mol in C-C bonds. In fluorocarbon resins, the bond energy in C-F bonds is 490 KJ/mol, one of the strongest single bonds to carbon (Wood 2002).
Preston and Chittenden (1978) experimented with silicone-acrylic and fluorocarbon-acrylic (Fig. 2.12) resins as clear coatings on radiata pine and reported outstanding performance only if the wood had been pretreated with inorganic reactive chemicals before accelerated weathering. However, due to their high cost, silicone and fluorocarbon resins are less attractive commercially for use on wood exposed outdoors (Preston and Chittenden 1978).

There is a widespread interest in featuring the natural appearance of wood used outdoors (Bravery and Miller 1980). Clear coatings play a role in timber preservation (Uiterwaal and Blom 1973), but have limited longevity due to photodegradation of the underlying wood surface, as mentioned above (Miniutti 1967). Usually, such coatings require maintenance after only months to 2 years from initial application (Ashton 1967, Cassens and Feist 1991). In contrast, pigmented coatings (paints) on wood can last 7-10 years without any maintenance (Cassens and Feist 1991). Polymer manufacturers are able to formulate binders for use in clear coating that have excellent resistance to weathering (Damusis and
Frisch 1967). Therefore, there is a gap between the durability of the coatings and their ‘on-wood durability’ (Schneider 1972). Despite this gap, Black and Mraz (1974) stated that “it is not unreasonable to expect clear coatings for exterior wood in the future to be as durable as paints” assuming that wood could be made photostable!

2.1.4 Assessing clear coating performance

“…varnish films on wood could be regarded as satisfactory only as long as the color in the wood remained…” Gray (1961)

A wide range of environmental factors influence the performance of clear coatings on wood including: thermal, light, mechanical and chemical forms of energy (Feist 2007). Additionally, the degree of severity of the effect of an energy form depends on whether the coating is exposed indoors or outdoors. The relative effects of various energy forms on uncoated wood are listed in Table 2.1.

Coated or uncoated, wood is challenged by similar factors, but with different severity (Feist 2007). These factors include sunlight, water, heat, environmental pollutants and micro-organisms (Fig. 2.13). Photo-irradiation is the main factor influencing clear coating performance on wood as mentioned above (Miniutii 1967).

Table 2.2: Relative effects of various energy forms on wood (Feist 2007)

<table>
<thead>
<tr>
<th>Form of Energy</th>
<th>Indoors</th>
<th>Outdoors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Result</td>
<td>Degree of effect</td>
</tr>
<tr>
<td>Thermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intense</td>
<td>Fire</td>
<td>Severe</td>
</tr>
<tr>
<td>Slight</td>
<td>Darkening of color</td>
<td>Slight</td>
</tr>
<tr>
<td>Light*</td>
<td>Color change</td>
<td>Slight</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical</td>
<td>Wear and tear</td>
<td>Slight</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>Staining</td>
<td>Slight</td>
</tr>
<tr>
<td></td>
<td>Discoloration</td>
<td>Slight</td>
</tr>
<tr>
<td></td>
<td>Color change</td>
<td>Slight</td>
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<td></td>
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</tbody>
</table>

*aBoth visible and ultraviolet light
Figure 2.13 has been removed due to copyright restrictions. It was a diagram of the stressing elements, influencing factors, and weathering effects that contribute to wood-finish system performance. Original source: Feist, W. C., 2007. Exterior wood finishes. In: *Coatings materials and surface coatings* (ed Tracton, A. A.), pp. 66:1-12, CRC Press, Boca Raton, FL.

Because of the complicated matrix of stressing elements, influencing factors and weathering effects, assessing the performance of clear coatings on wood exposed outdoors is not a trivial task. Initially, assessments of clear coating durability on wood were done by means of visual rating schemes where authors graded the appeal of the film, on a numerical scale, after natural and artificial exposure (Estrada 1958, 1967, Ashton 1967, Black and Mraz 1974). Ashton (1980) correlated the visual ratings with clear film properties such as water absorption, water vapor permeability, tensile strength and elongation at break. Assessments have also been based on one numerical variable such as gloss retention (Kiefer 1967). Today assessments are generally done based on a combination of variables such as color change, gloss retention and ratings on film failure after exposure. These parameters will be explained in my section on evaluation of clear coating performance on plasma treated wood (Chapter 4).

Regardless of the parameters measured, the end user expects clear coating on wood to be durable. Dawson *et al.* (2005) suggested that coating performance “must not only negate the influence of the weathering processes, but fulfill the market need for an environmentally friendly product.” As mentioned above, clear coatings have traditionally ranked low in their resistance to weathering, but they are
demanded because their transparency permits wood’s grain to be seen. The following section focuses on how sunlight limits clear coating performance outdoors. An understanding of the mechanisms of clear coating failure on wood has stimulated research to improve clear coating performance on wood.

2.2 Mechanisms of clear coating failure on wood

2.2.1 Loss of interfacial adhesion due to photodegradation of wood

Clear coatings are designed to “highlight, preserve the natural beauty” of wood and ultimately work better when they are correctly applied to wood (Schaller and Rogez 2007). Coatings are expected to adhere well to wood’s surface, have good cohesive strength, resist weathering and chemical deterioration, and impede permeability of water, harmful substances or corrosives (Weldon 2002). On exposure to environmental factors (Fig. 2.13), coatings may fail if stressed at their weakest point (Weldon 2002). Clear coating’s failure on wood has been ascribed to loss of wood’s cohesive strength resulting in delamination of the film (MacLeod et al. 1995, Singh and Dawson 2003). It is the purpose of this section to explain the mechanisms that promote this type of failure.

Sunlight is responsible for the photodegradation of wood, but our appreciation of wood’s grain and color is due to the action of a range of solar wavelengths reflecting and being absorbed by its surface (Hon and Minemura 2001). Hence, the color of wood that we see is the portion of the visible light that is reflected when light strikes the surface. The wavelengths of sunlight that mainly interact with wood belong either to the ultraviolet (UV: 280-380 nm), visible (Vis: 380-780 nm) or near infrared (NIR: 780-2400 nm) parts of the electromagnetic spectrum (Hon 2001). But not all of wood’s main chemical constituents interact to the same extent with the different wavelengths (Chang et al. 1982, Hon 2001).

High energy wavelengths, those located in the UV range, may break the chemical bonds of wood’s constituents, particularly lignin, in a process termed photodegradation (Hon 2001). Lignin is a complex polymer composed of aromatic moieties (Fig. 2.14), which readily absorb UV light with a maximum absorption peak at 280 nm (Hon 2001). Aromatic extractives also absorb UV light and contribute to wood’s photodegradation (Pandey 2005). Cellulose and hemicelluloses are aliphatic and do not absorb UV component of sunlight to the same extent as lignin (Table 2.3).
Table 2.3: Chemical constituents of softwoods and UV-sensitiveness (Walker 2006\(^1\), Hon 2001\(^2\))

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Abundance (%)(^1)</th>
<th>UV-sensitiveness(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>42±2</td>
<td>Low</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>27±2</td>
<td>Low</td>
</tr>
<tr>
<td>Lignin</td>
<td>28±3</td>
<td>High</td>
</tr>
<tr>
<td>Extractives</td>
<td>3±2</td>
<td>High</td>
</tr>
</tbody>
</table>

*Note that cellulose and hemicelluloses are rapidly degraded by sunlight, as a result of the photodegradation of lignin (Evans et al. 1992, 1996)

Figure 2.14 has been removed due to copyright restrictions. It was a model of the structure of softwood lignin showing two (A & B) chromophoric groups. Original source: George, B., Suttie, E., Merlin, A. & Deglise, X., 2005. Photodegradation and photostabilisation of wood — the state of the art. *Polymer Degradation and Stability, 88*(2), 268-274.

The photodegradation of wood depends on the penetration of light into wood and its absorption by the wood’s polymers (Evans et al. 2005). Initially, the penetration of UV light into wood was reported by Browne and Simonson (1957) as “negligible, no more than a few mils” (1 mil = 25.4 µm). Later, UV light was reported to penetrate approximately 75 µm into uncoated wood surfaces, while visible light penetrated to a depth of 200 µm (Hon and Ifju 1978). Kataoka et al. 2004 observed that 90% of UV light
(350 nm wavelength) was absorbed by the first 75 µm layer, but 1% could reach depths of up to 150 µm. They also observed that 90% of visible light (420 nm wavelength) was absorbed by the first 220 µm layer, but 1% could penetrate to depths of 440 µm. In radial faces of the earlywood of sugi (*Cryptomeria japonica* (L.f.) D. Don), Kataoka *et al.* (2007) found a positive correlation between the penetration of light and the wavelength of the incident radiation within the range of 246-496 nm (Fig. 2.15). Kataoka *et al.* (2005) also reported that there was an “inversely proportional relationship between depth of photodegradation and wood density”, confirming the statement of Horn *et al.* (1994), that “a more dense (wood) structure would make it more difficult for the penetration of light” to occur.

\[\text{Figure 2.15 has been removed due to copyright restrictions. It was a diagram of the percentage of transmission of monochromatic light with wavelengths ranging from 246 to 496 through sections of varying thickness of sugi earlywood (semi-logarithmic scale). Original source: Kataoka, Y., Kiguchi, M., Williams, R. S. & Evans, P. D., 2007. Violet light causes photodegradation of wood beyond the zone affected by ultraviolet light. Holzforschung, 61(1), 23-27.}\]

As mentioned above, wood mainly absorbs UV light and both absorbs and reflects visible light. A clear coating’s role is to transmit visible light and therefore reveal the underlying wood surface (Kiguchi 1997). Unmodified clear coatings for wood also transmit much of the UV spectra. In a study by the Philadelphia Society for Paint Technology (Kiefer 1967), it was found that transmission of UV radiation
through clear films ranged from 35% for a tung oil phenolic varnish, to 65% for an oil modified polyurethane varnish and up to 80% for an alkyd resin varnish (Fig. 2.16).

Fig. 2.16 has been removed due to copyright restrictions. It was a diagram of the transmission curves of a tung oil phenolic varnish, a polyurethane varnish, and an alkyd resin varnish before and after 500 hours in a Fadometer. Original source: Kiefer, J. R., Jr., 1967. Ultraviolet light absorbers in clear coatings for wood. *Journal of Paint Technology, 39*(515), 736-751.

The transmission of light through the film “permits wood’s visualization and enhancement of its surface” (Horn *et al.* 1994). But when light reaches the underlying wood, it is absorbed and photodegradation of wood occurs. Regular clear coatings have been found to reduce the speed of these processes by a ratio of 30:1 when compared to unprotected wood (Horn *et al.* 1994). Nevertheless, their performance is limited when compared to pigmented systems (Cassens and Feist 1991).

Discoloration of the wood surface is the first change occurring during early exposure of uncoated wood to sunlight (Derbyshire and Miller 1981) and artificial light sources (Tolvaj and Mitsui 2005). A
decrease in brightness and a change from pale yellow to brown and to gray occurs when softwoods are exposed to light (Hon 2001). Such color changes provide evidence for the formation of new pigmented compounds termed chromophores (Hon and Minemura 2001). Chromophores are present in lignin and extractives and they can also be produced by the photodegradation of these compounds (Leary 1994, Horn et al. 1994, Hon 2001).

Chromophores in lignin contribute to 80-95% of the UV absorption by wood (Hon 2001). Such UV absorption readily excites the electrons in lignin’s aromatic rings and cleaves the lignin molecule resulting in the formation of aromatic radicals (Leary 1994). These radicals (Fig. 2.17) in the presence of oxygen further oxidize into a wide variety of low molecular weight molecules such as quinones and vanillin (Leary 1994, Hon 2001). These smaller molecules, unlike their parent polymer, display increased mobility within the wood’s microstructure. These by-products can be leached from wood by water (Derbyshire and Miller 1981, Horn et al. 1994, Evans et al. 1996) thus creating a partially delignified surface at the wood surface or under transparent films (Horn et al. 1994, MacLeod et al. 1995).

Photodegradation of lignin has severe effects on the surface integrity of wood. Lignin is not the most abundant of wood’s polymers (Table 2.3), but its importance in the context of the failure of clear coating lies in its distribution within the cell wall (Fig. 2.18). Lignin is wood’s ‘natural glue’ and it reaches a high concentration in the middle lamella (Fergus et al. 1969). The middle lamella is readily degraded by UV light causing tracheids in softwoods or fibers in hardwoods to separate from each other (Derbyshire and Miller 1981, Chang et al. 1982, Evans 1989). Under an irradiated clear coating, tracheids debond from each other after only six months of natural weathering (Singh and Dawson 2003).

Degradation of wood beneath coatings occurs before failure of the coating. Singh and Dawson (2003) showed delignified cells still attached to a delaminated clear coat after the coating had failed (Fig. 2.19).
Figure 2.17 has been removed due to copyright restrictions. It was a diagram of the mechanisms of free radical formation from lignin degradation. Original source: George, B., Suttie, E., Merlin, A. & Deglise, X., 2005. Photodegradation and photostabilisation of wood — the state of the art. *Polymer Degradation and Stability*, 88(2), 268-274.

Figure 2.18 was removed due to copyright restrictions. It was a micrograph of a cross section of tracheids of black spruce earlywood photographed in ultraviolet light of wavelength 240 nm. Original source: Fergus, B. J., Procter, A. R., Scott, J. A. N. & Goring, D. A. I., 1969. The distribution of lignin in sprucewood as determined by ultraviolet microscopy. *Wood Science and Technology*, 3(2), 117-138.
Figure 2.19: Light micrographs of transverse sections of radiata pine sapwood with varnish applied on the tangential surface; coatings were stained with Sudan IV and the wood tissue with aqueous toluidine blue. (a) Intact coating in close contact with the wood surface before outdoor exposure for 6 months in Rotorua, New Zealand; (b) the coating has detached due to separation of weathered surface cells, arrowhead points to a fully penetrated ray still in contact with the film layer; (c) region where the coating (arrow) detached from the wood together with some cells that were part of the wood surface and; (d) higher magnification view of (c) Scale bar = 40 µm in (a), (b) and (d), 100 µm in (c) (Singh and Dawson 2003, c/o IAWA Journal)
Photodegradation of lignin under an acrylic clear coating was also examined by MacLeod et al. (1995). Using Fourier transform infra-red spectroscopy, they found no evidence of photo-oxidation of the transparent film before failure, but the fibers that adhered to the coating had lost all their lignin. In conclusion, photo-induced processes result in the delignification of wood beneath the clear coating, tracheids detach from the underlying wood and the overlying clear coating fails due to loss of interfacial adhesion (MacLeod et al. 1995, Singh and Dawson 2003). This is one of the basic mechanisms of clear coating failure on wood. Hence efforts to increase the service life of clear coatings on wood have focused on improving the photostability of wood (prior to clear coating). Section 2.3 reviews some of this research, but I first examine the role that water and micro-organisms play in the failure of clear coatings on wood.

2.2.2 Effects of water on performance of clear coatings

Water, in the form of rain or moisture, is one of the main elements stressing clear films during outdoor exposure (Yaseen and Ashton 1970). Beneath paint films, for example, where wood is protected from UV, there is “a considerable surface degradation due to the action of water alone” (Banks 1971). Evans and Banks (1988) reported that water by itself may cause hydrolysis and loss of strength of thin wood strips, and such degradation was positively correlated with water temperature. Additionally, photodegradation and loss of strength of thin wood strips occurs more rapidly in the presence of water than when water is excluded (Derbyshire and Miller 1981). UV photochemical processes are enhanced more by moisture than by heat, but under a varnish film, the rate of photodegradation is reduced when compared to uncoated surfaces (Horn et al. 1994).

Wood is a hydrophilic substrate and when clear coated there is “an added possibility that moisture will reach the back of the film” (Yaseen and Ashton 1970). Popular clear coatings, such as varnishes, are permeable to moisture and may absorb water (Yaseen and Ashton 1970). In fact, “no organic coating is completely impervious” to water (Yaseen and Ashton 1978). When high moisture contents develop under clear coatings and under intense solar radiation, weakening of the surface beneath the clear coating is possible. Such an effect may contribute to the detachment of coating films on wood.
(Evans and Banks 1988). Uiterwaal and Blom (1973) stressed that moisture permeability of coatings is the “main cause of failure” of coatings upon exposure to the weather.

Feist (1990) reported a large proportion of coating failure outdoors was a direct result of moisture changes in wood and subsequent dimensional movement. Coatings slow down the rate at which wood changes moisture content (Borgin et al. 1975, Cassens and Feist 1991, Feist 2007), but, nevertheless, changes in wood moisture still cause the coated wood to shrink and swell (Spalt 1958), which imposes strains on the coating resulting in cracks in the film (Ashton 1967, Borgin et al. 1975, Feist 1990). There is little difference between the sorption and desorption of moisture by varnish films (Fig. 2.20a, Yaseen and Ashton 1970), whereas wood attains higher moisture content on desorption than on absorption in a phenomenon termed hysteresis (Fig. 2.20b, Spalt 1958). As suggested by Imamura (1976a, 1976b), coating failure (delamination and cracking) on wood is “induced mainly by the internal stress in the paint film.” This internal stress is “generated by the difference between the elongation or the contraction of the coating film and that of the wood” during dry-wet-dry cycles, such as those present when wood is exposed outdoors (Imamura 1976a).

Figure 2.20: (a) Water sorption isotherm for 20-gal tung-phenolic varnish at 23 °C compared to (b) sorption isotherms for previously air-dried white spruce (Picea glauca (Moench) Voss) and acetylated spruce at 32 °C (Spalt 1958, Yaseen and Ashton 1970)
2.2.3 Effects of microorganisms on performance of clear coatings

The damaging effects of water and sunlight on wood outdoors are often grouped as physico-chemical changes involved in weathering (Derbyshire and Miller 1981). Simultaneously, wood and also clear coated surfaces are colonized by microorganisms, particularly ‘blue stain fungi’ (Dickinson 1971). Dickinson (1971) reported that “the colonization of decorative timbers by stain fungi is the principal means by which the aesthetic appearance of timber is reduced.” Blue stain fungi cause the graying of wood surfaces both in uncoated and clear-coated wood. They also limit the performance of clear coatings on wood exposed to the weather (Dickinson 1971).

In Northern climates, *Pullularia pullulans* (syn. *Aureobasidium pullulans* (De Bary) G. Arnaud) has been identified as the main contributor to the graying of unprotected timber causing disfigurement and surface breakdown of wood (Sell 1968, Kühne *et al.* 1970, Dickinson 1971). Physical weathering causes clear films to crack and detach, and this allows the fungi to become established on and in these imperfections (Dickinson 1971). The colonization occurs first at small imperfections on the surface of the clear coating and via loose wood fibers which extend through the film, but it may also reach below the film causing staining of the wood (Butin 1961, Dickinson 1971). Dickinson (1971) states that in order to renovate a stained surface one must “cut back to clean wood.”

Besides staining, ‘inner colonization’ of the coating/wood interface by *A. pullulans* also reduces the performance of clear coatings on wood (Butin 1961). Dickinson (1971) reported that the fungus can grow under polyurethane, phenolic and alkyd varnish films and form pustules which can erupt through and cause “gross damage to the film.” In an effort to prevent the development of blue-stain fungi on coated wood, fungicides are often added to clear finishes or used as a wood pre-treatment (Sell 1968). Sell (1968) mentioned that if moisture, is excluded from exposed timber then blue-stain attack can be prevented. Hence, wood pre-treatments often combine a fungicide with water repellent substances (wax/oil) (Bravery and Miller 1980).
2.3 Improving clear coating performance

Attempts to improve the performance of clear coatings on wood have focused on changing the coating formulation and/or stabilizing the wood/coating interface. The approaches that have been used are reviewed in the following section.

2.3.1 Coating formulation

2.3.1.1 Resin type

A major contribution to the field of improving clear coating performance on wood was made by Ashton and co-workers at Division of Building Research, National Research Council, Ottawa, Canada. Their first exposure tests started as early as 1955 in Ottawa. Western red cedar (*Thuja plicata* Donn ex. D. Don) and white pine (*Pinus* sp.) siding panels were protected with several clear coatings (16 phenolic varnishes of different oils and lengths, 9 alkyds of different oils and 3 epoxy-fatty-acid-esters of different oils) and left to weather for 3 years (Harris *et al.* 1964, Ashton 1967). After such exposure, the only recoatable surfaces were the ones coated with 30- and 40-gallon tung oil phenolic varnishes. For the phenolic varnishes, it was apparent that those containing tung oil were superior to linseed oil, and both were better than ones containing dehydrated castor oil or soya oil. However, for the long length alkyds, the soya based coatings were better than the linseed based coatings. The researchers concluded that alkyds failed in a different manner to the phenolics when used as clear coatings on wood. The poorest performing clear coatings were the epoxy esters, and both short and medium length alkyds. Clear coatings applied to western red cedar panels were less durable than those applied on white pine. It was also noted that the degradation of the films was faster during summer months.

