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THE INFLUENCE OF WOOD EXTRACTIVES ON DURABILITY PROPERTIES OF HARDWOODS AND SOFTWOOD EXPOSED TO ARTIFICIAL WEATHERING

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THE INFLUENCE OF WOOD EXTRACTIVES ON DURABILITY PROPERTIES OF HARDWOOD AND SOFTWOOD SPECIES EXPOSED TO ARTIFICIAL WEATHERING

By

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Abstract

The Influence of Wood Extractives on Durability Properties of Hardwoods and Softwoods Exposed to Artificial Weathering

By

Pascal Nzokou

Wood is the prime building material for various structures in outdoors applications. It is widely used for structures such as decking, railroad crossties, and playground equipment. However, when exposed to outdoor conditions, wood is susceptible to weathering degradation.

This project investigated the influence of wood extractives on the weathering of red oak (*Quercus rubra*), black cherry (*Prunus serotina*), and red pine (*Pinus resinosa*).

The first hypothesis of the study was that wood extractives occupy moisture sorption sites in wood and prevent water absorption. Therefore, removal of extractives by the weathering process leads to higher moisture absorption, which in turn leads to higher shrinkage and higher cracking of the wood surface. The second hypothesis was that wood extractives acts as antioxidants protecting the wood surface against photodegradation.

To test these hypotheses organic solvents were used to remove extractives from red pine, red oak, and black cherry wood specimens. Their physical, chemical and aesthetic degradation processes were monitored during laboratory conducted artificial weathering.

Fourier Transformed Infrared and X-Rays Photoelectron spectroscopy analysis demonstrated the removal of high carbon contents (from extractives and lignin), and increased exposure of cellulose and hemicellulose on the extracted wood surfaces.

Water sorption of extracted wood surfaces was higher than that of un-extracted surfaces at high relative humidities as a result of availability of moisture sorption sites previously occupied by extractives, which became available follow extraction. Application of the Hailwood Horrobin model and calculation of the free energy change for the hydrated water showed that lower energy was required to swell the wood structure due to the increase in hydrophilic sites available. The contact angle decreased significantly following extraction as a consequence of the higher ability of wood surfaces to absorb water.

Analysis of the surface roughness, weight loss and microscopic degradation, however, showed no statistically significant difference between control and extracted samples for red oak and black cherry, and a significant difference in the direction disproving our hypothesis for red pine. These observations suggest that the increased susceptibility to absorb water demonstrated in the sorption study did not result in higher susceptibility to physical degradation when exposed to artificial weathering.

The photo-discoloration study of wood surfaces evidenced a significant influence of water extractives on the overall discoloration of wood surface when exposed to artificial weathering. The presence of extractives slowed the discoloration process with polyphenolic water extractives acting as antioxidant protecting the wood against photodegradation.

These results suggest that extractives affect the chemical processes occurring on the wood surface, but their influence on the physical degradation of wood, which is more affected by the wood structure, is limited.

DEDICATION

To my late parents, Richard Nzokou and Jeanne Mawe Nzokou

To my beloved wife Caroline and my children Aristarque and Richard,

To my brothers and sisters for their patience, and sacrifices.

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Chapter 1

Introduction

Wood is the material of choice for several exterior applications such as poles, fencing, decking, siding, and walls. However, like other biological materials wood is susceptible to degradation. When exposed to the weather, wood undergoes a complex process of physical, chemical, and mechanical degradations commonly known as weathering (Feist 1982; Feist and Hon 1984). This process results from the combined action of weather factors such as oxygen, ultraviolet light, relative humidity, and wind, that induce discoloration and physical deterioration of wood surfaces (Feist and Hon 1984; Owen et al. 1993). The wood color quickly changes towards a brown color, and later to a whitish gray (Browne 1960; Feist and Hon 1984). These factors destroy the aesthetic quality of wood and reduce its service life.

Wood in exterior applications faces stiff competition from various substitutes and there is a great need to investigate and understand all the factors causing its degradation in outdoor uses. This will help develop strategies to overcome those shortcomings.

Several intrinsic wood factors have been reported to affect the weathering process. These include wood density, the presence of earlywood and latewood, juvenile wood, and wood extractives (Feist and Hon 1984). A great deal of research has been performed to describe the influence of density and juvenile wood on the weathering process, but there are only limited published results describing the mechanisms by which wood extractives interact with other weathering factors to degrade wood in outdoor applications.

Wood extractives are defined as components of wood removable by leaching or extraction with water or organic solvents (Dadswell and Hillis 1962; Hillis 1987). They usually include many different classes of organic compounds, ranging from relatively simple molecules such as phenols and sugars, to highly complex coloring matters like tannins and resins.