In 1960 a second exposure test was carried out using only white pine, but including more clear coating formulations (Harris *et al.* 1964, Ashton 1967). For the phenolic varnishes, the very long, poorly performing 50-gal types containing tung or linseed oil were eliminated, the 30-gal tung oil was cooked for different times to obtain a range of viscosities and the starting material was varied from *p-*phenylphenol to: 1 commercial resin, 1 reactive, and 2 *p-tert*-butylphenol (non reactive, *p* = para). Soya alkyds were tested in the complete range of oil lengths using *o*-phthalic anhydride, while only one very
long oil isophthalic alkyd was included \((o = \text{ortho})\). Epoxy-esters were discarded and three different epoxy precursors were tested: an amine, an amine adduct and a polyamide resin. A castor-oil-cured urethane was also tested and all of the above clear coatings were applied as 3 coats to the panels. After 2 years of exposure, only the 30- and 20-gal tung oil \(p\)-phenylphenolic varnishes, a \(p\)-\(\text{tert}\)-butylphenol varnish and the castor-oil-cured urethane had excellent ratings. Because of the influence of oil content and type of oil on durability (Fig. 2.21), and the higher rating of phenolic varnishes, Ashton (1967) recommended that “the resin should be \(p\)-phenylphenolic and the oil should consist mostly of tung oil and comprise 65-75\% of solids.” Ashton (1967) observed that the alkyds were still quite durable, but because they transmitted more UV light they were inferior to the phenolic varnishes. However, the linseed oil alkyd had the best gloss retention of all clear coatings tested in their trial (Harris et al. 1964). Delamination was the primary mode of failure of the clear coatings and was pronounced in the urethanes because of high tensile strength of their films. Nevertheless, epoxies showed a different type of failure in that films flaked and degraded. Again, the summer months were the most destructive to the clear coatings applied to the white pine panels.

Following observations of Ashton and co-workers of the superior performance of phenolic varnishes on wood exposed outdoors, the Division of Building Research directed more attention to the effects of water, as a “chief element of weather”, on the performance of clear free films (Yaseen and Ashton 1970, 1977, 1978). They observed that for phenolic varnishes, for example, with any one oil, the lower the oil content the lower the amount of water absorbed (Yaseen and Ashton 1970). \(P\)-phenylphenolic varnishes formulated with tung oil absorbed less water than those containing linseed oil at similar oil lengths, and this correlated well with their higher durability on western red cedar panels (Ashton 1967, Yaseen and Ashton 1970). Tung oil \(p\)-phenylphenolic varnishes were also less permeable to water vapor than other oil formulations and this was explained by the fact that tung oil has a higher degree of conjugated unsaturations and crosslinks compared to the other oils (Yaseen and Ashton 1978). For the alkyds, a lower oil content also reduced water permeability, but their permeability was higher than that of the phenolics. Hence it was concluded that there was an inverse correlation between the permeability of clear coatings and their durability on wood used outdoors (Ashton 1967, Yaseen and
Further work permitted Ashton (1979, 1980) to relate the durability of clear coatings on wood exposed outdoors with variables such as water absorption, water vapor permeation, tensile strength and elongation at break of clear films. Water vapor permeation and water absorption correlated well with durability for both phenolic varnishes ($r = 0.92$) and alkyds ($r = 0.94$). Flexibility variables measured through tensile strength and elongation at break “were found to be less important in relation to the performance of clear finishes than water absorption, water vapor permeation or transparency to UV light even on such a dimensionally unstable substrate as wood” (Ashton 1979).

Figure 2.21: Effect of oil content and type on the durability of para-phenylphenolic varnishes on white pine siding exposed to weathering (Ashton 1967). Durability rating according to the state of degradation of the clear coats on the panels where $10 = $ no change, $8 = $ slight change, $6 = $ moderate change, $4 = $ marked change, $2 = $ severe change and $0 = $ complete failure

Estrada (1967), on behalf of the Golden Gate Society for Coatings Technology, noticed that the durability of tung and tung-linseed oil $p$-phenyl phenolic varnishes on edge grained western red cedar and pine diminished quickly during the third summer of outdoor weathering in Cloverdale, California, a severe exposure site. However, the performance of the phenolic varnishes was rated as fairly good at both Portland, Oregon, and Sayville, New York. In contrast to the observations of Harris et al. (1964) and Ashton (1967), the clear coatings performed “equal” on redwood ($Sequoia sempervirens$ (D.Don) Endl.) and western red cedar but their performance on white pine was poorer (Estrada 1958). This case illustrates the discrepancies that arise when assessing performance of coatings through natural weathering.
trials in different exposure sites, and also the large effect that the substrate can have on clear coating performance on wood.

Estrada (1958) found that long oil alkyds performed better than varnishes, epoxy and silicone materials on redwood after a two year exposure trial in Sayville, New York; Tulsa, Oklahoma; Portland Oregon; Long Beach, California and Cloverdale, California. A long oil pentaerythritol phthalate soya alkyd performed the best, while isophthalic alkyds performed “quite good” at the most severe site, (Cloverdale). However, even the most durable systems failed by delamination due to breakdown of the wood surface itself, rather than direct failure of the coating (Estrada 1958). In a later study, the performance of some 31 different two package (i.e. catalyzed) clear coating systems was evaluated on edge-grain redwood panels exposed at three sites: Willits, California; El Monte, California; and Highstown, New Jersey, was compared. After 33 months of exposure, the 2-3 coat systems were assessed for their recoatability. The urethane coatings performed the best, especially a castor polyol cured with TDI-pre-polymer, when compared to epoxies and polyesters. Estrada (1967) concluded that the urethane system appeared to have the “greatest probability of providing a satisfactory answer to the need for a suitable clear finish for redwood for exterior exposure.” Estrada (1967) regretted that his finding of the enhanced durability of urethane clear coatings was not “illustrated with photographs” as they may have provided information on other important variables such as color changes. Damusis and Frisch (1967) reported that urethanes based on aromatic diisocyanates were susceptible to yellowing while those based on aliphatic and cycloaliphatic diisocyanates were UV stable.

The absorption of UV by phenolic coatings contributes to their good performance on wood (Ashton 1967). Conversely, UV transparent silicone coatings do little to restrict the photodegradation of wood (Miniutti 1967). Hence, UV “transparent” clear coatings (e.g. some acrylics, aliphatic polyurethanes) on wood must be stabilized with organic or inorganic UV absorbers to obtain satisfactory performance (Ashton 1973, Boxall et al. 1984). There are two main approaches to stabilizing clear coatings. The first approach uses additives that absorb UV light or terminate radical reactions. This area will be reviewed in Section 2.3.1.2. The second approach also involves ultraviolet absorbers (UVA’s), but
these are reacted with the resin during its synthesis. This approach reduces losses of UVA by volatilization or leaching (Nielsen and Wicks 1975).

Hon et al. (1985) reported that a clear coating containing a co-polymer of a UV absorber (HMHBTP: 2-hydroxy-4(3-methacryloxy-2-hydroxy-propoxy) benzophenone) and an acrylic binder performed better than a commercial phenolic varnish and polyurethane clear on southern pine (Pinus sp.). Scanning electron microscopy (SEM) revealed that after 1000 hours UV irradiation the wood beneath the coating containing the copolymer had “no noticeable surface deterioration.” The coated wood also retained its color and brightness much better than wood coated with the other coatings. Evans and Chowdhury (2010) synthesized a HEPBP (2-hydroxy-4-(2,3-epoxypropoxy) benzophenone)-phthalic anhydride copolymer (i.e. a polyester) in wood and found that it was able to photostabilize thin yellow cedar (Chamaecyparis nootkatensis (D. Don) Spach) wood veneers. Previously, Sundell and Sundholm (2004) had polymerized in bulk the components of a polyester with commercial benzotriazole UV absorbers (Tinuvin 320 and Tinuvin 213). Contrary to expectations they found that the “improved clear coating” on Scots pine (Pinus sylvestris L.) panels yellowed more than the regular clear coating after 30 days of artificial weathering (Sundell and Sundholm 2004).

2.3.1.2 Use of additives

2.3.1.2.1 Ultraviolet absorbers

Rothstein (1967) states that “ultraviolet absorbers (UVA’s) can inhibit photodegradation of coatings by absorbing UV radiation energy and dissipating the energy either by transferring it to its surroundings or by re-emitting it at longer wavelengths through phosphorescence, fluorescence, and heat.” For example, for an organic UVA such as 2,4-DHBP (2,4-dihydroxybenzophenone), Hon et al. (1985) states that the mechanism within the molecule responsible for UV protection “involves the formation of hydrogen bond between hydroxyl and carbonyl groups” leading to a “ketone-enol tautomerism” that provides a “facile pathway for dissipation of absorbed energy” (Fig. 2.22).
One important property of UV stabilizers is that they should contribute as little color as possible to the clear coating (Rothstein 1967). Kiefer (1967) notes that besides absorbing UV, some organic UVA’s will also absorb a portion of the visible spectrum in the blue-violet range, imparting a yellow color to the clear coating. This is not a problem for varnishes, “which tend to have a slightly yellow cast”, however inorganic UVA’s, such as nickel chelates may produce an undesirable intense green color (Kiefer 1967). The absorption curves of some important commercial organic UVA’s used for improving clear coating performance on wood are shown below (Fig. 2.23).

Mixed outcomes were reported in early work on the use of UVA’s to improve clear coating performance on wood. Estrada (1958) observed improved durability of clear coated panels when solvent and water-borne coatings contained 0.5% UVA (benzophenone type) and 1.25% UVA (benzophenone type) respectively. Conversely, Harris et al. (1964) and Ashton (1967) reported that a UVA (No. 9) at
0.5% concentration was ineffective at slowing exterior degradation of clear coatings on wooden panels. They also noted that increasing the UVA concentration to 10% would double the cost of the coating. However, for epoxy catalyzed systems, a coating containing 10% of the UVA Univel 400 (phenylmethanone type) gave the best results in an exterior weathering trial, although the system was still less durable than most of the better performing urethane systems, which lacked UVA’s (Estrada 1967).

Because of these discrepancies, the performance of UV absorbers in clear coatings for wood, but applied to plastic panels, was evaluated by Rothstein (1967). He noted that the performance of an alkyd varnish was enhanced more by the addition of UVA’s at 3% concentration than either an oil modified polyurethane or a tung-oil phenolic spar varnish. For example, after artificial light exposure, yellowing and surface degradation of the alkyd varnish containing 2(2’-hydroxy-3’,5’-di-tert-butylphenyl)benzotriazole was not observed (Rothstein 1967). Kiefer (1967) tested 11 different UVA’s at concentrations ranging from 3 to 7% on maple (Acer saccharum Marsh.) panels. He tested the same three types of clear coatings that were evaluated by Rothstein (1967), but the coating’s durability was assessed on their ability to retain gloss (60º) after two years exposure in Miami, Florida. The coating containing benzophenone type UVA’s performed the best and had outstanding gloss retention when they contained 2-8% of UVA. Both Rothstein (1967) and Kiefer (1967) found that substituted acrylonitriles did not perform well in exterior clear coatings. Hence, they concluded that the performance of a specific UVA is influenced by the type of varnish that it is mixed with, but the presence of UVA’s in the films improves the durability of wood-coating systems (Kiefer 1967, Rothstein 1967).

Adding to the above complexity are the results of Ashton (1973). He studied the effect of Cyasorb UV24 (2-hydroxy-4-methoxyphenyl)-(2-hydroxyphenyl) methanone in various clear coating systems on western red cedar by rating the durability (fail = 1 to very good = 10) of the coating after 4 years exposure in Ottawa. The UVA at a concentration of 7.5% slightly increased the durability of 3 coats of phenolic varnish (3.5) compared to the control (2), while fair durability of alkyds (4.75) was observed when they contained 5% UVA. However, the best durability was obtained with a phenolic-alkyd combination containing 5% UVA (Table 2.4). The control almost completely failed (0.5) after 4 years exposure.
Table 2.4: The effect of adding a UV absorber on the durability of phenolic-alkyd clear coating combinations exposed to four years outdoors in Ottawa, Canada (Ashton 1973)

<table>
<thead>
<tr>
<th>Combination</th>
<th>Type</th>
<th>No. of coats</th>
<th>UV absorber (%)</th>
<th>Avg. rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenolic</td>
<td>2</td>
<td>0</td>
<td>2.75</td>
</tr>
<tr>
<td>1</td>
<td>Alkyd</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Phenolic</td>
<td>2</td>
<td>5</td>
<td>6.25</td>
</tr>
<tr>
<td>2</td>
<td>Alkyd</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
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Note: See Fig. 2.21 for explanation on ratings

Recently, the effect of adding organic UVA’s on the performance of clear coatings on wood has been reported by Chou et al. (2008). They observed that 2% Tinuvin-1130 (hydroxyphenyl benzotriazole UVA) reduced the photoyellowing of an aromatic polyurethane when coated Chinese Fir (Cunninghamia lanceolata (Lamb.) Hook) panels were exposed to artificial accelerated weathering for 24 days. Additionally, Aloui et al. (2007) reported that organic UV absorbers in clear coatings provided better color stabilization for a range of hardwoods than inorganic absorbers (Fe₂O₃), which also act as reflectors by scattering UV light. Conversely, Forsthuber and Grüll (2010) reported that inorganic (TiO₂) were better than organic UVA’s at restricting color changes in Norway spruce (Picea abies (L.) H. Karst), but the panels had a “hazy appearance”. Furthermore, inorganic UV absorbers (CeO₂ and TiO₂ pastes) were found to reduce the flexibility of clear films and, hence, coatings containing the inorganic UVA’s cracked on grand fir (Abies grandis Douglas ex. D. Don.) Lindl) and European oak (Quercus sp.) panels exposed to artificial accelerated weathering (Aloui 2006). A two part urethane modified with an extender type inorganic UV absorbers (pulverized fuel ash [PFA]) on European beech (Fagus sylvatica L.) rated well after 6 years exposure in the UK. The PFA and urethane combination produced “a stronger less extensible film” that failed during exposure by first losing its gloss (chalking) and then through the usual mechanism of cracking and delamination of the film. Inorganic UV absorbers can offer improved protection in the UV range when added to clear coatings, but they reduce the transparency of the coating (Boxall et al. 1984). The translucency of inorganic absorbers has been improved by reducing their size to 2-50 nm in diameter (nano-sized additives) since shorter wavelengths of light are more efficiently scattered by smaller particles (Allen et al. 2002). For example, adding 5% nano-rutile (i.e. a TiO₂ polymorph) to
acrylic clear coatings was as effective as a 5% organic UVA in restricting color changes of coated pine exposed to 160 hours of artificial weathering (Allen et al. 2002). Similar color stability was obtained by adding nanoparticles of ZnO and TiO₂ to clear acrylic emulsions applied to black spruce (Cristea et al. 2010). Various researchers have also reported improvements in the photostability of wood pre-treated with reflectors such as micronized TiO₂ (Blackburn et al. 1991) as well as iron oxide and cerium oxide nanoparticles (George et al. 2005, Liu et al. 2010). The improvements in photostability obtained by adding inorganic nanoparticles to clear coatings on wood contrast with some earlier finding which discounted the use of colloidal iron oxide for clear coatings on wood because of “considerable darkening” of redwood panels upon exterior exposure (Estrada 1958, 1967).

2.3.1.2 Hindered amine light stabilizers

The photooxidation of clear coatings exposed to sunlight can be reduced by adding compounds that scavenge free radicals. The most common of these additives are the hindered amine light stabilizers (HALS) (Pospíšil and Nešpurek 2000). The invention and development of HALS was “a breakthrough in polymer stabilization” according to Pospíšil and Nešpurek (2000). The HALS that are now in commercial use invariably contain a 4-substituted 2,2,6,6-tetramethylpiperidine group (Fig. 2.24, top left). The mode of action of HALS is complex and “based on chemical transformations of HALS with oxidizing species arising in a photooxidized polymer matrix and identification of nitroxide (NO‘), the key free-radical intermediate accounting for photoantioxidant performance” (Pospíšil and Nešpurek 2000). The Denisov cycle describes how HALS are “transformed into stable nitroxide radicals in the presence of atmospheric oxygen by high energy radiation” and are “capable of trapping the radicals which destroy the film and inactivate them by later combining them with other radicals” (Goldshmidt and Streitberger 2007, Schaller and Rogez 2007).
HALS do not absorb UV radiation themselves (NO\' excited states do), but they may protect the UVA’s in coatings and polymers against free radical attack. Thus they perform better (synergistically) in combination with UVA’s (Pospíšil and Nešpurek 2000, Rogez 2001). For example, an acrylic clear coating on maritime pine (*Pinus pinaster* Ait.) that contained a HALS performed better than the same coating containing an organic UVA when samples were exposed to artificial and natural weathering (Pereira and Eusébio 2006). However, the combination of UVA + HALS was better than either of the additives on their own at enhancing the durability of the coating (Pereira and Eusébio 2006). Recently, Forsthuber and Grüll (2010) confirmed that the combination of UVA’s and HALS was better at restricting the photodegradation of an acrylic clear coat on Norway spruce than a UVA on its own. Chang and Chou (2000) observed that a combination of an organic UVA + HALS reduced the color change of red oak (*Quercus rubra* L.) wood underneath a detached film of an aromatic acrylic-polyurethane by 70% and also that of panels underneath an aliphatic acrylic-polyurethane by 80% when panels were exposed to UV light. However, Allen *et al.* (2002) reported undesirable color changes during artificial weathering of Scots pine panels coated with a clear acrylic finish containing either an organic UVA or nano-rutile TiO\(_2\) with 1% HALS.
2.3.2 Interface stabilization

“...whatever we are going to do to the wood we have got to protect that surface and the breakdown of the surface...” J.F. Levy, 1980

Coatings can dimensionally stabilize the wood surface by excluding some water vapor (Fig. 2.25), but this does not greatly improve the clear coating’s performance (Ashton 1967, Borgin et al. 1975). A consensus has been reached that efforts to improve clear coating performance on wood must focus on photostabilizing the underlying wood surface (Black and Mraz 1974, Derbyshire and Miller 1981). Therefore, as pointed out by Evans (2008), “considerable research has been devoted to finding pre-treatments for wood that will provide a photostable interface prior to clear coating.”

A wide array of photoprotective treatments have been tested, but on a limited number of wood species. I review these treatments, but I focus on those that restrict the photodegradation of wood. I also omit treatments designed to protect wood from fungal decay which often alter the wood’s color (Estrada 1958). Evans (2008) points out that the “most effective photoprotective treatments photostabilize lignin”, and these are examined in greater detail. However, as pointed out by Evans (2008) “most of the pre-treatments designed to improve clear coating performance have not been commercialized.”

Figure 2.25 has been removed due to copyright restrictions. It was a graph detailing the water absorption variation with time for polyurethanes and a long oil alkyd brushed on tangential faces of Pinus sylvestris in Stellenbosch, South Africa. Original source: Borgin, K., Lowe, A. & Gate, P. A., 1975. Evaluation of polyurethane systems as clear lacquers on four types of wood. Journal of the Oil and Colour Chemists’ Association, 58(4), 113-124.
2.3.2.1 Reactive inorganic chemicals

Treatment of wood with reactive inorganic chemicals can increase the resistance of wood to degradation by UV irradiation, reduce surface swelling by water, increase water repellency and improve the durability of clear coatings (Black and Mraz 1974). Black and Mraz (1974) found that the most effective inorganic chemicals at stabilizing the wood interface were: copper chromate, ammonium chromate, acid and ammoniacal copper chromate, ammoniacal copper chromate arsenate, cupriethylene diamine, copper and iron molybdate and copper ferricyanide.

One of the aims of the work by Black and Mraz (1974) was to produce a stable clear coating-wood interface which could increase the durability of the clear coat so that it gave 5 years maintenance free performance outdoors. They tested a polyurethane varnish, an acrylate and a UV transparent silicone resin on western red cedar and redwood that had been brush-treated with aqueous solutions containing a range of reactive inorganic compounds (above). They found that the silicone coating applied over the copper chromate treatment showed no major change in appearance on either of the species tested. The polyurethane did best on western red cedar, but failed after 5 years, and the acrylate performed the worst, usually failing at 3-4 years. The copper chromate treatment improved the performance of the above three coating types more so than a water-repellent preservative doped with an organic UVA (dibenzoyl resorcinol) or a phenol-resin pretreatment (Black and Mraz 1974).

Black and Mraz (1974) found that among the inorganic treatments listed above, ammonium chromate was one of the few that “markedly improved the performance of the acrylic coating as well as the silicone coating.” The improvement in the performance of the UV transparent silicone (retention of flexibility, absence of checking or embrittlement of the film) on treated wood was attributed to a photostable wood surface (Black and Mraz 1974). Preston and Chittenden (1978) confirmed the improved weathering performance of a clear acrylic on both acid copper chromate-treated and ammoniacal copper chromate-treated radiata pine. Subsequently, chromium compounds received much attention as primers to improve the performance of clear coatings on wood (Feist 1979, Williams and Feist 1988).

A disadvantage of all the brush on applications of inorganic solutions was the marked color change of treated surfaces (Black and Mraz 1974). For example copper chromate-treated western red
cedar, changed color, from an initial mottled yellow-brown or orange brown or yellow-green, to a brown cast or greenish tan after 36 months of exterior exposure. Such color changes are not liked by all end-users (Dickinson 1971), but the green color does indicate that toxic chromium VI has been reduced to the less toxic chromium III (chromous oxide) (Black and Mraz 1974). Under clear films, copper-chromate treated surfaces are brown to black, which indicates the reduction of hexavalent chromium to the less harmful chromium III compound, chromium dioxide (Black and Mraz 1974).

Feist and Ellis (1978) recommended the use of chromium trioxide, instead of copper chromate, as surface photoprotective treatments for wood because it ‘fixed’ more rapidly. Such fixation could be accelerated by heating the wood surface for 10 minutes at 135°C, thus ensuring that hexavalent chromium could not be leached by water (Feist and Ellis 1978, Williams and Feist 1984). Feist (1979) reported that the performance of clear finishes on chromic acid modified surfaces was directly related to Cr (VI) concentration, the chromium valence state which is reported as toxic, carcinogenic and mutagenic (Sax 1975). This led Williams and Feist (1985) to examine the use of chromium nitrate, where chromium is present as Cr (III). The performance of a polyurethane clear coating on chromium nitrate modified surfaces of western red cedar siding was inferior to that of the same coating on chromic acid treated surfaces (Williams and Feist 1988). However, a silicone clear coating performed “exceptionally” well on chromic acid and chromic nitrate treated surfaces of western red cedar and Douglas fir (Pseudotsuga menziesii (Mirb.) Franco) after 30 months of outdoor exposure (Williams and Feist 1988).

As an alternative to Cr there was interest in the use of iron (III) compounds as photoprotective treatments for wood (Pandey and Pitman 2002). Chang et al. (1982) observed that ferric chloride protected pine surfaces to the same extent as chromic acid. However, their samples were only exposed to UV light (without water spray). Evans and Schmalzl (1989) reported that treating radiata pine veneers with the iron (III) compounds, ferric chloride and ferric nitrate, resulted in significant losses of tensile strength before weathering. Even greater strength losses occurred when the treated veneers were exposed outdoors. This finding confirmed the important role of water in the degradation of wood (Evans and Banks 1988). Further studies by the same authors led them to hypothesize that enhanced UV stability of chromium trioxide treated wood was due to the formation of photostable lignin-chromium complexes.
(Evans and Schmalzl 1989, Evans et al. 1992). Hon and Chang (1985) had reasoned that such complexes were able to reduce the formation of peroxide radicals and thus limit photodegradation. However, Schmalzl et al. (2003) argued that chromic acid oxidizes lignin phenols and that the weather stability of chromium (VI) treated wood was due to the formation of chromium (III) quinone complexes (i.e. antioxidants and UV protectants). Today, chromium is still used in some wood preservatives, for example chromated copper arsenate (CCA) and copper chrome borate (CCB), and clear finishes perform better on wood that has been treated with these preservatives than on untreated wood (Feist and Ross 1995, Yalinkılıç et al. 1999).

Concerns about the unappealing green color of “chromium” treated surfaces and the toxicity of Cr (VI) led researchers to see if other less toxic inorganic compounds could provide the same level of photoprotection as chromium trioxide without changing the wood’s color. Schmalzl and Evans (2003) identified some promising titanium, zirconium and manganese compounds which were able to restrict tensile strength losses and mass losses of radiata pine veneers exposed to the weather. These compounds, however, were unable to photostabilize lignin. In contrast, potassium permanganate and manganic acetate were more effective than chromium trioxide at restricting tensile strength losses. However, these manganese compounds also discolor the surface. Titanium and zirconium compounds tended to whiten wood surfaces. Some of the titanium and zirconium compounds (as primers) were able to improve the durability of clear coatings on radiata pine, but they were much less effective than chromium trioxide (Schmalzl and Evans 2003).

2.3.2.2 Water repellents

Water repellents are generally transparent, but they do not form a film and their mode of action is different from that of clear coatings. Banks and Voulgaridis (1980) noted that water repellents are applied to wood by immersion or vacuum processes and that they coat the external and to some extent the internal pore surfaces in wood with hydrophobic films. Such films are formed following evaporation of the carrier solvent (Banks and Voulgaridis 1980). Water repellents reduce the rate, but not the magnitude of water absorption (Banks and Voulgaridis 1980). Water repellents do not significantly affect the rate at
which wood loses surface fibers during weathering and their component are leached from treated surfaces by rain. Hence, they require constant maintenance to maintain their protective effects on wood exposed outdoors (Black and Mraz 1974, Banks and Voulgaridis 1980). Because of the improved dimensional stability that water repellents impart to wood, there has been some interest in their use as primers to improve the performance of opaque coatings (Borgin 1961, F.P.R.L. 1970, Banks and Voulgaridis 1980, Feist 1990) and to a lesser extent clear coatings (Black and Mraz 1974).

2.3.2.3 UV stabilizers as primers

Recently, brush applications of transparent solutions containing low concentrations of HALS have been used to photostabilize wood surfaces prior to application of clear coatings (Hayoz et al. 2003, Schaller and Rogez 2007, Forsthuber and Grüll 2010). Such ‘wood pre-treatments’ enhanced the performance of clear coatings (3 coats) containing a UV absorber and HALS. These clear coating systems were able to restrict color changes of various woods exposed to either artificial (Hayoz et al. 2003) or artificial or natural weathering (Schaller and Rogez 2007).

A noteworthy study by Chang and coworkers (1998) tried to stabilize the valuable red color of the heartwood of Taiwania (*Taiwania cryptomeriodes* Hay.) using a primer containing UVA/HALS and clear coating formulations doped with photostabilizers. The system reduced discoloration of wood exposed to a short period of accelerated weathering. The best system consisted of a pretreatment containing UVA/HALS and polyethylene glycol (PEG) and a clear coating containing a UVA.

2.3.2.4 Polyethylene glycol as primer

Hon *et al.* (1985) observed that the copolymer of an acrylic clear coating-HMHBP (UVA) applied on pine wood surfaces pretreated with polyethylene glycol (PEG-400) exhibited excellent photostability. Kiguchi *et al.* (1997) reported that a pre-treatment of Douglas fir plywood with a 10% solution of PEG prevented film failure of clear finishes when the coated composite was exposed outdoors for two years. Chang *et al.* (1998) pretreated the red heartwood of Taiwania with PEG (30%) and found that PEG was able to reduce discoloration of clear coated (polyurethane + UVA) wood to the same extent as a solution of UVA + HALS. However, the authors reported the brightness of the heartwood beneath
the PEG/clear coating was increased. They attributed this increase in brightness to the photodegradation of PEG and the production of hydroperoxides which bleached the heartwood (Chang et al. 1998). Ohkoshi (2002) observed that PEG-4000 did not restrict color changes in four Japanese wood species exposed to UV radiation, but it did decrease the rate of photodegradation of lignin. However, the PEG molecule was degraded by light, and hence Ohkoshi (2002) suggested that this might limit its effectiveness in the long term. Because PEG affords some dimensional stability to wood and it is compatible with clear coatings, research has focused on the modification of this molecule and its grafting to wood as means of enhancing the photostability of wood surfaces (Grelier et al. 1997, Grelier et al. 2007).

2.3.2.5 Grafting

The observation that chromium trioxide bonded to wood, restricted the degradation of lignin, and enhanced the performance of clear coatings led Williams (1983) to investigate chemically bonding (grafting) organic UV stabilizers to wood as a pretreatment for clear coatings. UV absorbers require: (i) proximity to the wood to achieve energy transfers and; (ii) permanence at the interface to avoid leaching (Williams 1983). Successful grafting required a molecule that could react with the hydroxyl groups in wood and also contain a UV stabilizing group. Thus Williams (1983) tested 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone (HEPB) (Fig. 2.26). Williams (1983) synthesized HEPBP and impregnated 2% HEPBP, in the presence of an amine catalyst, into thin western red cedar panels. These panels were coated with a commercial spar varnish or a clear polyurethane, and exposed to 2400 h of accelerated weathering. Grafting also improved the color retention of the clear coated specimens during accelerated weathering and reduced damage to the clear coating (Williams 1983).

Later, Kiguchi and Evans (1998) and Kiguchi et al. (2001) built on the work of Williams (1983). Sugi specimens grafted with HEPBP (1.5% and 5.6%) and coated with a silicone-urethane clear varnish showed reduced film failure during accelerated weathering when compared to untreated clear coated controls (Kiguchi and Evans 1998). Kiguchi and Evans (1998) observed that the ability of grafting to enhance clear coating performance was influenced by the type of clear coating, because a silicone-
urethane on grafted wood outperformed a polybutadiene clear varnish during an artificial weathering trial. Subsequently, Kiguchi et al. (2001) observed the opposite during a natural weathering trial as the percentage film failure of the polybutadiene varnish on HEPBP grafted wood was lower than that of the silicone-urethane varnish on grafted wood. These findings indicate that the effectiveness of grafting as a pre-treatment beneath clear coatings should ultimately be evaluated using natural weathering trials.

Figure 2.26 has been removed due to copyright restrictions. It was a diagram of the synthesis of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPB) and its grafting on wood. Original source: Kiguchi, M., Evans, P. D., Ekstedt, J., Williams, R. S. & Kataoka, Y., 2001. Improvement of the durability of clear coatings by grafting UV-absorbers on to wood. Surface Coatings International Part B: Coatings Transactions, 84(4), 263-270.

Grelier et al. 1997 used a different approach to grafting UV stabilizers to that used by Williams (1983) and Kiguchi and co-workers (1998, 2001). They grafted a UVA containing an isocyanate group to fir and European oak. Grafting was accelerated by microwaves and the UVA was combined with antioxidants. The best treatments at restricting color changes of fir exposed to UV-Vis light were UVA/PEG and UVA/HALS, while the UVA and UVA/PEG treatments were the best at stabilizing the color of oak. Grelier et al. (2007) impregnated Scots pine wood with an aqueous solution of POLN3 (poly[styrene-co-PEG maleate-co-acyl azidure]) and HPBTN3 (hydroxyl-phenyl-benzotriazole) and then grafted both molecules to the wood using microwaves. The treatment improved the wood’s color stability during exposure to UV-Vis light and the adhesion of an acrylic clear coating on Scots pine samples exposed to accelerated weathering. Impregnation of wood with these compounds, however, limited coating penetration, and thicker top coats were observed on grafted wood coated with both water-borne and solvent-born acrylic clear coats. The ability of PEG to act as a radical scavenger protecting the phenol
function of the UVA, was thought to explain the improved photostability of the interface (Grelier et al. 1997, Grelier et al. 2007).

2.3.2.6 Others

Experiments conducted by Tarkow et al. (1966) with phenol resin add weight to the evidence that clear coating performance can be enhance by photostabilizing the wood-clear coat interface. Tarkow et al. (1966) treated two pines and redwood by diffusion and impregnation with phenol resin. The resin was then cured and two clear coatings, an oil-modified polyurethane and a UV transparent acrylic, were applied to the treated wood samples. The UV transparent acrylic performed better than the polyurethane over phenol treated wood; the former retained its gloss and no checking was observed in the finish or wood after 8 weeks of artificial weathering. The authors suggested that it was unlikely that improvements in weathering performance of phenol treated wood were due to dimensional stabilization alone, because of the very low level of penetration of the resin solution into the wood’s microstructure. Tarkow et al. (1966) suggested that the stabilization of the interface was due to phenolic resin acting as a “massive” UV absorber. However, the brown discoloration of phenol treated surfaces has discouraged its use beneath clear coatings. Impregnation of wood with melamine or dimethylol resins can also improve the performance of clear coatings, but since these resins have limited ability to photostabilize wood, any improvements in coating performance are likely to be due to the increased dimensional stability of the treated wood substrate (Rapp and Peek 1999, Xie et al. 2005, 2006, 2008).

Hill (2006) reported that acetylation as a wood modification provides a limited degree of UV stabilization to the wood surface. The bulking effects of acetylation in wood cell walls provide good dimensional stability (Spalt 1958, Hill 2006). Plackett et al. (1992) and Dunningham et al. (1992) observed that acetylation reduced the checking of uncoated wood during natural and artificial weathering trials and it also reduced the color changes of clear coated wood during artificial weathering. Acetylation reduced the surface erosion and checking of radiata pine finished with a semi-transparent alkyd stain and exposed to artificial weathering for 3000 h (Plackett et al. 1992). However, Beckers et al. (1998)
observed that an acrylic stain on acetylated Scots pine performed worst (lost adhesion) than the untreated finished control during 12 weeks of accelerated weathering.

Dawson et al. (2008a, 2008b) used an unconventional approach to stabilizing the interface and improving clear coating performance on radiata pine. The rationale behind their approach was that a delignified wood surface would be less susceptible to photodegradation. They delignified surfaces by exposing them to 450 h of artificial weathering or by reacting them with peracetic acid. The former pre-treatment delignified wood to a depth of 100 μm, while the latter modified the wood to a depth of 2-3 mm from the surface. The color of peracetic acid-treated boards coated with clear polyurethane was similar to that of unexposed specimens after 3000 hours of artificial weathering (Dawson et al. 2008b). Interestingly, the yellowness component (b*) measured on the latter specimens declined during artificial weathering, while in untreated specimens it increased due to photodegradation of lignin. The polyurethane clear coating performed better than an acrylic clear coating over peracetic acid and preweathering pre-treatments after a 3 year outdoor weathering trial in Rotorua, New Zealand. However, both pretreatments weakened the surface and promoted the checking of boards which prevented the further development of this novel approach to improving the performance of clear coatings on wood (Dawson et al. 2008b).

Other pretreatments that stabilize wood surfaces and could presumably improve clear coating performance are: benzyol chloride (Evans et al. 2002, Pandey and Chandrashekar 2006), vinyl benzoate (Jebrane et al. 2009) and phenol-formaldehyde resins (Stamm and Seborg 1936, 1939, Sudiyani et al. 1999, de la Caba et al. 2007; building on the work of Tarkow et al. (1966)).
2.3.3 Increasing clear coating penetration and adhesion

Wood clear-coating systems are often ranked on their ability to restrict changes in the color of wood. A decrease in color change is equated with reduced photodegradation of lignocelluloses (Hon 2001), and hence performance improvement. Less consideration has been given to the influence of different pre-treatments and clear coatings on penetration and adhesion of coatings (Black and Mraz 1974, Grelier et al. 1997, Dawson et al. 2008b). Photodegradation of wood occurs to depths of up to 500 µm but degradation by UV light is mainly restricted to depths of 100 µm or less, as mentioned above (Section 2.2.1). Hence, there could be benefits as hypothesized in Chapter 1 on creating a deeper more stable interface between clear coats and wood (Schneider and Côté 1967).

2.3.3.1 Coating adhesion

Wood adhesion theories have been developed for adhesives in cases where wood surfaces are brought together to form a “true contact area” generally under heat and pressure. Thus their applicability to coatings may be limited (Marian and Stumbo 1962, Paul 1982). Paul (1982) suggested that coating adhesion depended on adsorption phenomena followed by mechanical interlocking. Hence, the properties of the clear coating and its ability to interact with the substrate via secondary forces (van der Waals, hydrogen bonds, etc.) are theorized to dominate the film’s adhesion to wood (Paul 1982, Pizzi 1992, Rijckaert et al. 2001b). According to the mechanical interlocking theory, the “macroscopic substrate roughness provides a mechanical locking of the deposited film and a larger surface area for bonding” (Paul 1982).

Marian and Stumbo (1962) tried to separate the relative contributions of mechanical and specific (physico-chemical) factors in wood adhesion with double shear tests on Scots pine. They treated wood blocks with silane to render them hydrophobic and glued them together; a set of untreated wood blocks were also glued together. The shear strength of silane-treated samples was 10-20% of that of untreated samples, suggesting that “mechanical adhesion contributes very little to total adhesion” (Marian and Stumbo 1962). However, the study of clear coating performance on wood suggests a higher contribution of mechanical interlocking to adhesion (Vasishth et al. 1974). In the extensive durability tests of clear
coatings on wood reported by Harris et al. (1964) and Ashton (1967), they observed that low viscosity phenolic varnishes were superior to other formulations. They hypothesized that this was “due to the ability of lower molecular weight materials to penetrate and reinforce the top layer of wood.” Such reinforcement was also reported by Miniutti (1967) from microscopic observations of a transparent silicone coating on wood after prolonged UV irradiation. Miniutti (1967) reported that the silicone maintained its original position on wood by means of resin fingers that penetrated into the wood substrate. When the film detached, these fingers pulled free from the surface lumens looking “curly and twisted with fragments of cell wall”. This brittle failure of the walls led Miniutti (1967) to observe that the coating was relying on mechanical adhesion to perform adequately on wood. Furthermore, studies that have measured coating adhesion on wood have recorded lower percentages of adhesion failure at the fracture zone, suggesting the important role of mechanical anchoring (Boxall et al. 1984, Williams et al. 1987, Williams et al. 1990).

2.3.3.2 Coating penetration

"Penetration" refers to wetting conditions that occur when a liquid works its way up along the walls of a solid capillary. "Spreading" refers to wetting conditions involved when a liquid flows out over a surface (Collet 1972). Hence, wetting of the wood surface is a pre-condition for penetration and spreading. Furthermore, a high surface energy is a pre-condition for good wetting and optimal coating application (Nussbaum 1995). However, in unmodified fresh surfaces, wetting is not a limiting factor since the surface energy of coatings tends to be lower than that of wood (Nussbaum 1995, de Meijer 2004).

Mechanical interlocking between coating and wood depends on penetration of the coating into the porous wood substrate (Miniutti 1967, Vasishth et al. 1974). Schneider (1972) pointed out the importance of first (µm) and second (nm) order levels of wood porosity to achieve contact between coatings and the wood’s microstructure. The first level of porosity consists of pathways for coatings to flow into wood (Schneider 1972, de Meijer et al. 1998). These pathways in softwoods are (as illustrated in Fig. 2.27): (i) Open ends of longitudinal tracheids, (ii) Open ends of ray parenchyma and ray tracheids,
and (iii) Pits from ray parenchyma to longitudinal tracheids in latewood (de Meijer et al. 1998). The relative importance of each pathway depends on the angle made by a particular surface with the wood’s grain (Gray 1961, de Meijer et al. 1998). Thus, coatings penetrate transverse surfaces more than tangential or radial surfaces, i.e. axial penetration is greater than lateral penetration (de Meijer et al. 1998, 2001a).

First order porosity can be resolved using light microscopy, but more powerful imaging techniques have been used to visualize whether coatings can penetrate cell walls (van Loon 1966, Schneider and Côté 1967, Schneider 1979, Smulski and Côté 1984). Some authors maintain that such cell wall penetration and the creation of secondary molecular bonds between the coating and wood’s molecular constituents plays a vital role in increasing coating adhesion to wood (Paul 1982, Pizzi 1992). Wood-coating interactions via second order porosity are influenced to a large extent by coating formulation (Tarkow et al. 1966). Tarkow et al. (1966) reported that the effective sub-microscopic void size of cell wall’s capillary network in green Sitka spruce (Picea sitchensis (Bong.) Carriére) is similar to that of a PEG 3000 molecule (radius of gyration = 1.8 – 2.0 nm). Microscopically, pigments penetrate less than the solvent (van Loon 1966) because they block flow paths (Nussbaum 1994). Furthermore, most pigments in paints are too large to penetrate wood cell wall’s nano-capillary network (de Meijer et al. 2001a). Clear coatings have been reported to penetrate deeper into wood than paints (de Meijer et al. 1998).
Figure 2.27 has been removed due to copyright restrictions. It was a diagram of a radial cross-section of a tangential-coated softwood showing the different ways a coating can penetrate into a softwood: (1) Flow into open ends of longitudinal tracheids; (2) Flow into ray tracheids; (3) Flow into ray parenchyma; (4) Flow from ray parenchyma into longitudinal latewood tracheids; (5) Flow from ray tracheids into longitudinal tracheids. Original source: de Meijer, M., Thurich, K. & Militz, H., 1998. Comparative study on penetration characteristics of modern wood coatings. Wood Science and Technology, 32(5), 347-365.

2.3.3.3 Influence of coating penetration and adhesion on the performance of clear finishes

Several authors have stressed the primary role of the interface and depth of coating on the durability of wood-coating systems (van Loon 1966, Schneider and Côté 1967, Williams et al. 1987). The penetration of a primer into wood may improve water repellency and dimensional stability, which has beneficial effects on the durability of coatings (Smulski and Côté 1984). An increase in coating penetration could increase adhesion due to greater mechanical entanglement between the resin and deeper sub-surface layers of wood, in accord with the finding of Vasishth et al. (1974). Penetration of finishes is greater in earlywood than in latewood and, there is less failure of finishes on earlywood than on latewood (Williams and Feist 1994, Thay and Evans 1998, Rijckaert et al. 2001b). Nevertheless, the opposite occurred when wood was preweathered before finishing, because weathering increases coating penetration into latewood and degrades earlywood more than latewood (Williams et al. 1990, Williams and Feist 1994, Thay and Evans 1998). Ahola (1995) reported that pre-weathering increased the
penetration of a solvent-borne alkyd paint into wood, but there was no increase in coating adhesion. Evans et al. (1996) found that natural weathering decreased the adhesion of acrylic primers to preweathered wood samples more on radial surfaces than on tangential surfaces. They also reported that an oil modified acrylic paint penetrated weathered wood to a greater extent than standard acrylic paints and its adhesion to wood was better (Evans et al. 1996).

Therefore, the coating formulation influences its penetration and adhesion and possibly the durability of the coating/wood system (Nussbaum et al. 1998, de Meijer et al. 1998, 2001a, 2001b, Rijckaert et al. 2001a, 2001b, Van den Bulcke et al. 2008). Middleton (1993) suggested that “if the film composition remains constant throughout the entire level of penetration then its performance is dependent on its formulation, however, if preferential migration of certain components of the coating into specific parts of the film or wood substrate occurs then the relationship of the original coating (formulation) to performance is limited.” For example, studies have observed that water-borne coatings penetrate into earlywood more than they penetrate into latewood, while the opposite has been observed with solvent-borne coatings (although solvent-borne coatings penetrate wood more than water-borne coatings) (de Meijer et al. 1998, 2001a, 2001b, Rijckaert et al. 2001a, 2001b). Additionally, Nussbaum et al. (1998) reported that increases in coating penetration results in better surface dimensional stabilization with both solvent-borne and water-borne formulations. Rijckaert et al. (2001b) observed that deeper penetration in paints, which was not detrimental to adhesion, was achieved by lowering the pigment volume concentration, modifying the resin type (e.g. increasing oil length in alkyds), lowering the solids content and decreasing the viscosity. Rijckaert et al. (2001a) reported that the lateral penetration of clear stains, solvent-borne alkyds and water-borne acrylics into wood, is less than that observed with paints. Van den Bulcke et al. (2008) reported that solvent-borne coatings perform better than water-borne coatings and suggested a service-life-rank based on coating features such as: deeper penetration, higher adhesion, thicker coat, reduced color changes and high gloss retention.