It is well established that the presence and amount of extractives in wood plays a significant role in wood properties, including affecting physical and mechanical properties, equilibrium moisture content, and dimensional stability (Chen and Chong 1994). Wood extractives also play an important role in the natural decay resistance of several temperate wood species such as osage orange, black locust, and redwood (Schultz et al. 1995; Kamdem 1994; Nzokou and Kamdem 2003) and in tropical woods such as teak (*Tectona grandis*) and grenadillo (*Platymiscium yucatanum*) (Waterman 1946; Reyes-Chilpa et al. 1998, Rudman 1963; Thevenon et al. 2001).

Frequently the influence of extractives on physical properties of wood are explained by the following hypotheses:

a) A bulking effect. It is suggested that large molecules of wood extractives keep the wood structure in a semi-swollen condition and hinder the number of available sites for the formation of intermolecular lignin-cellulose and/or lignin-lignin bonds (Ajuong and Breese 1997). In addition, studies during non-steady state drying from green condition have suggested that the presence of extractives induce significant reductions in both creep and shrinkage at lower temperature, while increasing both phenomena at higher temperature (Ajuong and Breese 1997)

b) A plasticizing effect. The presence of extractives may promote plastic flow (Narayanamurti 1957)

c) An effect of stiffening the cell walls. This is supported by claims that extractives exert a small but significant increase in short term mechanical properties of wood (Panshin and De Zeeuw 1980; Ajuong and Breese 1997).

In addition, Pizzi and Cameron (1986) demonstrated that tannin extractives within the cell wall of drought resistant species act as springs limiting the cracking of cell walls.

Although there are numerous references characterizing wood extractives and investigating their influence on water related and durability properties of several wood species, the relationship between wood extractives content and the weathering properties of wood surfaces is not well understood.

The goal of this project was to investigate possible correlations between wood extractives and the susceptibility to weathering. This will help in explaining and predicting the durability or weathering resistance observed in some species.

It is anticipated that the removal of extractives and their washing out by the weathering process would induce increased shrinkage, leading to a higher susceptibility to cracking. In addition, the modification of the extractive content and wood composition by weathering may affect wood structure by increasing the hydrophilic nature of wood and subsequently its susceptibility to decay fungi.

The experimental hypotheses are based on the likely mechanisms on how extractives influence the weathering of wood.

Hypothesis I: Wood extractives bulk cell walls, lower shrinkage, and affect specific gravity (Nearn 1955; Ajuong and Breese 1997). *Therefore, the removal of extractives makes available additional moisture sorption sites and induces higher dimensional change, leading to more cracks when exposed to weathering.*

$H_{1.1}$: *Extracted wood will be more physically unstable than non-extracted wood, and will therefore display increase in surface roughness, and weight loss, higher and more injurious macroscopic and microscopic cracks after weathering.*

Hypothesis II: Extractives are the cause of wood color, and have a plasticizing effect in wood. Flavonoids, lignans, and tannins are polyphenolic substances with the natural tendency to greasiness (Ajuong and Breese 1997). They act as antioxidants capable of protecting wood surface against photooxidation (Maldas and Kamdem 1999). *Therefore extracted wood will be more susceptible to photodegradation caused by the weathering process than un-extracted wood.*

$H_{2.1}$: *Extracted wood samples will be more prone to discoloration due to weathering compared to un-extracted wood samples due to the loss or reduction of its antioxidant protection.*

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Chapter 2

Literature review

2.1 Wood Structure and Anatomy

The anatomical structure, the chemical composition and the physical properties of wood play an important role in the weathering of wood.

Wood is the secondary xylem formed by cell division of the vascular cambium in a living tree (Kollman and Cote 1984). Wood cells make up the xylem portion of the tree as contrasted to the phloem (bark), which forms the protective layer surrounding the xylem. Softwood shows a simple structure with tracheids arranged in radial rows representing the only major type of longitudinal elements. Tracheids represent 90 to 95% of the total structure in softwoods. They are long cells with flattened or tapered ends (Haygreen and Bowyer 1996). Their cell walls contain pits, which provide pathways for conduction of fluids to adjoining cells. In hardwoods, in addition to fibers, there are cells of relatively large diameter known as vessels or pores. These cells are the main conduits of the movement of liquid and sap. The other cell types found in hardwoods are fiber tracheids, rays, and parenchyma. The wood rays are horizontally oriented tissue through the radial plane of the tree. They vary in size from one cell wide and a few millimeters high to more than 25 cells wide and several centimeters high. The rays connect various layers from pith to bark for storage and transfer of starch and food.