Coating penetration into wood is irregular (Gray 1961, Schneider and Côté 1967, Schneider 1979, Nussbaum 1998) and the adhesion of the coating is further influenced by how the surface is prepared prior to finishing. Rougher surfaces provide reinforcement for the first coating layer (Gray 1961) and
absorb more coating (Williams and Feist 1994, Nussbaum et al. 1998) which can lead to improved performance of some coatings, for example, film forming stains (Feist 1990, de Meijer 2004). Van Loon (1966) reported that film durability was increased when the surface was both planed and sanded, because a thicker coating developed on such surfaces compared to ones that were only planed. Although coating penetration can be lower on sanded surfaces, sanding can improve the performance of stains and improve the adhesion of coatings to wood compared to planing (Richter et al. 1995, de Meijer et al. 1998, de Moura and Hernandez 2004). Sanding improves finish performance by roughening the surfaces and removing contaminants (Wolkenhauer et al. 2009). Plasma can also etch (i.e. roughen) wood surfaces and remove contaminants (Denes et al. 2005). Therefore, it is possible, as mentioned in Chapter 1, that plasma modification (as a surfacing technique) could enhance the performance of clear coatings on wood.

2.4 Plasma modification

Plasma modification of wood is a process, together with chemical and thermal treatments, that lies in the domain of wood modification (Hill 2006). Unlike modification techniques such as acetylation or heat treatment, however, plasma treatments for wood have not been commercialized. Nevertheless, this novel technology represents a contemporary approach to making improvements to wood, compared to conventional bulk processes that have been used in the past to enhance wood’s performance. Some of the commercial applications of plasma processing are in the semiconductor industry where it is being used to both clean and/or coat silicon wafers, and also in the plastics industry, where plasma is used to improve the finishing of otherwise hydrophobic plastic surfaces (Boenig 1982, Inagaki 1996).

2.4.1 Plasma types and effects

Plasma is known as the fourth state of matter and consists of a highly energetic gaseous mixture of atoms, molecules, ions, free electrons and metastable species (Boenig 1982, Inagaki 1996). Plasmas are widely known for their ability to etch polymers, and plasma etching is employed commercially by the semiconductor industry for cleaning silicon, as mentioned above (Flamm and Herb 1989, Inagaki 1996). Another use of plasma is to deposit a thin layer of material on a substrate, for example to coat silicon
wafers (Chapman 1980, Inagaki 1996). Plasmas may also be used to substitute atoms at the surface of polymers with ones particular to the excited mixture (Inagaki 1996). Such reactions functionalize the surface and, for example, facilitate finishing of plastics by making the surface more wettable (Inagaki 1996).

Plasmas used to modify wood have been obtained from organic or inorganic moieties. Plasma derived from organic gases or vapor makes wood surfaces hydrophobic (Denes and Young 1999, Podgorski et al. 2001, Bente et al. 2004). Conversely when inorganic gases are employed, the resulting plasma can increase the surface energy of wood and also gluing ability (Chen and Zavrin 1990, Sakata et al. 1993, Podgorski et al. 2000, Ramos 2001, Rehn and Viöl 2003, Mertens et al. 2006, Evans et al. 2007). The modification of wood by plasma, including plasma etching, has been reviewed by Chen (1989) and Denes et al. (2005).

2.4.2 Effects of plasma modification on wood structure and permeability

The degree of permeability of wood depends on the species and their anatomy (Liese and Bauch 1967a). Softwoods are mainly composed of longitudinal tracheids (95%), which are connected by bordered pits. Simple pits connect parenchyma cells while half-bordered pits permit passage of solutions between both cell types (Fig. 2.28). After air-drying, bordered pits may close or aspirate hindering the permeability of wood to liquid flow (Liese and Bauch 1967a).

Flynn (1995) reviewed the permeability, fluid flow and its relation to anatomy in spruce wood (Picea Dietr. A.). Unlike pine, spruce is classified as a refractory species, meaning that it is difficult to treat with liquids such as wood preservatives (Liese and Bauch 1967a). Flynn (1995) points out that the low permeability of a refractory wood species is due to many interrelated factors including: wood density, earlywood/latewood differences, heartwood formation and structure of rays, tracheids, resin ducts, bordered pits and cell walls. Flynn (1995) suggests that in spruce the presence of an abundance of aspirated pits, small ray size, and a high percentage of heartwood contribute to its refractory nature. Additionally, the permeability and fluid flow in spruce differs between the axial and lateral (radial and tangential) directions (Flynn 1995). Flow through bordered pits and rays constitute the main paths for the
lateral penetration of coatings into softwoods (de Meijer et al. 1998). The blocking of liquid flow due to pit aspiration is greater on radial than on tangential surfaces of softwoods (Wardrop and Davies 1961).

Liese and Bauch (1967a) reported that all of the earlywood bordered pits in Norway spruce and Scots pine were aspirated after air drying, compared to only 20-25% and 50% of the pits in the latewood of Norway spruce and Scots pine, respectively. Hence, penetration of fluids into dry softwood often occurs via latewood (Wardrop and Davies 1961, Liese and Bauch 1967a). Liese and Bauch (1967b) reported that “the main reason for the refractory behavior of spruce-wood is due to the structure of ray cells” and most of all the “presence and penetrability of ray tracheids”. In spruce, ray parenchyma cells connect with each other through small channels of a few microns in diameter with a separating membrane through which only very small plasmodesmata occur, according to Liese and Bauch (1967b). Additionally, ray tracheids above and below the parenchyma rows are “mostly not continuous”, and the radial penetration has been reported to end at the boundary of the annual ring (Liese and Bauch 1967b). The bordered pits in ray tracheids of spruce remain unaspirated even after air-drying (Liese and Bauch 1967b). However, the pit membranes of ray tracheid pits are invariably “always heavily incrusted” with extractives which would block the movement of liquids across the pits in the heartwood (Liese and Bauch 1967b).

The area of interconnections between ray tissue and longitudinal tracheids is termed a cross-field. The pits in the cross-field constitute an important flow path for coatings into wood (de Meijer et al. 1998). The small size of the elliptic piceid pits (ø 2-5 µm) in spruce is another feature responsible for the refractory nature of spruce (Fig. 2.28), especially compared to Scots pine which has large fenestriform pits (ø 10-25 µm).
Plasma treatment can etch and remove membranes from bordered pits and also enlarge pits (Chen and Zavrin 1990, Jamali and Evans 2011). Prolonged exposure to a glow discharge plasma treatment can also create voids in tracheid walls by etching pit borders and cell wall material in between the pits (Jamali and Evans 2011). The etching also opens up the rays as well as simple and half bordered pits (Fig. 2.29). Jamali and Evans (2011) reported that the etching of sub-surface layers of wood can occur when voids are created in the surface layer of wood cells. Plasma treatment appears to be capable of re-opening the main flow paths in wood (Jamali and Evans 2011) and, accordingly, previous research has shown that plasma treatments can improve wood’s permeability (Chen and Zavrin 1990, Ramos 2001).

**2.4.3 Effects of plasma on coating penetration and performance**

Chen and Zavrin (1990) reported that plasma treatment can increase the permeability of wood because it widened the “internal passages of wood.” The authors reported that plasma treatment is able to ablate material from the surface of tracheid walls and particularly from the bordered pits in two ways: (i) Physical sputtering and (ii) Chemical etching. Physical sputtering refers to “knocking-out fragments” of woody material, while chemical etching suggests the oxidation of wood by plasma. Chen and Zavrin (1990) also noted that the plasma may be formed both inside and outside of the wood’s microstructure.
Figure 2.29: Radial (a,b) and tangential (c,d) longitudinal surfaces of Californian redwood (*Sequoia sempervirens* (D. Don) Endl.) before and after plasma treatment: (a) Untreated earlywood showing bordered pits in tracheids, note intact pit membranes; (b) Earlywood tracheids after plasma treatment for 667s, note etching of bordered and half-bordered cross-field pit membranes (arrowed left of centre) and etching of the raised border of a bordered pit (arrowed top right); (c) Untreated earlywood showing uniseriate ray (centre) and bordered pits in tangential walls (arrowed left of centre); (d) Earlywood subjected to plasma treatment for 1,333 s, note thinning of ray parenchyma cells in a ray (centre), severe etching of cell walls (arrowed centre right) and contents of a longitudinal parenchyma cell remaining at the surface (arrowed far right) (c/o Arash Jamali)
Limited literature is available on the effect of plasma treatment on coating penetration and performance. Podgorski and Roux (1999) found no effects of plasma treatment on the adhesion (cross-hatch) of oil-borne alkyd and water-borne acrylic-alkyd systems to Scots pine wood samples that were subjected to six weeks of artificial weathering. Lukowsky and Hora (2002) plasma treated Scots pine before applying a water-borne or solvent-borne clear coating. Pull-off and cross-cut wet adhesion tests on the water-borne coating suggested that the plasma treatment improved adhesion to wood. Interestingly, the authors also reported on the feasibility of integrating a plasma treatment process into a production line and estimated the cost of treatment to be 0.3€ per window.

Blanchard et al. (2009) estimated the penetration of a UV-curable coating into plasma-treated sugar maple wood using confocal Raman spectroscopy. Coating penetration was deeper in samples treated with plasmas derived from inorganic gases. Penetration and coating adhesion were positively correlated with treatment time and power. These findings were explained by increased surface energies and chemical changes to wood as a result of plasma treatment.

2.5 Summary

This review has established the link between photodegradation of wood occurring under clear coatings with their underperformance (MacLeod et al. 1995, Sing and Dawson 2003). Loss of adhesion between the photodegraded wood and coating leads to film failure (Miniutti 1967). Moisture and micro-organisms also contribute to the failure of clear finishes (Ashton 1967, Dickinson 1971, Evans and Banks 1988).

Attempts to improve the performance of clear coatings have combined both UV-stabilization of the film formulation and that of the underlying wood. UV absorbers and hindered amine light stabilizers are commonly added to commercial clear-coatings systems, but the performance of the clear coatings containing these additives still do not match consumer expectations. The performance of clear coatings has been based on measurements of the clear coating’s ability to retain its original characteristics as well as prevent changes to the underlying wood during accelerated or natural weathering trials. Less
importance has been directed towards understanding the wood/coating interactions resulting from the use of wood pre-treatments or improved clear coatings (Grelier et al. 1997, Dawson et al. 2008)

Various authors have identified the integrity of the wood/coating interface as the key element determining the performance of clear coatings on wood (van Loon 1966, Schneider and Côté 1967, Schneider 1972, Smulski and Côté 1984, Williams et al. 1987). It has been suggested that coating adhesion, which has been linked by some authors to improved coating performance, could be improved by increasing coating penetration (Bravery and Miller 1980, Boxall et al. 1984, Williams et al. 1987, Williams et al. 1990, Evans et al. 1996, Bardage and Bjurman 1998). Coating penetration has been studied by several authors who have concluded that penetration depends on the wood’s anatomy and coating formulation and (obviously) the extent to which the coating flows into the wood’s porous microstructure (first order porosity) and then interacts with cell walls (second order porosity) (Schneider 1970, 1972, 1979, Smulski and Côté 1984, de Meijer et al. 1998, 2001b). Techniques that roughen wood surfaces are a simple and efficient means of increasing the adhesion and penetration of finishes into wood (Williams et al. 1994, de Moura and Hernández 2005).

Plasma etching is a novel technique that can roughen wood and increase its permeability (Chen and Zavrin 1990, Jamali and Evans 2011). This study aims to increase clear coating penetration and adhesion on wood as means of rendering a more stable wood/coating interface. Singh et al. (1998) noted improvements in coating penetration due to bacterial etching of bordered pit membranes. Plasma can also etch and open-up aspirated pits (Jamali and Evans 2011). Plasma treated wood is more permeable as a result of etching, which could also improve coating penetration and possibly performance, as hypothesized in Chapter 1.
3. Effect of plasma treatment of wood on clear coating penetration and adhesion

3.1 Introduction

Clear coatings perform badly on timber during exterior exposure due to photodegradation of wood beneath the coating and loss of interfacial adhesion between the coating and wood (MacLeod et al. 1995). UV radiation and the photoactive component of the visible spectrum (380 to 410 nm), penetrate and degrade wood to a depth of approximately 500 microns, depending on wood density (Kataoka et al. 2007). Normally coatings do not penetrate beyond this depth and hence their performance outdoors is badly affected by surface photodegradation of wood.

The performance of clear coatings might be increased, however, if they could penetrate into wood and bond with the subsurface layers that are less affected by light. The penetration of coatings into wood can be increased by treatments that increase the permeability of wood. For example, Singh et al. (1998) showed that storing wood in ponds, where wood is colonized by bacteria that destroy pit membranes (Dunleavy et al. 1973), significantly increased the penetration of coatings into radiata pine wood. Pit membranes in wood can also be degraded by plasma (Jamali and Evans 2011), and a previous study showed that the permeability of wood could be increased by plasma treatment (Chen and Zavarin 1990).

It is hypothesised here that plasma pre-treatment of wood will increase the penetration of clear finishes into wood and this might have beneficial effects on the adhesion of the coating. The aim of this Chapter is to test this hypothesis by examining clear coating penetration in wood samples treated for different periods of time with a glow-discharge plasma. A modified pull-off adhesion test was used to measure the adhesion of oil-borne and water-borne clear polyurethane coatings to plasma treated samples. Both light and scanning electron microscopy were used to examine clear coating penetration into plasma treated wood. Some of my results were published in the Proceedings of the 5th European Conference on Wood Modification, Riga, Latvia (Haase and Evans 2010, See Appendix 5).
3.2 Materials and methods

3.2.1 Experimental designs

Two designed experiments are described in this Chapter. The first experiment examined the effect of two fixed factors: (i) coating type (2 levels); and (ii) plasma treatment (5 levels), on the penetration of coating into black spruce wood. Four black spruce panels (blocks) were planed and cross-cut into two equally-sized samples. Each half from one panel (the sample) was randomly allocated to a coating type, either water or solvent borne polyurethane (whole plot). Each sample was further cross-cut to obtain five specimens (40 in total) and these were allocated at random to the different plasma treatments including the untreated control (split plot). The second experiment examined the effect of the same factors on the adhesion of the coatings to black spruce wood. In this case, 7 black spruce panels (blocks) were converted into samples and specimens, and allocated, as above, to the different experimental factors (70 specimens in total).

3.2.2 Wood samples and coatings

Air-dry, planed, quarter-sawn black spruce heartwood sample boards measuring 60 mm (width) x 25 mm (thickness) x 450-500 mm (length) were obtained from the Centre de recherche sur le bois at the Université Laval, Québec (Fig. 3.1a). Boards were conditioned at 20 ± 1°C and 65 ± 5% relative humidity prior to treatment for 15 days. The basic density of three black spruce specimens from each board was determined by the water displacement/oven-drying method as follows (Table 3.1). Smoothly cut wood cubes (10 x 10 x 10 mm) were vacuum-impregnated with distilled water for approximately two days. Distilled water was added to a beaker and the weight of the beaker was measured using an analytical balance. A metal dissecting needle was inserted in one of the ends of the cubes and the cube was carefully submerged in the water inside the beaker. The change in weight of the beaker was used to estimate the green volume of the block of wood. The wood cube was then dried at 105 ºC until it reached constant weight. The basic density of the cube was recorded as the oven dry mass of the wood block divided by its green volume (Walker 2006). The wood boards were viewed under a 10x magnifying lens and a scaled ruler was used to help count the number of rings per centimetre. Basic density measurements
were in the normal range (332 kg/m³ – 442 kg/m³) for black spruce reported by Risi and Zeller (1960); however, various factors (stand properties, genetics, etc.) have been shown to influence the basic density of black spruce wood (Hall 1960).

Figure 3.1: Cutting pattern used to convert boards into the samples and specimens that were allocated to experimental factors; (a) Board; (b) Samples; (c & d) Cross-cut samples and (c1-c5 & d1-d5) specimens

Table 3.1: Ring number and basic density of the different black spruce boards used in Chapter 3

<table>
<thead>
<tr>
<th>Board Number</th>
<th>No. of Growth rings/cm</th>
<th>Basic Density (kg/m³) ± Standard Deviation (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15-17</td>
<td>470.7 ± 13.3</td>
</tr>
<tr>
<td>2</td>
<td>25-28</td>
<td>494.4 ± 0.6</td>
</tr>
<tr>
<td>3</td>
<td>9-10</td>
<td>438.4 ± 2.0</td>
</tr>
<tr>
<td>4</td>
<td>22-24</td>
<td>505.5 ± 16.5</td>
</tr>
<tr>
<td>5</td>
<td>8-11</td>
<td>415.5 ± 1.8</td>
</tr>
<tr>
<td>6</td>
<td>11-20</td>
<td>453.0 ± 5.8</td>
</tr>
<tr>
<td>7</td>
<td>7-11</td>
<td>464.5 ± 6.9</td>
</tr>
</tbody>
</table>

For the first experiment, four boards were selected and one of their radial faces was planed using a Martin planer (T44/V4133680/5000 rpm) with 2 blades in the cutting head. One single face-planed piece measuring 18 x 6 x 450 mm (Fig. 3.1b) was cut from each board and cross-cut into two samples (Fig. 3.1c, 3.1d) using a band saw (Ryobi BS902). Five specimens 18 x 6 x 20 mm in size were cut from each sample half (Fig. 3.1c1-5, 3.1d1-5). For the adhesion experiment, 7 boards were selected and each of the sawn and planed samples measured 30 x 3 x 500 mm. Specimens for this experiment measured 30
x 3 x 30 mm. Two different types of clear coatings (Table 3.2) were purchased commercially from Home Depot in Richmond, British Columbia: (1) Oil-borne urethane; (2) Water-borne urethane (See Appendix 2 for each product’s Material Safety Data Sheet).

Table 3.2: General information on commercial clear coatings tested

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Solvent</th>
<th>Viscosity (Poise)(^a)</th>
<th>Solids content (%)(^b)</th>
<th>Recommended spread rate (m(^2)/L)</th>
<th>Recommended Number of coats</th>
<th>Experimental spread rate (m(^2)/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Minwax® Helmsman® Spar Urethane</td>
<td>White spirit</td>
<td>1.1</td>
<td>52.2</td>
<td>8-10</td>
<td>2-3</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Varathane® Diamond™ Spar Urethane</td>
<td>Water</td>
<td>0.7</td>
<td>28.1</td>
<td>9-10</td>
<td>4</td>
<td>36</td>
</tr>
</tbody>
</table>

\(^a\) ASTM D1200 Ford cup efflux, \(^b\) ASTM D1644 Non volatile content

3.2.3 Plasma treatment and coating application

Planed and conditioned specimens were cleaned with a jet of compressed air and then exposed to glow discharge plasma for 0.5, 3, 10 or 20 minutes in a plasma reactor as follows (Fig. 3.2). First the air filter valve in the reactor was opened to release any pressure inside the chamber. The top plate was raised and secured to allow access to the inside of the chamber using sterile tweezers. Specimens were held with sterile tweezers and were placed on top of a sample dish inside the chamber. The top plate was lowered and the air-filter valve was closed. The vacuum pump was turned on and the pressure inside the chamber was monitored until it reached 13.33 Pa. At this point the water flask valve was opened. The pressure inside the chamber was monitored again until it reached 19.99 Pa. Then the radiofrequency (RF) unit, which was set to deliver 150 watts/125 MHz during treatment, was turned on. A purple glow-discharge developed within the chamber. Once specimens were exposed to this plasma for the desired length of time, the RF generator was turned off, the vacuum valve and water valve closed and the pressure was gently released inside the chamber by opening the air-filter valve. The specimens were removed carefully from the inside of the chamber using sterile tweezers, and taking care to avoid contact with their upper modified surface. Specimens subjected to a vacuum (19.99 Pa) for 1 minute in the plasma reactor acted as a control.
In both experiments, the first coating layer was applied using a calibrated micropipette and a pre-soaked fine brush. The amount of coating applied was calculated to equal the sum of the number of coats recommended for these products, multiplied by the spread rate recommended for each coating (Table 3.2). The coated surfaces were air dried at 20 ± 1°C and 65 ± 5% RH for 20 days. For the first experiment a second identical coat to the first one was brushed on to the surface of the specimens after light sanding with P220 grit aluminum oxide abrasive sandpaper. The second coat was applied to prevent the coating from detaching during sectioning because preliminary experimentation showed that a single layer of coating often detached from the sample block when it was sectioned. The second layer was applied 10 days after the first layer to ensure the first coat had completely cured and hardened.

### 3.2.4 Coating penetration measurement

#### 3.2.4.1 Microscopy

A sliding-microtome (Spencer Lens Co. Buffalo, NY) and blade was used to cut transverse sections from plasma-treated coated specimens and controls, as follows. Specimens were secured with their transverse face uppermost in the sample holder of the sledge microtome (Fig. 3.3). A distilled water droplet (~ 0.08 ml) was placed on the transverse face and left to soak into the specimen for 5 minutes. A disposable microtome blade (Feather Type S35) secured in a blade holder was used to section the specimen perpendicular to the longitudinal axis of the specimen and at ~30° relative to the radial-longitudinal direction. Approximately one hundred and fifty 30 µm thick sections were cut from each specimen (Fig. 3.3a, 3.3b, 3.3c). After each section was cut, a droplet of water (~ 0.08 ml) was placed on the freshly exposed surface to facilitate further sectioning. Sections were stained (Fig. 3.3d) with 0.1% Sudan IV (in 80% ethanol) for 2 minutes to make it easier to see the coatings in cell lumens, as recommended by Singh and Dawson (2004).

Immediately after staining, sections were mounted in distilled water on a glass slide and examined under a 6.3X lens with a Zeiss microscope (Large Universal). Sections were mounted so that
the age of the growth ring increased from left to right: earlywood to latewood. Measurements of coating penetration were made in the center region of the clear coating/wood interface of each section.

Figure 3.2: Plasma reactor used to modify wood samples prior to clear coating: (a) Schematic diagram of the reactor and its different parts (c/o Anthony Hyde, The Australian National University); (b) Purple glow discharge plasma inside the reactor chamber (c/o Philip Evans, UBC)
The microscope was equipped with an Olympus DP71 digital camera that was used to record one representative digital photograph (JPG) of a complete growth ring from each specimen (Fig. 3.4). Images were 4080 x 3072 pixels in size and had a resolution of 432 dpi.

Figure 3.3: Method of cutting thin sections from plasma-treated coated specimens and controls: (a) Clear coated specimen (i) being rotated to secure it in the sample holder of the sliding microtome (ii) showing area discarded and arrow pointing (iii) at surface where sections were obtained; (b) Sliding microtome and blade used to section specimens, (i) blade holder, (ii) sample holder, arrow indicates direction of sectioning; (c) Close-up of a specimen being sectioned with arrow indicating clear-coated face and; (d) Staining of sections in Sudan IV (i), washing of sections in distilled water (ii) and final sections (iii) clearly showing the stained coating

In the following section, I describe the methodology and three different software packages that were used to quantify clear coating penetration from the surface into black spruce wood.
3.2.4.2 Software 1: image analysis

I used Definiens object-based software (Definiens GmbH, München, Germany, formerly known as eCognition) to differentiate cell lumina elements (5x5 pixel arrangements) on each selected image as either coated (red cells) or non-coated (empty cells) (Fig. 3.5). The software was able to differentiate coated and non-coated elements because they were different colors. The rule set in Table 3.3, or process used to solve a defined image analysis task, was based on previous applications of the software for remote sensing (Coggins 2011). I am not aware of any applications of the software to analyze images of wood microstructure.
Figure 3.5: (a) Light microscopy image of a clear coating penetrating into black spruce wood. Arrow indicates magnified section in (b) and (c); (b) Image combining multi-resolution segmentation and classification; (c) Multi-resolution segmentation and chessboard segmentation into 5 x 5 pixel elements. Both (b) and (c) are snapshots from the software Definiens

3.2.4.3 Software 2: baseline definition

Shapefiles from Definiens were loaded into the AutoCad (2007) drawing platform and overlaid with the original image (Fig. 3.6). Using the latter image the roughened upper surface was located and traced on the image as a sequence of short lines that together formed a poly-line. This poly-line was divided by a number of segments equalling the amount of visible open cell lumina on the drawn surface. The resulting line defined a series of points that represented the entry points for flow of coating into wood. These points together defined the baseline (depth = 0). Coordinates (x,y) of all points on the drawn surface (≈25 ± 6 points/image), red cells (≈9900 ± 7900 points/image) and empty cells (≈54700 ± 10500 points/image) on each image were obtained using the data extraction command, which permitted the generation of an Excel spreadsheet (*.xls).
Table 3.3: Rule set for separating coating filled lumina (red cells) area from non-filled lumina (empty cells) area

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Process Name</th>
<th>Definition</th>
<th>Parameters</th>
</tr>
</thead>
</table>
| 1        | Multiresolution segmentation | A basic procedure for largely knowledge free and unsupervised segmentation of homogeneous image object primitives at any chosen resolution. The technique was developed to work even on highly textured image data. For a given number of image objects, it minimizes the average heterogeneity and maximizes their respective homogeneity. (Figs. 3.2b & 3.2c) | Shape: 0.1 \( w_1 \)  
Color: 0.9 \( 1-w_1 \)  
Compactness: 0.2 \( w_2 \)  
Smoothness: 0.8 \( 1-w_2 \)  
Scale parameter: 100 |
| 2        | Classification | A procedure that associates image objects with an appropriate class. Through the process of classification, each image object is assigned to a certain (or no) class and thus connected with the class hierarchy. The result of the classification is a network of classified image objects with concrete attributes, concrete relations to each other and concrete relations to the classes in the class hierarchy (Fig. 3.2b) | Red cells and (min)  
Area < 14,000 Pixel  
Mean red > 70  
Ratio red > 0.4  
Roundness < 3.5  
Empty cells and (min)  
Area < 18,000 Pixel  
Brightness ≥ 90  
Mean green > 60  
Ratio red < 0.4  
Roundness < 3.5 |
| 3        | Chessboard segmentation | Chessboard segmentation is the simplest segmentation algorithm. It cuts the scene, or later the dedicated image objects, into equal squares of a given size (Fig. 3.2c). | 5 x 5 pixel element |
| 4        | Export | Creates files from the system to be used in other applications. | Exported center of elements as a point shapefile (*.shp). Red cells and empty cells separate. Undo classification process i.e. red cells and/or empty cells. |
| 5        | Undo | Goes back to a previous state in process editing | |

\(^1\text{Definiens Developer 7 User Guide Document Version 7.0.2.936}\)

3.2.4.4 Software 3: element to baseline measurements

Van Loon (1966) defined the depth of coating penetration as the shortest distance from the wood surface to the deepest point of penetration of the coating. Hence, depth of penetration was defined as the minimum Euclidean distance from the center point of a 5x5 pixel element to the closest point on the
surface. This iterative process was computed using a minimum distance routine written using Statistical Analysis Software (SAS: Valerie Lemay, Fall 2009) because of the large number of elements (> 50,000 points/image) to be referenced back to the surface points. The software generated a separate spreadsheet listing the (i) depth of penetration in pixels of (ii) an element filled/empty to the (iii) closest surface point.

![Image processing in the Autocad 2007 drawing platform. First the shapefile is loaded (a), the original image is overlaid (b), the roughened surface is drawn (c), and inspected for points outside the surface boundary (d).](image)

Depths of penetration in pixels were converted to microns and depth of penetration was calculated for successive 25 µm intervals from the surface: 0-25 µm, 25-50 µm, 50-75 µm, etc. Coating penetration (CP) was defined as the ratio of coated elements to the total elements for a given interval depth from the surface. For example, on a given image, for the first 25 µm from the surface there were 25 coated elements and 25 non coated elements classified (element = 5 x 5 pixel arrangement). Therefore the coating penetration was 50% (i.e. CP = 25/[25+25]).
### 3.2.5 Pull-off adhesion tests

In my second experiment, a modified pull-off test (ISO 4624) was used to measure the adhesion of the two coatings to plasma-treated specimens and controls. Using this test I assessed the breaking load (MPa) and nature of failure (cohesive, adhesive, etc.) when a test cylinder (ø 20 mm, Elcometer) was pulled-off coated samples (Fig. 3.7). Two drops of cyanoacrylate adhesive (Instant Krazy Glue Advanced Formula) was used to glue the test cylinder to the lightly sanded (P220 grit aluminum oxide abrasive sandpaper) coated sample. Each test specimen was glued using phenol resorcinol formaldehyde (PRF) adhesive (Arclin, 2.5/1 resin-to-hardener ratio) to a wooden Douglas fir base measuring 30 x 20 x 140 mm. Clamping (torque of 5 Nm) was used to help bond the test cylinder to the coated sample and the sample to the holder. The sample was tested in an Instron universal testing machine (model 4200, crosshead speed 1/2 mm/min).

The breaking load (MPa) required to pull the test cylinder from the sample was recorded. The test cylinders (and the holder/sample system to a lesser extent) were then examined to assess the percentage of cohesive failure of wood (wood present) or adhesive failure between the clear coating and the wood (clear coating present without wood). A transparent grid divided into 16 areas was overlaid on the test cylinder after the adhesion test (Fig. 3.7d). Type of failure was recorded as percentage of area on the test cylinder covered by either wood or coating. Other failure types (test cylinder/Krazy glue, Krazy glue/clear coating, specimen/PRF, PRF/wooden base) were not of experimental interest and hence are not reported (Bardaje and Bjurman 1998).
3.2.6 Statistical analyses

My experiments used factorial principles to assess the effect of coating type and plasma treatment on penetration of coating into samples (experiment 1) or the adhesion of coatings to samples (experiment 2). Random effects arise in both experiments due to variation in wood properties between boards and elapsed time between measurements. Analyses of variance (ANOVA) were performed to assess the effects of fixed (coating type and plasma level) and random factors on coating penetration and adhesion (Appendix 1). Statistical computation was performed using Genstat (v. 11.0). Before the final analysis, diagnostic checks were performed to verify if data conformed to the assumptions of ANOVA: (i) observations are independent, (ii) normal distribution of error terms around each treatment mean and (iii) the variances of the error terms around each treatment mean are homogeneous for all treatment means. In experiment 1 (coating penetration), ANOVA was performed only at three depth intervals: 0-25 µm, 25-50 µm and 50-75 µm. ANOVAS were not performed at further depth intervals ( > 75 µm) because many 0's
were present in the data. Before analysis of the adhesion tests, response variables such as breaking load and percentage of cohesive failure were transformed into variables that met the assumptions of ANOVA. The transformations used to meet the latter requirements were: (i) arcsin: $y' = 2 \sin^{-1} \sqrt{y}$ and (ii) natural logarithm: $y' = \ln(y)$. Significant results are presented in graphs, which include error bars (± 2 standard error or 95% confidence intervals) to estimate the significance of differences between individual means.

3.2.7 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to examine the etching of black spruce wood by plasma. Plasma modified and unmodified black spruce specimens measuring 5 x 5 x 5 mm were dried over silica granules for 24 h and attached to aluminum mounting stubs using double-sided adhesive tape, with the radial surface facing up. Afterwards, the specimens were coated with a layer of gold (8 nm) in a sputter coater (Nanotech SEMPrep II) and coated surfaces were examined using a Hitachi S-4700 field emission scanning electron microscope operating at 5.0 kV. Selected images of plasma modified and unmodified surfaces were recorded as TIFF files.

Scanning electron microscopy (SEM) was also used to examine the wood-clear coating interface and the penetration of clear coatings into radial surfaces of black spruce. A clear coating layer was brushed on to plasma modified (20 minutes) and unmodified radial surfaces of black spruce wood, as described above (Table 3.2). An ultraviolet (UV) laser was used to produce transverse sections measuring 4 x 10 x 15 mm as described by Wålinder et al. (2009). In this procedure, the “laser beam passes through a series of lenses and masks to create a suitable focal point where the specimen surface is placed with the help of a positioning device” (Wålinder et al. 2009). The UV laser ablates the surfaces and produces a clean section from the specimen. These sections were trimmed with a blade (Carbon Steel Injector Blade) to produce specimens measuring 5 x 5 x 5 mm. Sections were dried over silica granules for 24 h and then attached to aluminum mounting stubs using double-sided adhesive tape, with their transverse surfaces facing up. The specimens were sputter coated with a layer of gold and coated transverse surfaces were examined using a Cambridge Instruments S360 SEM operating at 5.0 kV. Selected images of plasma modified and unmodified clear coated surfaces were recorded as TIFF files.
3.3 Results

3.3.1 Clear coating penetration into the wood microstructure

Analysis of variance showed significant (p < 0.05) effects of plasma treatment on the ratio of coating to total lumen void space (Table 3.4). Amongst plasma treatment levels, significant differences were also observed on the latter response variable at each depth interval (Table 3.5).

Table 3.4: Statistical significance of coating effects (C), plasma treatment effects (P) and coating x plasma interactions (C x P) on lumen space filled with coating at different depth intervals (** p < 0.01, NS = Not significant / p > 0.05)

<table>
<thead>
<tr>
<th>Depth</th>
<th>Statistical significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth</td>
<td>Coating (C)</td>
</tr>
<tr>
<td>0-25 µm</td>
<td>NS</td>
</tr>
<tr>
<td>25-50 µm</td>
<td>NS</td>
</tr>
<tr>
<td>50-75 µm</td>
<td>NS</td>
</tr>
</tbody>
</table>

Table 3.5: Ratio of coating to total lumen void space at different depths for black spruce specimens treated with plasma for different times. Treatments sharing the same letter are not significantly (p > 0.05) different

<table>
<thead>
<tr>
<th>Depth</th>
<th>Lumen space filled with coating (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth</td>
<td>Plasma treatment time (min)</td>
</tr>
<tr>
<td>Depth</td>
<td>0</td>
</tr>
<tr>
<td>0-25 µm</td>
<td>0.492 a</td>
</tr>
<tr>
<td>25-50 µm</td>
<td>0.229 a</td>
</tr>
<tr>
<td>50-75 µm</td>
<td>0.160 a</td>
</tr>
</tbody>
</table>

The oil-borne clear coating penetrated untreated black spruce wood to a depth of ~300 µm (Figs. 3.8, 3.9). The penetration of the water-borne coating into untreated black spruce wood was approximately half that of the oil-borne coating (Fig. 3.10), although occasionally cells that contained water-borne coating material could be found much deeper in the wood. Both the oil and water-borne coatings filled approximately 55 percent of the void space at depths of up to 25 µm in untreated wood (Figs. 3.9, 3.10). Thereafter there was a drop in the percentage of void space filled with coating, which was more pronounced for wood coated with the water-borne coating (compare Fig. 3.9 with Fig. 3.10). Prolonged plasma treatment for 10 and 20 minutes increased the penetration of the oil-borne coating into wood to
500 µm, compared to 300 µm in the untreated control, although at a depth of 500 µm less than 10 percent of cell lumens were occupied by coating material (Fig. 3.8). Prolonged plasma treatment for 20 minutes also increased the penetration of the water-borne coating to 200 µm compared to 150 µm in the untreated control (Fig. 3.10). The observations on coating penetration for all of the different boards coated with the oil-borne polyurethane are detailed in Figure 3.11, while those coated with the water-borne polyurethane are shown in Figure 3.12.

![Figure 3.8: Effect of plasma treatment on the penetration of an oil-borne polyurethane clear coating into black spruce wood](image)

Prolonged plasma treatment for 20 minutes also significantly increased the percentage of void space occupied by coating material. Figure 3.13 compares the effects of the different plasma treatments on the percentage of lumen space occupied by coating material at depths of 0 to 25 µm, 25 to 50 µm and 50 to 75 µm. The results are the averages for both the oil-borne and water-borne coatings because analysis of variance revealed no significant (p > 0.05) interaction of coating type and treatment on the percentage of void space occupied by coating material. Plasma treatment for 0.5, 3, 10 and 20 minutes significantly (p < 0.05) increased the percentage of void space occupied by coating material in the zone immediately below the wood surface (from 0 to 25 µm). However, at depths of 25 to 50 µm and 50 to 75
µm only prolonged plasma treatment for 20 minutes significantly ($p < 0.05$) increased the percentage of void space occupied by coating material.

Figure 3.9: Effect of plasma treatment on the penetration of the oil-borne clear coating into the first 200 µm of black spruce wood

Figure 3.10: Effect of plasma treatment on the penetration of the water-borne polyurethane clear coating into the first 200 µm of black spruce wood
Figure 3.11: Effect of plasma treatment on the penetration of the oil-borne polyurethane clear coating to a depth of 500 µm in black spruce wood

The effects of prolonged plasma treatment on coating penetration are easily seen in light microscopy sections in Figs. 3.14 and 3.15. The penetration of the oil-borne clear coating into untreated black spruce wood and wood treated with plasma for 20 minutes are shown in Figure 3.14.
Figure 3.12: Effect of plasma treatment on the penetration of the water-borne polyurethane clear coating to a depth of 500 µm in black spruce wood

Figure 3.15 shows the penetration of the water-borne coating into untreated black spruce wood and wood treated with plasma for 20 minutes. These photographs clearly demonstrate that prolonged plasma treatment for 20 minutes increased the penetration of clear coatings into black spruce wood.
3.3.2 Scanning electron microscopy

Under the scanning electron microscope the unmodified radial surfaces of black spruce wood show many aspirated bordered pits on radial walls of longitudinal tracheids (Figs. 3.16a, 3.16b). After 10 minutes exposure to plasma, tangential cell walls have been etched and removed from the surface and the raised borders of bordered pits have been partially or completely etched from the surface (Fig. 3.16c). The outer borders of some bordered pits were still present in samples exposed to plasma treatment for 10 minutes (Fig. 3.16d). However, they were completely etched and removed from samples exposed to plasma for 20 minutes. In such samples etching extended up to 3 cells deep (Fig. 3.16e). Etching of simple and half bordered pits in ray parenchyma occurred (Figure 3.16e), as well as bordered pits in ray tracheids (Fig. 3.16f).

SEM photomicrographs of the interface of the clear coating and wood showed more crushed cells in unmodified specimens (Fig. 3.17a, Fig. 3.17c) than in plasma treated specimens (Figs. 3.17b, 3.17d). This might be due to the reinforcement of sub-surface layer by coating material in plasma treated specimens. There was more filling of cell lumens with coating material in specimens coated with the oil-borne coating (Figs. 3.17a, 3.17b) than in specimens coated with the water-borne coating (Figs. 3.17c, 3.17d).
Figure 3.14: Penetration of oil-borne clear coating into untreated black spruce wood (left) and wood treated with plasma for 20 minutes (right). Stain in lumens of tracheids indicates the presence of coating material (after staining with Sudan IV). Scale bar = 100 µm

Figure 3.15: Penetration of water-borne clear coating into untreated black spruce wood (left) and wood treated with plasma for 20 minutes (right). Stain in lumens of tracheids indicates the presence of coating material (after staining with Sudan IV). Scale bar = 100 µm
Figure 3.16: Scanning electron microscope images of unmodified and plasma treated radial longitudinal surfaces of black spruce wood: (a) Untreated surface showing aspirated bordered pits in tracheids with uniseriate arrangement of pits, note intact pit membranes; (b) Unmodified surface showing raised tangential walls in longitudinal tracheids; note aspirated and intact pits; (c) Tracheids subjected to plasma treatment for 10 min, note etching of the raised border of a bordered pit (arrow right) and intact bordered pit in subsurface layer (arrow left); (d) Tracheids subject to plasma treatment for 10 min, note etching of cell wall material separating etched bordered pits (arrow right) and intact bordered pit in subsurface layer (arrow left); (e) Tracheids subjected to plasma treatment for 20 min, note etching of half-bordered cross-field pit membranes (arrow), note etching has extended up to three subsurface layers deep; (f) Tracheids, ray parenchyma (arrow top) and ray tracheids (arrow bottom) subjected to plasma treatment for 20 min; note etching has opened-up flow paths in the surface and subsurface layers of wood.
3.3.3 Clear coating adhesion to wood

Analysis of variance (ANOVA) revealed significant (p < 0.05) effects of coating type on the load required to pull the aluminum test cylinder off coated samples (hereafter referred to as ‘breaking load’). However, there was no significant (p > 0.05) effect of plasma treatment on breaking load and no significant interaction of coating x plasma treatment on breaking load. Higher loads were required to pull the test cylinder from the water-borne coating, compared to the oil-borne coating, irrespective of plasma treatment (Fig. 3.18). For example, the mean breaking load for the water based clear coating (6.8 MPa) was double that of the oil-borne coating (3.5 MPa). The breaking loads for the water-borne coating were also less variable than those of the oil-borne coating. However, there were some outliers (black circles) for the oil-borne coating that were well above the average breaking load.
of the water-borne coating. These outliers, labelled on Figure 3.16, were not associated with any particular treatment.

ANOVA revealed a significant (p < 0.05) effect of coating type on the two types of failure modes associated with the pull-off test. No significant (p > 0.05) plasma effect or coating x plasma interaction were recorded. Firstly, there was a significant (p < 0.05) effect of coating type on the cohesive failure of wood (Fig. 3.19). In other words, test cylinders that were glued on to water-borne clear coated samples had more wooden material adhering to them compared to the cylinders on to samples coated with the oil-borne finish. For example, test cylinders glued on to water-borne clear coated samples showed on average 68% cohesive failure while 28% less cohesive failure was observed in oil-borne samples. Conversely, a significant coating effect was also observed for the adhesive failure between the clear coating and black spruce wood (Fig. 3.20). In this case, the test cylinders glued to the oil-borne clear coating had a greater area (54%) that was free of woody material compared to the cylinders that were glued to the water-borne clear coating (20%).
summary, the oil-borne coating failed due to an adhesive rather than the preferred cohesive failure on the wood, whereas the latter was common in the water-borne coating (Fig. 3.21).

**Figure 3.19:** Percentage of the area of test cylinder which contained wood after the pull-off test

**Figure 3.20:** Percentage of area of test cylinder face that was free of wood after the pull-off test
3.4 Discussion

My results partially support the hypothesis that plasma treatment will increase the penetration of clear coatings into black spruce wood. All plasma treatments increased penetration of the clear coatings into the first layer of cells, but only prolonged plasma treatment resulted in increased penetration beyond the surface layer of cells, which was the zone of particular interest (0-75 μm). Evans et al. (2007) found that glow discharge plasma treatments derived from water increased the wettability of eucalypt wood surfaces and this effect may explain why the plasma treatments increased the penetration and filling of the first layer of cells (0-25 μm) with coating material. However, only the prolonged, 20 minute plasma treatment, significantly improved ‘sub-surface filling’. Previous research has shown that such increased coating penetration into wood occurs as a result of the opening up of flow paths within the wood. For example, Singh et al. (1998) observed that degradation of bordered pits in radiata pine as a result of bacterial activity allowed coatings to penetrate deeper into wood. It is well known that aspiration of bordered pits reduces the permeability of softwoods, Liese and Bauch (1967a) found that 75-80% of bordered pits were aspirated in the latewood of Norway spruce while only 50% were aspirated in Scots pine. They argued that this effect accounted for the lower permeability of spruce compared to pine (Liese and Bauch 1967a). Furthermore, spruce contains small piceoid cross-field pits which are less permeable that the larger fenestriform and numerous pinoid pits found in the cross-fields of pines (Phillips 1968). As observed
in the SEM pictures (Fig. 3.16), prolonged plasma treatments etched bordered pits in tracheids and ray tracheids as well as cross-field pits. The degradation of these pits and the opening up of flow paths explain why clear coatings penetrated deeper into the wood that was plasma treated for 20 minutes (especially when compared to the untreated control). Significantly greater quantities of coating material were found at the three depth intervals in black spruce wood specimens treated with plasma for 20 minutes compared to the untreated control (Fig. 3.13). However, the ratio of coating to total lumen void space in the specimens decreased from 82% in the surface to 25 µm layer, to 63% in the 25-50 µm layer and down to 40% in the 50-75 µm layer. Such a centripetal decrease in coating penetration with depth has been described previously (Gray 1961, Schneider 1979).

My finding that prolonged plasma treatment increased coating penetration into wood accords with those of Blanchard et al. (2009). They found increases in the penetration of a waterborne UV-curable polyurethane/polyacrylate resin when sugar maple wood was exposed to prolonged (20 and 60 min) R.F. plasma treatments. Their coating was able to penetrate sugar maple to a depth of up to 100 µm after the wood was exposed to an argon plasma (180W) for 20 minutes. Shorter periods of exposure (0.5 and 10 min) and the use of lower R.F. (150W) power did not have the same effect on coating penetration; penetration depths of 5-25 µm were recorded. Blanchard et al. (2009) reported that prolonged plasma treatment increased coating penetration, but did not report on the cause of this increase, whereas I observed that the anatomical changes to black spruce wood following plasma treatment could account for increases in clear coating penetration.

Previous studies have not quantified coating penetration into wood using the approach adopted here. Early studies described penetration of finishes into wood qualitatively using light or fluorescent microscopy of microtome sections (Gray 1961, Wardrop and Davies 1961, Erickson and Balatinecz 1964, van Loon 1966, Schneider and Côté 1967) or scanning electron microscopy of coated wood blocks (Schneider 1970, Zicherman and Thomas 1972, Vasishth et al. 1974, Schneider 1980). Rødsrud and Sutcliffe (1994) provided numerical estimates of coating penetration into spruce and pine based on centripetal changes in fungicide concentration. Nussbaum et al. (1994) and de Meijer et al. (1998) quantified coating penetration in terms of rows of cells filled with coating. Later,
Rijckaert et al. (2001a) developed an image analysis technique to obtain a mean value for the penetration of paints and stains into Scots pine sapwood. Subsequently Van den Bulcke and coworkers (2003) wrote a program in the computer language C that calculated the mean depth of penetration of opaque and clear coatings into beech and pine wood using image analysis of grouped pixel columns. Their technique differed from that used here. Rijckaert et al. (2001a) pointed out the limitations of visualizing coating penetration in 2D, but they suggested that the approach still has the potential to improve our understanding of this phenomenon.

A second hypothesis posed in the introduction was that increased penetration of coatings in black spruce would have beneficial effects on coating adhesion. My results do not support this hypothesis because there was no significant effect of plasma treatment on coating adhesion. Rijckaert et al. (2001b) suggested that deep penetration of coatings into wood is not detrimental to their adhesion. De Meijer et al. (1998) indicated that deeper penetration could further improve adhesion by providing more sites for mechanical interlocking. Earlier, Gray (1961) observed that the penetration phenomenon was “so sporadic that it cannot have much reinforcing effect on the wood.” Later, van Loon (1966) suggested that “deep penetration does not ensure good adhesion” but the depth of the interfacial zone is critical to the durability of wood-coating systems (Schneider and Côté 1967). Bardage and Bjurman (1998) suggested that because deep penetration enables the binder to interact with a large contact area, it might be an important factor in the adhesion of paints to wood. My findings support the suggestions of Gray (1961) and van Loon (1966) that coating penetration and adhesion are not positively correlated, however, it is possible that positive effects of plasma treatment on coating penetration did not increase coating adhesion because plasma degraded the wood's microstructure.

My finding that plasma treatment did not improve coating adhesion does not accord with previous findings. Blanchard et al. (2009) found that plasma treatment for 20 minutes using N₂, Ar or N₂/H₂ gas sources slightly increased the pull-off adhesion of test cylinders glued to a waterborne UV-curable polyurethane/polyacrylate coating on sugar maple. Adhesion improvements as a result of plasma treatment were also reported by Lukowsky and Hora (2002). They tested clear and pigmented
coatings on plasma modified Scots pine sapwood. The wet adhesion of a waterborne acrylic coating measured using both cross-cut and pull-off tests was improved by their atmospheric plasma treatment, whereas the same plasma treatment had no effect on the adhesion of a solvent-borne formulation (Lukowsky and Hora 2002).

I found a significant difference in the adhesion of the oil and water-borne polyurethane clear coatings to wood. There are few reports on the adhesion of either water- or oil-borne polyurethane clear coatings on wood and none that have tested the adhesion of these finishes using the pull-off test (de Moura and Hernandez 2004). Most of the published literature in the area has focused on the adhesion of pigmented oil and water-borne coatings (Williams et al. 1987, Ahola 1995, Bardage and Bjurman 1998). Furthermore, there has been very little research on the adhesion of polyurethanes to wood even though they have excellent gloss and abrasion, solvent, and chemical resistance (Damusis 1967, Weldon 2002). Research on coating penetration and adhesion has more often examined the adhesion of alkyds, acrylics and combinations of the latter resin types on wood (Williams et al. 1987, Williams et. al. 1990, Ahola 1995, Bardage and Bjurman 1998, Thay and Evans 1998, Rijckaert et al. 2001b). There is no common benchmark value for pull-off breaking load when evaluating coating adhesion to wood, which limits the extent to which my findings can be compared with those of previous studies.

3.5 Conclusion

One hypothesis posed in the introduction to this Chapter was that plasma treatment would increase clear coating penetration into wood. My results partially support this hypothesis. A 20 min glow discharge plasma treatment significantly increased clear coating penetration whereas shorter treatments for 0.5, 3 and 10 minutes were less effective at increasing coating penetration. Therefore I conclude that plasma treatments can increase clear coating penetration into wood, but increases in coating penetration depend upon duration of treatment.
The image analysis procedure used here to quantify clear coating penetration into the wood microstructure advances the field as it permits more precise estimates of coating penetration at different depths.

A second hypothesis posed in the introduction to this study was that plasma treatment and increased coating penetration would lead to increases in coating adhesion. My results did not support this hypothesis. However, the adhesion of the water-borne coating to black spruce was significantly greater than that of the solvent-borne coating. Therefore I conclude that coating type has a greater effect on adhesion than plasma treatment. As a result it is possible that the water-borne coating will perform better during weathering than the solvent-borne coating.
4. Performance of clear coatings on plasma treated wood

4.1 Introduction

In Chapter 3 I showed that the penetration of clear coatings into quarter sawn wood could be increased with plasma treatments, particularly those lasting 20 minutes. It suggested that this was due to the opening up of flow paths, such as aspirated bordered pits and rays, permitting better uptake of the finishes into the wood’s microstructure. Here, I hypothesize that clear coatings should perform better on plasma treated black spruce wood because they will penetrate into sub-surface layers that are less affected by surface photodegradation of wood caused by UV light. The degree to which increases in clear coating penetration may improve the performance of the wood-coating system to weathering was not examined in Chapter 3 and hence it is the subject of this experimental Chapter.

4.2 Materials and methods

4.2.1 Experimental designs

Two designed experiments are described in this Chapter. Both experiments examined the effect of two fixed factors (coating type and plasma treatment) on the performance of clear coatings on black spruce wood. In the first experiment, two planed quarter-sawn (radial) black spruce samples were cut from the parent blocks of wood and randomly allocated to coating type (2 levels). Each sample was then cross-cut to yield five specimens (3 x 15 x 75 mm), which were randomly allocated to the different plasma treatments (5 levels). In the second experiment, two flat-sawn (tangential) samples were also cut from the parent blocks of wood (as above), and then cross-cut to obtain five specimens, which were allocated to plasma treatment.

4.2.2 Preparation of wood specimens

Air-dry, planed, quarter-sawn black spruce heartwood sample boards measuring 60 mm (width) x 25 mm (thickness) x 450-500 mm (length) were obtained from the Centre de recherche sur le bois at the Université Laval, Québec (Fig. 4.1). Boards were conditioned at 20 ± 1°C and 65 ± 5% relative humidity prior to treatment for 15 days. The basic density of three black spruce
specimens from each board was determined by the water displacement/oven-drying method as described above (Section 3.2.2). The wood boards were viewed under a 10x magnifying lens and a scaled ruler was used to count the number of rings per centimetre (Table 4.1).

![Image](image.png)

Figure 4.1: Front (a) and isometric (b) views of the cutting pattern followed to obtain quarter-sawn (radial: g3-g7) and flat-sawn (tangential: e2-e6) panels from the same piece of wood (Step I). Step II details radial boards (a,g) and tangential boards (b, e), as well as extra pieces shown in light yellow (c, e, f). In the front view of step III all pieces shown were discarded. The isometric view of Step III shows how half of the radial (g3-g7) and tangential (e2-e6) pieces were obtained and also the pieces that were discarded (g1,g2, g8, e1, e7). The same procedure detailed in step III was used in boards b and a shown in step II and is omitted for ease of presentation.

<table>
<thead>
<tr>
<th>Board Number</th>
<th>No. of growth rings/cm</th>
<th>Basic Density (kg/m³) ± Standard Deviation (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7-9</td>
<td>416.9 ± 16.0</td>
</tr>
<tr>
<td>2</td>
<td>8-10</td>
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</tr>
<tr>
<td>3</td>
<td>6-8</td>
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</tr>
<tr>
<td>4</td>
<td>8-9</td>
<td>412.7 ± 6.5</td>
</tr>
<tr>
<td>5</td>
<td>8-10</td>
<td>418.1 ± 26.2</td>
</tr>
<tr>
<td>6</td>
<td>7-8</td>
<td>439.3 ± 17.6</td>
</tr>
</tbody>
</table>
4.2.3 Plasma treatment and coating application

Planed and lightly air-blown specimens were exposed to glow discharge plasma for 0.5, 3, 10 or 20 minutes as described in Chapter 3. Specimens subjected to a vacuum (19.99 Pa) for 1 minute in the plasma reactor acted as a control. Immediately after plasma treatment, specimens were brushed-coated with the same coatings used in Chapter 3. For both radial and tangential surfaces, one layer of coating was applied using a calibrated micropipette and a pre-soaked fine brush. The amount of coating applied was calculated to equal the sum of the number of coats recommended for these products times the spread rate recommended for each coating (Table 3.2). Afterwards, the remaining five faces of each wooden specimen were brush coated with black enamel paint (Cloverdale 11147 Flat Black), as recommended by Kiguchi et al. (2005). The coated surfaces were air dried at 20 ± 1°C and 65 ± 5% RH for 20 days.

4.2.4 Accelerated weathering test cycle

There are numerous accelerated weathering tests reported in literature to test coating performance on wood. The closest to being accepted as a standard was proposed by Podgorski and coworkers (2003) and validated in seven European laboratories that had previously developed their own cycles. The authors note that this optimized cycle “enables differentiation between coating performance on different wood substrates” (Podgorski et al. 2003). Hence, this cycle was selected and used to assess clear coating performance on plasma treated wood. The cycle consists of separate condensation, UV irradiation and water spraying steps together with sub-cycling steps as described in Table 4.2. This cycle was programmed into a QUV/SPRAY weatherometer (Q-Panel Lab Products, 0.68W/m² at 340 nm).

Coated specimens were exposed to accelerated weathering for a total of 3024 hours divided into six 504 hour exposure periods. Exposure periods are rounded off and described in this Chapter to the nearest hundredth hour. For example, the 504h exposure period is given as 500 h, the 1008h exposure period as 1000 h, and so on.
Table 4.2: Accelerated weathering cycle used to test the performance of clear coatings on plasma treated wood. The cycle is the same as that described in the European Prestandard: prENV927-6: Coating materials and coating systems for exterior wood. Part 6: Method, assessment and evaluation for an artificial weathering test for wood coatings based on fluorescent lamp apparatus (Podgorski et al. 2003)

<table>
<thead>
<tr>
<th>Step</th>
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<th>Duration (h)</th>
<th>Remark</th>
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</thead>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>Subcycle step 3+4</td>
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</tr>
<tr>
<td>3</td>
<td>UV</td>
<td>60°C</td>
<td>2.5</td>
<td>UVA-340 nm</td>
</tr>
<tr>
<td>4</td>
<td>Spray</td>
<td>0.5</td>
<td>6-7 Liters/min</td>
<td>UV light off</td>
</tr>
</tbody>
</table>

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

4.2.5 Evaluation of coating performance

The methods used to evaluate the performance of the coatings on the weathered panels were similar to those described by Kiguchi et al. (2005) in their paper on service life prediction of coatings on wood. Observations were made at the start of the test (0 h) and after the completion of each 504 h exposure period for the duration of the trial (Fig. 4.2). A description of each of the methods used to evaluate coating performance follows:

4.2.5.1 Color (L*, a*, b*)

A Minolta CM-2600d spectrophotometer was used to quantify color (10°/D65) changes on clear coated wood panels. Color measurements are expressed using the CIE (Commission Internationale de Enluminare) LAB (L*, a*, b*) space system (CIE 1976). In this three-dimensional system the positive and negative directions of the perpendicular a* and b* axes describe the magenta (red) to green, and yellow to blue color range, respectively, whilst the L* axis (perpendicular to a* and b*) is the measure of luminosity from white (+) to black (-).

Color measurements after each exposure period are expressed as the ratio of L*, a* or b* to the initial unexposed values of L*, a* or b* (Table 4.3). A transparent template with three holes (ø 7 mm) punched into it was used to make sure that color measurements were made in the same places on the weathered coated surface throughout the trial. The average of these three measurements on the different specimens was used to estimate color changes that occurred during weathering.
4.2.5.2 Film defects (D*)

Clear coated panels were overlaid with a transparent template containing a grid of 90 rectangles, each measuring 2 x 5 mm. Surfaces were observed under iridescent light aided with a 10x hand lens. Defects that reduce the integrity of coatings, such as film delamination or peeling, in each grid were recorded. The total number of defects was divided by 90 to estimate overall degradation of the coating on each specimen. Film defects that developed during exposure are expressed as the ratio of film defects to the film defects at 1000 h, because film defects did not develop in specimens until they were exposed for 1000 h of accelerated weathering (Table 4.3).

4.2.5.3 Gloss (G*)

Gloss is a measure of the light reflected off the surface of coatings (Goldschmidt and Streitberger 2007). Surface gloss was measured at 60° on the center of each specimen using a Micro-TRI-Gloss Meter (BYK Gardner Model 4551/HWS 5820). High gloss values (~100%) are indicative of high reflection as the gloss meter measures the intensity of the reflected light sent from a lamp to the specimen and then back to a photocell. Gloss measurements after each 500 h exposure period are expressed as the ratio of measured gloss to the initial unexposed gloss parameter (Table 4.3).

Table 4.3: List of properties that were used to assess the performance of plasma treated and coated specimens exposed to artificial accelerated weathering

<table>
<thead>
<tr>
<th>Performance Parameter</th>
<th>Response variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lightness (L*)</td>
<td>Ratio of L* n / L* 0 h</td>
</tr>
<tr>
<td>Yellowness (b*)</td>
<td>Ratio of b* n / b* 0 h</td>
</tr>
<tr>
<td>Redness (a*)</td>
<td>Ratio of a* n / a* 0 h</td>
</tr>
<tr>
<td>Gloss (G*)</td>
<td>Ratio of G* n / G* 0 h</td>
</tr>
<tr>
<td>Film defects (D*)</td>
<td>Ratio of D* m / D* 1000 h</td>
</tr>
</tbody>
</table>

(i) Measurement after n exposure period divided by the measurement at the beginning (0 h); n = 500 h, 1000 h, 1500 h, 2000 h, 2500 h or 3000 h; (ii) In this case m = 1500 h, 2000 h, 2500 h or 3000 h
4.2.6 Statistical analyses

Analysis of variance was used to examine the effects of coating and plasma treatment on the variables listed in Table 4.3. All variables measured were analyzed as the ratios of the measured variable for weathered specimens to the initial (unweathered) value of that variable. This approach made it possible to follow changes in the performance of clear coats through the accelerated weathering test. All transformed response variables met the requirements of equal variance and a normal distribution of residuals. Statistical computation was performed using Genstat v11. Significant results are presented in graphs, which include least significant difference (LSD based on 95% confidence intervals) bars for plasma effects and coating × plasma interactions, or ± 2x standard errors of the difference (SED) bars for coating effects. These error bars allow the reader to estimate the significance of differences between individual means.
4.3 Results

A summary of the statistical significance of all experimental factors on the response variables for both radial and tangential surfaces is presented in Table 4.4. Accordingly, only those results that were statistically significant (p < 0.05) are described in this results section.

Table 4.4: Statistical significance of coating effects (C), plasma treatment effects (P) and coating x plasma interactions (C x P) on response variables measured on clear coatings on wood exposed to 3000 hours of accelerated weathering. Measurements were made every ~500 hours. P-value that are highlighted in yellow are statistically significant (p < 0.05)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Coating(C)</th>
<th>Plasma(P)</th>
<th>CxP</th>
<th>Coating(C)</th>
<th>Plasma(P)</th>
<th>CxP</th>
</tr>
</thead>
<tbody>
<tr>
<td>L* 500 h / L* 0 h</td>
<td>0.649</td>
<td>0.522</td>
<td>0.05</td>
<td>0.063</td>
<td>0.821</td>
<td>0.553</td>
</tr>
<tr>
<td>L* 1000 h / L* 0 h</td>
<td>0.821</td>
<td>0.397</td>
<td>0.003</td>
<td>0.267</td>
<td>0.133</td>
<td>0.388</td>
</tr>
<tr>
<td>L* 1500 h / L* 0 h</td>
<td>0.153</td>
<td>0.567</td>
<td>0.118</td>
<td>0.375</td>
<td>0.578</td>
<td>0.407</td>
</tr>
<tr>
<td>L* 2000 h / L* 0 h</td>
<td>0.124</td>
<td>0.307</td>
<td>0.26</td>
<td>0.015</td>
<td>0.69</td>
<td>0.949</td>
</tr>
<tr>
<td>L* 2500 h / L* 0 h</td>
<td>0.031</td>
<td>0.26</td>
<td>0.922</td>
<td>0.003</td>
<td>0.658</td>
<td>0.855</td>
</tr>
<tr>
<td>L* 3000 h / L* 0 h</td>
<td>0.014</td>
<td>0.606</td>
<td>0.516</td>
<td>0.002</td>
<td>0.499</td>
<td>0.777</td>
</tr>
<tr>
<td>a* 500 h / a*0 h</td>
<td>0.008</td>
<td>0.776</td>
<td>0.05</td>
<td>0.002</td>
<td>0.198</td>
<td>0.063</td>
</tr>
<tr>
<td>a* 1000 h / a*0 h</td>
<td>0.004</td>
<td>0.755</td>
<td>0.036</td>
<td>0.001</td>
<td>0.178</td>
<td>0.122</td>
</tr>
<tr>
<td>a* 1500 h / a*0 h</td>
<td>0.006</td>
<td>0.619</td>
<td>0.08</td>
<td>0.008</td>
<td>0.795</td>
<td>0.638</td>
</tr>
<tr>
<td>a* 2000 h / a*0 h</td>
<td>0.006</td>
<td>0.342</td>
<td>0.097</td>
<td>0.002</td>
<td>0.121</td>
<td>0.077</td>
</tr>
<tr>
<td>a* 2500 h / a*0 h</td>
<td>0.014</td>
<td>0.615</td>
<td>0.055</td>
<td>0.001</td>
<td>0.148</td>
<td>0.138</td>
</tr>
<tr>
<td>a* 3000 h / a*0 h</td>
<td>0.014</td>
<td>0.261</td>
<td>0.15</td>
<td>0.001</td>
<td>0.178</td>
<td>0.265</td>
</tr>
<tr>
<td>b* 500 h / b*0 h</td>
<td>0.001</td>
<td>0.215</td>
<td>0.11</td>
<td>0.001</td>
<td>0.02</td>
<td>0.6</td>
</tr>
<tr>
<td>b* 1000 h / b*0 h</td>
<td>&lt;.001</td>
<td>0.03</td>
<td>0.09</td>
<td>&lt;.001</td>
<td>0.04</td>
<td>0.486</td>
</tr>
<tr>
<td>b* 1500 h / b*0 h</td>
<td>&lt;.001</td>
<td>0.009</td>
<td>0.174</td>
<td>&lt;.001</td>
<td>0.043</td>
<td>0.329</td>
</tr>
<tr>
<td>b* 2000 h / b*0 h</td>
<td>&lt;.001</td>
<td>0.013</td>
<td>0.379</td>
<td>&lt;.001</td>
<td>0.046</td>
<td>0.168</td>
</tr>
<tr>
<td>b* 2500 h / b*0 h</td>
<td>&lt;.001</td>
<td>0.04</td>
<td>0.454</td>
<td>&lt;.001</td>
<td>0.015</td>
<td>0.643</td>
</tr>
<tr>
<td>b* 3000 h / b*0 h</td>
<td>&lt;.001</td>
<td>0.035</td>
<td>0.034</td>
<td>&lt;.001</td>
<td>0.025</td>
<td>0.94</td>
</tr>
<tr>
<td>D* 1500 h / D* 1000 h</td>
<td>0.123</td>
<td>0.848</td>
<td>0.007</td>
<td>0.646</td>
<td>0.461</td>
<td>0.614</td>
</tr>
<tr>
<td>D* 2000 h / D* 1000 h</td>
<td>0.591</td>
<td>0.16</td>
<td>0.047</td>
<td>0.058</td>
<td>0.031</td>
<td>0.81</td>
</tr>
<tr>
<td>D* 2500 h / D* 1000 h</td>
<td>0.493</td>
<td>0.678</td>
<td>0.188</td>
<td>0.169</td>
<td>0.01</td>
<td>0.423</td>
</tr>
<tr>
<td>D* 3000 h / D* 1000 h</td>
<td>0.544</td>
<td>0.939</td>
<td>0.441</td>
<td>0.75</td>
<td>0.034</td>
<td>0.184</td>
</tr>
<tr>
<td>G* 500 h / G*0 h</td>
<td>&lt;.001</td>
<td>0.126</td>
<td>0.025</td>
<td>&lt;.001</td>
<td>0.05</td>
<td>0.138</td>
</tr>
<tr>
<td>G* 1000 h / G*0 h</td>
<td>&lt;.001</td>
<td>0.351</td>
<td>0.031</td>
<td>&lt;.001</td>
<td>0.158</td>
<td>0.356</td>
</tr>
<tr>
<td>G* 1500 h / G*0 h</td>
<td>0.001</td>
<td>0.597</td>
<td>0.855</td>
<td>0.001</td>
<td>0.561</td>
<td>0.234</td>
</tr>
<tr>
<td>G* 2000 h / G*0 h</td>
<td>0.004</td>
<td>0.087</td>
<td>0.033</td>
<td>0.001</td>
<td>0.089</td>
<td>0.015</td>
</tr>
<tr>
<td>G* 2500 h / G*0 h</td>
<td>0.011</td>
<td>0.069</td>
<td>0.043</td>
<td>0.002</td>
<td>0.15</td>
<td>0.039</td>
</tr>
<tr>
<td>G* 3000 h / G*0 h</td>
<td>0.057</td>
<td>0.019</td>
<td>0.012</td>
<td>0.086</td>
<td>0.813</td>
<td>0.26</td>
</tr>
</tbody>
</table>
4.3.1 Plasma effects

The following subsections present the response variables where statistically significant (p < 0.05) differences occurred due to plasma treatment.

4.3.1.1 Yellowing of surfaces

Analysis of variance showed significant (p < 0.05) effects of plasma treatment on the yellowing (yellowness ratio) of both radial and tangential surfaces during accelerated weathering (Table 4.4). For radial surfaces, these effects were significant after all exposure periods, except the 500 h and 3000 h periods (Fig. 4.3). After 1000 h, 1500 h, 2000 h and 2500 h of artificial weathering similar effects of plasma treatment on yellowing were observed: samples pre-treated with plasma for 0.5 and 20 min were yellower than the control. The samples treated with plasma for 0.5 min yellowed more than the samples treated with plasma for 10 min (Fig. 4.3).

For the tangential surfaces, analysis of variance revealed significant (p < 0.05) effects of plasma treatment on the yellowing of wood panels after all six periods of artificial weathering (Fig. 4.4). Samples treated with plasma for 3 min yellowed more than the control and samples exposed to plasma for 10 min for all six exposure periods (Fig. 4.4). Furthermore, samples exposed to plasma for 3 min yellowed significantly more during accelerated weathering than those pre-treated with plasma for 0.5 and 20 min (for the 2500 h and 3000 h exposure periods) (Figs. 4.4e, 4.4f).

4.3.1.2 Film defects

Analysis of variance showed significant (p < 0.05) plasma treatment effects on film defects (expressed as the ratio of defects in the film at 2000 h, 2500 h and 3000 h to that at 1000 h), which suggests that plasma treatment improved coating performance when samples were exposed to accelerated weathering for prolonged periods of time (Fig. 4.5). After 2000 h and 2500 h, all plasma treated samples showed significantly lower film defect ratios than the control (Fig. 4.5a, 4.5b). However, after 3000 h of artificial weathering, the level of film defects in samples treated with plasma for 10 min was not significantly different from that of the control. Furthermore, the 0.5, 3 and 20 min plasma treatments did improve the performance of the clear coatings when compared to the
control (Fig. 4.5c). The film failure in untreated and plasma treated samples is presented below (Fig. 4.6, 4.7).

![Graphs showing changes in yellowness (b*) ratio of plasma treated and clear coated radial black spruce surfaces following artificial weathering for different periods. Each graph represents a different weathering period: (a) 1000 h; (b) 1500 h; (c) 2000 h; (d) 2500 h. Changes in yellowness defined as the ratio of b* at a weathering period to that of unweathered specimens.](image)

Figure 4.3: Changes in yellowness (b*) ratio of plasma treated and clear coated radial black spruce surfaces following artificial weathering for: (a) 1000 h; (b) 1500 h; (c) 2000 h; (d) 2500 h. Changes in yellowness defined as the ratio of b* at a weathering period to that of unweathered specimens.
Figure 4.4: Changes in yellowness ($b^*$) ratio of plasma treated and clear coated tangential black spruce surfaces following artificial weathering for: (a) 500 h; (b) 1000 h; (c) 1500 h; (d) 2000 h; (e) 2500 h; (f) 3000 h. Changes in yellowness defined as the ratio of $b^*$ at a weathering period to that of unweathered specimens.
Figure 4.5: Changes in film defects (D*) ratio of plasma treated and clear coated tangential black spruce surfaces following artificial weathering for: (a) 2000 h; (b) 2500 h; (c) 3000 h. Changes in film defects defined as the ratio of D* at a weathering period to that at 1000 h.

4.3.1.3 Gloss retention

Analysis of variance revealed statistically significant (p < 0.05) plasma treatment effects on the ratios of gloss measured on tangential samples after 500 h. For such samples gloss retention was statistically higher in specimens pre-treated with plasma for 0.5 or 10 min when compared to samples pre-treated with plasma for 3 min (Fig. 4.8).
Figure 4.6: Occurrence of defects in an oil-borne urethane coating on untreated tangential black spruce wood surfaces exposed to artificial weathering for (a) 2000 h, (c) 2500 h and (e) 3000 h; and defects in the same coating type on samples pre-treated with plasma for 3 min and then exposed to accelerated weathering for (b) 2000 h, (d) 2500 h and (f) 3000 h.

Figure 4.7: Occurrence of defects in a water-borne urethane coating on untreated tangential black spruce wood surfaces exposed to artificial weathering for (a) 2000 h, (c) 2500 h and (e) 3000 h; and defects in the same coating type on samples pre-treated with plasma for 3 min and then exposed to accelerated weathering for (b) 2000 h, (d) 2500 h and (f) 3000 h.

Figure 4.8: Changes in gloss ($G^*$) ratio of plasma treated and clear coated tangential black spruce surfaces following artificial weathering for 500 h. Gloss changes defined as the ratio of $G^*$ at a weathering period to that of unweathered specimens.
4.3.2 Coating x plasma interactions

Statistical analysis of data revealed several significant plasma treatment x coating type interactions on response variables (Table 4.4). These interactions were recorded for specimens exposed to accelerated weathering for different periods of time as follows.

4.3.2.1 Color (L*, a*, b*)

Plasma treatment by coating interactions on the lightness ratio (L*) occurred for radial specimens exposed to accelerated weathering for 500 h and 1000 h (Fig. 4.9). After 500 h, all radial coated surfaces darkened, but specimens pre-treated with plasma for 0.5 min and coated with the oil-borne finish darkened significantly less than the following treatment x coating combinations: oil-borne (OB) x control, OB x 3 min, water-borne (WB) x 0.5 min, WB x 3 min and WB x 10 min (Fig. 4.9a). A similar effect was noted in specimens exposed to 1000 h of accelerated weathering. In this case the lightness of the oil-borne coating x 0.5 min plasma treatment combination was significantly higher than that of the OB x control, OB x 3 min, OB x 20 min, WB x 0.5 min, WB x 10 min and WB x 20 min (Fig. 4.9b). After 1000 h of accelerated weathering, the controls coated with the water-borne clear coating on radial surfaces were significantly lighter than the oil-borne control (Fig. 4.9b).

Figure 4.9: Changes in lightness (L*) ratio of plasma treated and clear coated radial black spruce surfaces following artificial weathering for: (a) 500 h; (b) 1000 h. Changes in lightness defined as the ratio of L* at a weathering period to that of unweathered specimens
Significant (p < 0.05) coating x treatment interactions were also observed for the a* parameter, which suggest that radial surfaces under both types of clear coating became redder after exposure to artificial weathering (Fig. 4.10). All water-borne (WB) x plasma treated specimens were redder than their oil-borne (OB) x plasma treatment counterparts after 500 h (Fig. 4.7a) as well as after 1000 h of exposure to accelerated weathering (Fig. 4.10b). Additionally, the OB x 3 min treatment combinations were significantly redder than the OB x control and OB x 0.5 min combinations after 500 h of exposure to accelerated weathering. These effects account for the significant coating x treatment interaction on the redness parameter a*. Furthermore, the same interaction was observed in the OB x 20 min combination when compared to the OB x control and OB x 0.5 min after 500 h of artificial weathering (Fig. 4.10a). After 1000 h, specimens coated with the water-borne coating were significantly redder than those coated with the oil-borne coating (Fig. 4.10b). The significantly higher redness ratios of the OB x 20 min combination compared to the OB x control and OB x 0.5 min combinations persisted after 1000 hours of artificial weathering. Also, the OB x 3 min combination had significantly higher redness ratios than the OB x control after 1000 h of exposure to accelerated weathering (Fig. 4.10b).

There were also significant coating x treatment interactions on yellowness (b*) ratio of radial surfaces of specimens exposed to 3000 h of artificial weathering (Fig. 4.11). All water-borne coating x plasma treatment combinations yellowed significantly more than the oil-borne coated specimens. The oil-borne x control combination yellowed significantly less than the oil-borne x plasma treatment combinations after 3000 h of artificial weathering (Fig. 4.11).
Figure 4.10: Changes in redness (a*) ratio of plasma treated and clear coated radial black spruce surfaces exposed to accelerated weathering for: (a) 500 h and (b) 1000 h. Changes in redness defined as the ratio of a* at a weathering period to that of unweathered specimens.

Figure 4.11: Changes in yellowness (b*) ratio of plasma treated and clear coated radial black spruce surfaces following artificial weathering for 3000 h. Changes in yellowness defined as the ratio of b* measured at a weathering period to that of unweathered specimens.

4.3.2.2 Film defects

Significant coating x plasma treatment interactions were observed in the ratio of film defects in tangential clear coated specimens exposed to 1500 h and 2000 h of artificial weathering (Fig. 4.12). After 1500 h, the oil-borne (OB) x control combination showed higher film defect ratios than the OB x 10 min, OB x 20 min, water-borne (WB) x control and WB x 3 min combination. The film on the OB x 3 min combination also had a significantly higher defect ratio than the OB x 10 min
combination after 1500 h of artificial weathering (Fig. 4.12a). Measurements of film defects (expressed as film defect ratio) revealed that the OB x control combination underperformed compared to all other coating x treatment combinations after 2000 h of artificial weathering (Fig. 4.12b). Some of these interactions can be observed in the panels below (Fig. 4.13).

**Figure 4.12:** Changes in film defects (D*) ratio of plasma treated and clear coated radial black spruce surfaces following artificial weathering for: (a) 1500 h; (b) 2000 h. Film defects defined as the ratio of D* at a weathering period to that at 1000 h.

**Figure 4.13:** Occurrence of defects in an oil-borne urethane coating on untreated radial black spruce wood surfaces following artificial weathering for: (a) 1500 h; (c) 2000 h; and defects in the same coating type on samples pre-treated with plasma for 10 min and following artificial weathering for: (b) 1500 h, (d) 2000 h. Occurrence of defects in a water-borne urethane coating on untreated radial black spruce wood surfaces following artificial weathering for: (e) 1500 h; (g) 2000 h; and defects in the same coating type on samples pre-treated with plasma for 3 min and following artificial weathering for (f) 1500 h; (h) 2000 h.
4.3.2.3 Gloss retention

Both tangential and radial clear coated surfaces showed significant coating x treatment interactions on the gloss of the coatings. These interactions were observed on tangential surfaces exposed to accelerated weathering for 2000 h (Fig. 4.14a) and 2500 h (Fig. 4.14b). In both cases, the oil-borne coating retained more of its gloss (original gloss = 1) than the water-borne coating, particularly on specimens that were pre-treated with plasma for 10 minutes (Fig. 4.14).

![Figure 4.14: Changes in gloss (G*) ratio of plasma treated and clear coated tangential black spruce wood surfaces following artificial weathering for: (a) 1500 h; (b) 2000 h. Gloss changes defined as the ratio of G* at a weathering period to that of unweathered specimens](image)

For radial clear coated surfaces, significant coating x plasma treatment interactions were observed at the end of every 500 h weathering cycle with the exception of the 1500 h cycle (Fig. 4.15). After 500 h, the oil-borne (OB) x plasma combinations had significantly higher gloss retention than the water-borne (WB) x plasma counterparts, particularly the specimens pre-treated with plasma for 10 min (Fig. 4.15a). A similar effect was observed for specimens exposed to 1000 h of artificial weathering. Significant coating x plasma interactions were observed after 2000 h (Fig. 4.15c) and 2500 h (Fig. 4.15d) of artificial weathering: OB x plasma combinations retained more gloss than WB x plasma combinations, but the difference was less pronounced in specimens that were pre-treated with plasma for 3 min. After 3000 h of accelerated weathering, only the OB x 0.5 and OB x 10 min retained gloss better than the WB x plasma treatment combinations (Fig. 4.15e).
Figure 4.15: Changes in gloss ($G^*$) ratio of plasma treated and clear coated radial black spruce wood surfaces following artificial weathering for: (a) 500 h; (b) 1000 h; (c) 2000 h; (d) 2500 h; (e) 3000 h. Gloss changes defined as the ratio of $G^*$ at a weathering period to that of unweathered specimens.
4.3.3 Coating effects

There were significant (p < 0.05) effects of the clear coating on the color (L*, a*, b*) and gloss of specimens exposed to artificial weathering. These coating effects were observed on both radial and tangential surfaces, as described below.

4.3.3.1 Color (L*, a*, b*)

There were significant effects of coating on the lightness (L*) of specimens after they were exposed to artificial weathering for 2500 h and 3000 h. The lightness of all specimens finished with both types of clear coatings decreased after prolonged exposure to artificial weathering, but the decrease was more pronounced in specimens finished with the oil-borne coating (Fig. 4.16).

![Graph showing lightness (L*) changes](image)

**Figure 4.16:** Lightness (L*) of specimens coated on their (a) radial and (b) tangential surfaces and exposed to artificial weathering. Changes in lightness defined as the ratio of L* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time.

Analysis of variance revealed significant effects (p < 0.05) of coating type on the redness of specimens. Redness is expressed as the ratio of a* measured at a weathering period to that of unweathered specimens. Redness ratios increased for specimens finished with both types of coatings when they were exposed to artificial weathering. Specimens finished with the water-borne coating were significantly redder than specimens finished with the oil-borne coating irrespective of the length of time specimens were exposed to artificial weathering (Figs. 4.17, 4.18). Increases in redness of
specimens exposed to artificial weathering were more pronounced at tangential surfaces compared to radial surfaces.

Figure 4.17: Redness (a*) of specimens coated on their radial surfaces and exposed to artificial weathering. Changes in redness defined as the ratio of a* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time.

Figure 4.18: Redness (a*) of specimens coated on their tangential surfaces and exposed to artificial weathering. Changes in redness defined as the ratio of a* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time.

There were significant effects of coating type on the yellowing of coated specimens (radial and tangential surfaces) exposed to artificial weathering. Yellowness (b*) ratios were higher for the water-borne coating on radial surfaces compared to the oil-borne coating for all but the 3000 h
exposure period (Fig. 4.19). In the latter period of exposure, a significant coating x treatment interaction occurred as previously mentioned (Fig. 4.11). Yellowness ratios for the water-borne coating on tangential surfaces were higher than those of the oil-borne formulation for all six periods of artificial weathering (Fig. 4.20).

Figure 4.19: Yellowness (a*) of specimens coated on their radial surfaces and exposed to artificial weathering. Changes in yellowness defined as the ratio of b* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time.

Figure 4.20: Yellowness (a*) of specimens coated on their tangential surfaces and exposed to artificial weathering. Changes in yellowness defined as the ratio of b* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time.
4.3.3.2 Gloss retention

There was a significant (p < 0.05) effect of coating type on the gloss of coated specimens when they were exposed to artificial weathering. The oil-borne coating showed better gloss retention on radial surfaces when compared to the water-borne coating for specimens exposed to 1500 h of artificial weathering (Fig. 4.21a). For all the remaining exposure periods significant coating x treatment interactions were observed (Fig. 4.15). However, on tangential surfaces, loss of gloss of the water-borne coating during artificial weathering was more consistent (Fig. 4.21b). Nevertheless, coating x treatment interactions on gloss were still observed on tangential surfaces for specimens exposed to artificial weathering for 2000 and 2500 h (Fig. 4.14).

![Figure 4.21: Gloss (G*) of specimens coated on their (a) radial and (b) tangential surfaces and exposed to artificial weathering for 1500 h (radial) or 500 h to 1500 h (tangential). Gloss changes defined as the ratio of G* at a weathering period to that of unweathered specimens. Results are averaged across specimens pre-treated with plasma for different periods of time.](image)

4.4 Discussion

My results partially support the hypothesis that plasma treatment of wood increases clear coating performance. Plasma treatments reduced the level of film defects in coatings on the tangential surfaces of specimens (Fig. 4.5). However, on coated radial surfaces, the beneficial effect of plasma treatment on the level of coating defects was less clear-cut as there were significant coating x treatment interactions. Nevertheless, the performance of the oil-borne coating x control combination...
was inferior to those of plasma treated specimens (Fig. 4.12). These findings are encouraging because they suggest that plasma treatment may be able to alter some properties of wood surfaces that improve the performance of finishes. The findings of Evans et al. (2007) that plasma treatment improves glue bonding of eucalyptus wood suggest that such improvements may be linked to the better wetting properties of plasma modified wood surfaces and increased penetration of adhesives into the wood’s microstructure. Although I did not measure wetting of plasma-treated surfaces by the coatings, I observed that, after placing the clear coatings with the micropipette on top of the plasma treated samples, the coatings spread much faster. This effect and the increased penetration of coatings into samples treated with plasma for prolonged periods of time could have produced films that were less susceptible to failure when they were exposed to artificial weathering. However, the increased yellowing of plasma-treated and coated specimens (Figs. 4.3, 4.4) is undesirable because clear coating seeks to maintain the natural appearance of wood (Derbyshire and Miller 1981). Additionally, plasma treatments had no statistically significant effect on many of other parameters that are used to assess coating performance (Table 4.4). Hence, glow discharge plasma treatments cannot be recommended as a means of significantly improving the performance of oil and water-borne polyurethane clear coatings on black spruce wood. However, many clear coating formulations are commercially available and because numerous coating x treatment interactions occurred, further experiments with other formulations may find that plasma treatments can improve the performance of other wood species/coating combinations.

Plasma treatment of wood is a diverse field, as previous studies have used many different plasma types to impart new properties to wood surfaces, which makes it difficult to compare my findings with those of other researchers. Furthermore, there have been no previous studies that have tested the performance (color, film defects or gloss) of clear coatings on plasma modified wood. For example, Lukowsky and Hora (2002) suggested that plasma treatments of Scots pine wood enhanced the performance of exterior coatings based on positive results obtained solely from adhesion tests. Despite the large gaps in our knowledge, plasma treatment has been shown to increase the adhesion
of adhesives to dense eucalyptus wood species (Evans et al. 2007) and, accordingly, it is possible that the adhesion and performance of clear coatings on dense wood species might be improved.

Various coating effects were observed which suggested that the oil-borne coating performed better during accelerated weathering than the water-borne coating. My finding that the oil-borne coating was better at restricting the discoloration of wood during weathering is in accord with those of Van den Bulcke et al. (2008). They also found that oil-borne clear coatings were better than water-borne coatings at restricting color changes of Scots pine exposed to accelerated weathering. However, Grelier et al. (2007) reported greater darkening and yellowing, but similar changes in redness, of oil-borne acrylic clear coatings compared to water-borne acrylics when coated Scots pine samples were exposed to artificial weathering. Oil-borne polyurethanes have also been found, as here, to retain their gloss better than water-borne polyurethanes during artificial weathering (Van den Bulcke et al. 2008). Miniutti (1967) observed that polyurethane coatings on redwood lose their gloss when they are exposed to UV radiation due to the formation of microchecks in the film. Such microchecks were not observed here, but Miniutti (1967) also reported that the loss of gloss was accompanied by a ‘milky’ appearance of the film, which was a characteristic of the water-borne polyurethane clear coating tested here. My finding that the oil-borne polyurethane coating performed better than the water-borne polyurethane accords with calorimetric measurements, which led Podgorski et al. (2004) to conclude that oil-borne alkyd and alkyd-modified clear coatings were more durable than water-borne acrylic-alkyd and acrylic coatings.

One unexpected finding was that plasma treated and coated specimens sometimes yellowed more during accelerated weathering than coated controls. Research on improving the performance of clear coatings on wood used outdoors has focused on developing systems that restrict color change to the substrate (Williams 1983, Chang et al. 1998, Chang and Chou 1999 and 2000, Kiguchi et al. 2001, Aloui et al. 2006 and 2007, Schaller and Rogez 2007, Forsthuber and Grüll 2010). Hence, many previous studies report on the ability of the clear coating to restrict the yellowing (b*) of wood, because yellowing is linked to the photo-degradation of lignin by UV radiation (Hon 2001, Müller et
al. 2003). However, Chou et al. (2008) reported that changes to polyurethane clear coatings also contributed (5-42%) to the discoloration of wooden panels exposed to light for 24 days. Here, I am unable to estimate how much of the discoloration of my specimens was due to changes in the color of the coating (rather than wood), but significant (p < 0.05) effects of coating type on this color parameter suggest that discoloration of coatings may have contributed to the discoloration of specimens. My finding that plasma modification can increase the yellowing of wood may have unexpected applications, for example artificially coloring wood. Mitsui et al. (2004) have shown that UV irradiation of heat treated wood through masks can be used to create photographic images on wood. Plasma modification may be able to create similar images, although further research would be needed to explore this application of plasma processing of wood.

The increased photo-yellowing of plasma treated and coated tangential surfaces was not correlated with increased film failure. For example, the untreated control which yellowed the least developed more coating defects than plasma treated and coated specimens. It is possible that unsaturated (yellow) quinone compounds, generated by plasma treatment and UV radiation, photo-stabilized the wood-clear coat interface. Alternatively, changes in the roughness as a result of plasma treatment may explain why coatings developed few defects on plasma treated specimens compared to the untreated control.

4.5 Conclusion

Plasma treatment reduced the level of defects that developed when black spruce specimens coated with two different polyurethane coatings were exposed to accelerated weathering. But plasma modification of black spruce wood did not improve the retention of gloss or color of coated specimens during the accelerated weathering trial. Therefore I conclude that plasma modification of black spruce wood improves the durability of coating films, but not their gloss or the color of the coated wood when coated specimens are exposed to accelerated weathering.
The oil-borne polyurethane coating performed better than the water-borne polyurethane in accord with the findings of other researchers, and I conclude that the type of coating applied to wood surfaces has a greater influence on coating durability than plasma pre-treatment.

Plasma treated and coated samples yellowed more than coated controls, which may create opportunities to use plasma treatments to artificially color wood.
5. General discussion, conclusions and suggestions for further research

5.1 General discussion

In Chapter 1, I hypothesized that plasma treatment would improve penetration of clear polyurethane coatings into wood and the performance of coatings when the coated samples were exposed to weathering. Results in Chapter 3 partially support this hypothesis because plasma treatment, particularly for longer periods of time (20 min), increased the penetration of clear coatings into black spruce wood. Deeper penetration of the clear coating into wood was hypothesized to result in better adhesion of the coating to the plasma treated wood. However, this was not the case as dry adhesion pull-off tests found no significant effect of plasma treatment on the adhesion of the clear coatings to black spruce wood. The latter finding runs counter to those of previous researchers who observed that plasma treatments increased the adhesion of polyurethane coatings to sugar maple (Blanchard et al. 2009), and the wet adhesion of a water-borne coating to Scots pine (Lukowsky and Hora 2002). However, there was a strong effect of coating type on adhesion: the water-borne coating adhered more strongly to black spruce wood than the oil-borne coating. In Chapter 4, I tested the performance of clear coatings on plasma treated samples exposed to artificial weathering. I found some improvements to coating performance as a result of plasma treatment. For example, visual quantification of film failure after prolonged weathering of plasma treated and coated specimens revealed that there was less film failure on plasma treated surfaces, than on the untreated controls. This finding supports my hypothesis that plasma treatment will increase the performance of clear coatings on wood. However, there was increased yellowing of plasma treated and clear coated samples even after they were exposed to artificial accelerated weathering for short periods of time. Yellowing was also more pronounced in samples coated with the water-borne formulation. Yellowing of clear coated wood exposed to weathering is undesirable (Rogez 2001, George et al. 2005) and hence my finding that plasma treated and clear coated specimens yellowed more than the untreated, clear coated specimens does not support the aforementioned hypothesis.
The influence of plasma treatment on the penetration of clear coatings into wood has received little attention. Furthermore, our understanding of how coating penetration influences the resistance of coatings to weathering is poor. Grelier et al. (2007) reported that an impregnation pre-treatment of wood limited the penetration of clear acrylic coatings into the first subsurface layer of radial surfaces of Scots pine. This effect increased the thickness of a second coat which “allows better compatibility between the finishes and the wood when weathering is occurring.” Plasma treatment did not have this effect because it tended to increase the penetration of the clear coatings into wood. Furthermore, only one coat of finish was applied to samples. Hence, it is unlikely that increased coating thickness explains why there was some improvement to coating performance on plasma treated wood. Dawson et al. (2008b) observed that delignification of radiata pine wood surfaces increased the penetration of clear coatings to zones further than 3-4 layers from the surface. They reported less yellowing of wood and better weathering performance of clear coats on delignified wood. However, the pretreated (peracetic acid) and coated wood checked more than the coated (untreated) control (Dawson et al. 2009b). Plasma etching of wood is a dry method of opening flow paths in wood and it preferentially removes hemicelluloses and cellulose from wood rather than lignin, which is responsible for the photo-yellowing of wood exposed to weathering (Leary 1968, Jamali and Evans 2011). The latter may explain why plasma treatment increased the yellowing of clear coated surfaces exposed to accelerated weathering.

The solvent-based polyurethane coating tended to perform better than the water-borne polyurethane coating. This finding accords with those of several previous studies. For example, Van den Bulcke (2008) ranked the service life of several opaque and clear coatings based on parameters, which separated ‘higher’ from ‘lower’ quality coatings, such as: deep penetration, thicker coat, high adhesion, low color changes and high gloss. Using this ranking they found that transparent solvent-based systems “scored a little better in general” than transparent water-borne systems. Other researchers also report that solvent-based coatings perform better than water-borne coatings on wood (Rødsrud and Sutcliffe 1993, Podgorski 2004, Goldschmidt and Streitherger 2007). I observed that
the oil-borne clear coating penetrated deeper, and after prolonged exposure to weathering it also yellowed less, reddened less, and retained gloss better than the water-borne formulation. Van den Bulcke et al. (2008) also noted that a semitransparent oil-borne polyurethane retained its gloss (60º) after 2000 h of artificial weathering and performed better than a semitransparent water-borne formulation, and all opaque oil- and water-borne formulations. I found better gloss retention for the oil-borne finish (90 & 98%) when compared to the water borne finish (30 & 80%) on both radial and tangential surfaces, respectively, after coated samples were exposed to accelerated weathering for 1500 h. However, the water-borne clear coating adhered better and darkened less than the oil-borne formulation after coated specimens were exposed to accelerated weathering for prolonged periods of time. No effect of coating type on film failure was observed. The deeper penetration of oil-borne formulations into wood compared to that of water-borne formulations is well documented (Ahola 1995, de Meijer et al. 1998, 2001a, Van den Bulcke et al. 2003). However, the technique of assessing coating penetration that I developed provided information on the pattern of coating penetration into wood as well as a measure of gross penetration. This aspect of my research is discussed in greater detail below, but it is worth noting that both coating types almost fully filled the uppermost layer of cells in wood that had been treated with plasma for 20 min.

The adhesion of the water-borne clear coating to black spruce was superior to that of the oil-borne coating. In accord with this finding, Rijckaert et al. (2001b) found that water-borne acrylic and alkyd paints adhered more strongly to Scots pine than solvent-based alkyd paints. However, Van den Bulcke et al. (2008) reported a significant linear relationship between penetration and adhesion (pre-weathered) of solvent-borne alkyd transparent coatings on Scots pine. In contrast, the penetration of the water-borne polyurethane here was lower than that of the solvent-borne polyurethane, but its adhesion to the black spruce wood was better. My adhesion tests were restricted to unexposed samples, and a better indicator of the adhesion of the polyurethane coatings may be their tendency to fail after each 500 hour cycle. There was less failure of the water-borne coating on untreated wood exposed to accelerated weathering for 1500 h and 2000 h.
One explanation why the water-borne clear coating adhered better to black spruce than the oil-borne clear coating might be related to the chemical composition of the two coatings. The oil-borne formulation was certainly a urethane oil (ASTM Type 1) because it was a one-pack formulation (McGinnis 1960, Damusis and Frisch 1967). Urethane oils are the only urethane ASTM type coating where the isocyanates are reacted i.e. no free isocyanates (Damusis and Frisch 1967). The water-borne coating was also bought as a one-pack solution and may have had free isocyanates because an “ammonia-like” odor is mentioned in its MSDS (See Appendix 2b). Isocyanates can form strong covalent bonds with hydroxyl groups in wood (Reichelt and Poller 1981, Ellis and Rowell 1984, Weaver and Owen 1995). For example, Nienhuis and Akkerman (2002) reported that the early adhesion of a clear coating on spruce was improved if isocyanates were added to the coating. Hence the higher adhesion of the water-borne formulation to black spruce wood here may be related to the presence of free isocyanates in the formulation. Additional information on the chemical composition of the coating is needed to confirm this suggestion.

The increased photo-yellowing of plasma treated radial and tangential panels was described in Chapter 4. Müller et al. (2003) explained the photo-yellowing of spruce (P. abies) wood surfaces with reference to the degradation of lignin and formation of quinones as reaction products of lignin degradation. Polyurethanes are also known to yellow on exposure to light due to the formation of amine groups in the film as discussed by Nielsen and Zeno (1975). Such photo-yellowing has been reported for clear coatings on wood (Borgin et al. 1975, Chou et al. 2008). Here, plasma treatments increased the photo-yellowing of black spruce coated with two different polyurethane finishes. Exposure to plasma for 0.5 min produced similar yellowing ratios during weathering than those observed in tangential surfaces that had been exposed to plasma for 3 min. Jamali (2011) has shown that modification of wood with the same glow discharge plasma used here results in a “lignin-rich” surface. Such a surface would be more susceptible to photoyellowing than unmodified surfaces, which might explain my findings. However, yellowing was most pronounced in surfaces exposed to plasma for short periods of time (0.5 min and 3 min) and the effect was not as pronounced in surfaces
exposed to plasma for 10 and 20 min even though such treatments would enrich the lignin content of wood surfaces more by preferentially degrading cellulose and hemicelluloses (Jamali and Evans 2011). Further research is needed to resolve this discrepancy.

The technique I developed to measure coating penetration into black spruce wood is novel as only one other research group has developed a method of image analysis techniques to quantify coating penetration into wood. This research group at the Laboratory of Wood Technology in Ghent University in Belgium developed a ‘timwin’ script to measure the penetration (20 equidistant measurements) of paints into Scots pine and Norway spruce from fluorescence microscopy images (Rijckaert et al. 2001a). Later, Van den Bulcke (2003) used a program written in C that analyzed images of coatings on wood, pixel by pixel based on their color value (1-256) and proximity to other pixels. The program decided if the pixel was ‘isolated coating’, ‘coating/wood interface’ or a wood pixel. Results from this C-program were in accord with manual measurements of coating penetration that used confocal laser scanning microscope images of painted pine and beech specimens. This program was also used to measure the penetration of solvent-based and water-borne paints and clear finishes into the earlywood of Scots pine sapwood (Van den Bulcke et al. 2008). The technique I developed is not fully automated, however, it takes into account the anatomy of the wood and also the colors in the image to measure the penetration of clear coating into both earlywood and latewood.

Plasma treatment increased the penetration of clear coatings into wood which would increase the clarity of wood’s grain (de Meijer 2004) and produce wood with a more attractive appearance (Estrada 1967). This application of plasma to the processing of wood might find a niche in products where appearance is important such as high-end wood furniture. Also in the wood finishing field, Hilditch (1983) reports that “penetration is mostly a desirable feature in a wood stain” and recently plasma treatments have been tested to increase the penetration of dye/stains into wood to alter (strengthen) the color of the dyed wood (Lötter and Evans 2011).
5.2 General conclusions

Plasma treatments can increase the penetration of oil and water-borne polyurethane coatings into black spruce wood, but increases in coating penetration depend on the duration of plasma treatment. For example, in samples exposed to plasma for 20 minutes the coatings were able to almost completely fill the uppermost layer of cells next to the wood surfaces and partially fill (~ 40%) the lumens to a depth of 75 microns. In contrast, plasma treatments of shorter duration were much less effective at improving coating penetration. Plasma treatment for 20 minutes etched bordered pits and rays at the wood surface. These anatomical features influence the permeability of spruce (Liese and Bauch 1967a, 1967b, Banks 1970). Therefore I conclude that plasma treatment can increase the penetration of coatings into wood if the plasma can etch the wood and open up important flow-paths.

Plasma treatments did not influence the adhesion of the water-borne or oil-borne polyurethane clear coating to black spruce wood even though some of the plasma treatments, as mentioned above, improved the penetration of the coatings into the wood. Coating adhesion was influenced much more by the type of polyurethane clear coating applied to the wood. For example, the breaking load during adhesion testing of the water-borne coating was twice (6.8 MPa) that of the breaking load of the oil-borne coating (3.5 MPa). Furthermore, the mode of failure of the water-borne coating differed from that of the oil-borne coating. The dominant type of failure after the pull-off tests for the water-borne clear coating was cohesive failure of the wood. The latter failure type is preferred over adhesive failure of the clear coating to the wood, which was more common with the oil-borne formulation. Therefore I conclude that plasma treatments have no positive effect on the adhesion of polyurethane coatings to black spruce wood and adhesion is influenced more by the type of coating (water-borne vs. oil-borne). Further research is needed (see below) to better understand why plasma treatments are able to improve the adhesion of coatings to some wood species, for example Scots pine (Lukowski and Hora 2002) and sugar maple (Blanchard et al. 2009), but did not improve the adhesion of polyurethane coatings to black spruce wood.
Plasma treatment influenced the weathering resistance of water-borne and oil-borne polyurethane coatings on black spruce wood depending on treatment time (0.5, 3, 10 and 20 minutes) and performance criteria (color, gloss, film failure) used to assess weathering resistance. Plasma treatments successfully reduced the degree of film failure of clear coatings on tangential black spruce surfaces during artificial weathering. However, plasma treatments increased the yellowing of coated radial and tangential surfaces exposed to artificial weathering, which is undesirable. The yellowing of UV irradiated samples is related to photodegradation of lignin under the clear coating (Leary 1968, Derbyshire and Miller 1981, Horn et al. 1994). Assessing the performance of coatings on wood exposed to weathering can involve the use of various criteria (Van den Bulcke et al. 2008). I conclude that plasma pre-treatments can have positive and negative effects on the exterior performance of coatings on wood depending on the criteria used to assess performance.

5.3 Suggestions for further research

Additional research is needed to confirm my finding that plasma treatment increases coating penetration, using different softwood and hardwood species, and a range of different coatings. I evaluated, the overall performance of a single clear coat for each of two different polyurethanes on plasma treated and untreated black spruce wood. This permitted more consistent material application. However, some clear coatings, for example marine varnishes, are applied as thick multilayer systems (3-6 coats) thus increasing the longevity of the coating on wood exposed outdoors (Chatfield 1967). Such multilayer systems are more prone to develop intercoat defects (Chatfield 1967) and hence applying one coat was preferred here. Thus, my conclusions are limited to the performance of one clear coat on plasma treated and untreated wood, however, multilayer systems may behave differently and further research would be needed to examine if plasma treatment improved their performance on wood exposed outdoors.

To assess the performance of clear coatings I used artificial accelerated weathering. Accelerated weathering reduces testing time (Podgorski et al. 2003), but it does not take into account important weathering factors such as atmospheric pollutants and staining fungi. Podgorski et al.
(2003) reported that the artificial weathering cycle used here accelerates the weathering of coatings on untreated wood by a factor of ten (x10) compared to exposure to natural weathering in Central Europe. Further research is needed to confirm whether the same correlation is relevant to plasma-treated wood, and also how plasma treatments influence the performance of clear coatings on wood exposed outdoors to natural weathering.

The performance of finishes on wood can be improved by modifying the surface roughness of wood, for example by sanding (Richter et al. 1995). Miniutti (1967) suggested that “a method of surfacing lumber that would eliminate or reduce the height of vertically projecting springwood tracheid walls without closing surface lumens by crushing or filling with wood fragments may improve the performance of exterior varnishes.” Results here and those of Jamali and Evans (2011) suggest that a surface with such attributes can be obtained by treating wood with a glow discharge plasma. Furthermore, my results showed that some aspects of the performance of clear coatings on tangential black spruce surfaces could be improved by pre-treating the wood with glow discharge plasma. Further research is required to determine if improvements in coating performance were due to changes in the surface morphology of the wood, or due to increased penetration of the coating into the wood’s microstructure.

The image analysis procedure developed here (Chapter 3) should be automated which would make it easier and faster to quantify penetration of coatings and adhesives into wood and possibly also labelled photoprotective additives (e.g. UVA’s, HALS). Knowledge of the distribution of such additives in the wood’s microstructure and their mobility and leaching from uncoated and coated substrates could help with the development of more effective photostabilizers for wood.
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Appendices

Appendix 1 – details on analysis of variance (ANOVA)

Table A1. ANOVA for Split-plot design used in all experiments

<table>
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<th>Df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
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<td>J - 1</td>
<td>SSBLK</td>
<td>MSBLK</td>
<td>MSBLK/MSE1</td>
</tr>
<tr>
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<td>K - 1</td>
<td>SSA</td>
<td>MS</td>
<td>MSB/MSE1</td>
</tr>
<tr>
<td>Exp Error # 1</td>
<td>(J - 1)(K - 1)</td>
<td>SSE1</td>
<td>MSE1</td>
<td>MSE1/MSE2</td>
</tr>
<tr>
<td>Factor B</td>
<td>L - 1</td>
<td>SSB</td>
<td>MS</td>
<td>MSB/MSE2</td>
</tr>
<tr>
<td>A x B</td>
<td>(K - 1)(L - 1)</td>
<td>SSAxB</td>
<td>MSAXB</td>
<td>MSAXB/MSE2</td>
</tr>
<tr>
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<td>MSE2</td>
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<tr>
<td>Total</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Main questions:

1. Is there an interaction between Factors A and B? A x B show a p < 0.05? If there is an interaction, look at treatment means for significant differences using t-tests.

2. If there is no interaction between Factors A and B:
   a. Are there differences between levels for Factor A? Coating type?
      i. p > 0.05: Do not report
      ii. p < 0.05: Since there are only two levels for coating, determine which is higher using a t-test.
   b. Are there differences between levels for Factor B? Plasma level?
      i. p > 0.05: Do not report
      ii. p < 0.05: Look at means for plasma levels to determine which are significantly different using t-tests.
Appendix 2 – material safety data sheet of coatings

a) Appendix 2a Minwax® Helmsman® Spar Urethane
   Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 2 -Material Safety Data Sheets/Minwax_Helmsman_MSDS_OB.pdf

b) Appendix 2b Varathane® Diamond™ Spar Urethane
   Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 2 -Material Safety Data Sheets/Varathane_Diamond_MSDS_WB.pdf

c) Appendix 2c Cloverdale® Alkyd Rust Resistant Flat Black
   Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 2 -Material Safety Data Sheets/Cloverdale_11147_PU_Alkyd_Black.pdf
Appendix 3 – statistical analyses: chapter 3

a) Effect of coating type, plasma treatment and coating type x plasma treatment interaction on penetration
Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 3 -Chapter 3 Stats/Penetration Tests

b) Effect of coating type, plasma treatment and coating type x plasma treatment interaction on pull-off strength and type of wood failure
Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 3 -Chapter 3 Stats/Adhesion Tests
Appendix 4 – statistical analyses: chapter 4

Effects of coating type, plasma treatment and coating type x plasma treatment interaction on color ratios, gloss ratios and film failure ratios

Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 4 -Chapter 4 Stats
Appendix 5 – paper presented at the Fifth European Conference on Wood Modification, Riga, Latvia, September 20-21, 2010


Location: ubc_2011_fall_haase_jonathan_appendices.zip/Appendices/Appendix 5 – ECWM5 Paper