Wood cell walls are complex in structure. Most are composed of primary (P) and secondary (S) layers. The secondary layer is composed of several layers: S_1, S_2, and S_3 from the outside to the inner layer lining the cell lumen (Kollman and Cote 1984). Within each layer the microfibrils are oriented more or less uniformly into a rather dense parallel

array. The S1 layer has its microfibrils oriented predominantly almost perpendicular to the long axis of the cell. The S2 is the principal layer of the wall. It is generally thicker than either the S1 or the S3 and since it is oriented approximately parallel to the cell axis, it contributes most of the mechanical properties of the cells. Finally, the S3 is a thin layer whose orientation runs parallel to that of the S1.

The structure and anatomy of wood and the presence of certain extractives in the cells can significantly affect the weathering properties of wood in use.

2.2 Wood extractives

Extractives are heterogenous chemical compounds naturally occurring in woody plants (Panshin and DeZeeuw 1980). Hillis (1987) defined extractives as non-structural constituents of plants. They have lower molecular weight than other polymeric constituents of wood and are distributed in lumina or in specific plant tissues. Extractives may be within the cell wall, but are not chemically attached to it. In addition to organic extractives, plant cells contain insoluble extraneous constituents such as crystalline inclusions of calcium oxalate and silica, starch granules, and other polymeric materials.

The term extractive covers a large number of compounds of different classes, which can be extracted from wood with polar and nonpolar solvents (Hillis 1987). A large number of compounds in extractives from different trees have been identified, and they represent several classes of organic compounds. The polyphenolic compounds, which do not include lignin, are the most common. Nearn (1955) classified wood extractives into two groups: (a) extractives soluble only in organic solvents which are distributed in the gross capillaries of the wood, (b) extractives which are soluble in water and are present in both the coarse capillary structure and within the fine cell-wall. The

chemical composition of extractives varies with species, different zones inside the tree, and various wood tissues.

Wood extractives can be divided in four major classes (Hillis 1987):

Galactans and Cyclitols: These are rarely found coniferous wood extractive compounds. They are heavily branched polysaccharides based on residues of arabinose and galactose.

Terpenoids: This is a large group of compounds, which are widespread and largely found in softwoods. They are built from a number of five carbon isoprene units. The terpenoids also have functional groups such as hydroxyl, carboxylic acid, carbonyl etc...

Fatty acids and related compounds: These include fats, fatty acids with glycerol and triglycerides, and waxes defined as esters of fatty acids with saturated straight chain alcohols with 16-28 carbon atoms. Waxes usually occur in smaller amounts than fats.

Phenolic compounds: These are the most widespread components of the wood extractives. There are thousands of polyphenols, which can be classified as follows;

- ***Lignans:*** These are dimeric phenylpropane units linked covalently at the β carbon atom.
- ***Stilbenoids (C_6-C_2-C_6):*** Stilbenes and Stilbenoids are diphenyl compounds joined by complex arrangement of the propane group, often involving a ring structure. They are present in both hardwoods and softwoods.
- ***Flavonoids (C_6-C_3-C_6):*** The flavonoids comprise many thousands of C_6-C_3-C_6 compounds subdivided into flavones, flavanes, flavanonols, and isoflavones. Many types of flavonoids can occur in hardwoods. The large number of flavonoids is not only due to the degree of saturation, but also to the variation of hydroxylation of the rings.

- ***Quinones biosynthesized from acetate units:*** Quinones are usually responsible for strong colors, high durability, and dermatitic properties of some woods.
- ***Polymerized polyphenols:*** Most of the phenolic extractives are present in wood in a polymerized form and with largely unknown constitutions (Hillis 1987).

Extractives are found in greater amounts in heartwood than in sapwood, and changes in content can be very abrupt in heartwood periphery. They are found largely in the parenchyma, but can also be found in vessels and fibers, and in some specialized cells (Hillis 1987). In most cases, the extractives of the heartwood are stable, and there is little or no change within plant species (Hillis 1968). However, several authors observed variation from normal in a few wood species of the genera *Cinnamomum*, *Pinus*, *Pterocarpus* (Hillis 1968), *Ocotea* (Gottlieb and Magalhaes 1959) and *Acacia* (Clark-Lewis and Dainis 1967). However the occurrence of these variants is rather uncommon (Hillis 1968).

There is considerable variation in the occurrence and distribution of extractives within vascular plants. No single species contains all of the possible compounds or even all of the different classes of compounds. However it is well established that extractives from related species are similar and are often used for taxonomic purposes (Buchanan 1963). In that sense, there are noticeable differences between extractives occurring in softwood species and those found in hardwood species.

2.2.1 Softwood extractives

According to Koch (1972), softwood extractives comprise a heterogeneous group of compounds present in low concentrations. Among the most important are terpenes and wood resins, both of which are composed of isopropene units, polyphenols such as

flavonols, anthocyanins, quinones, stilbenes, lignans and tannins, tropolones, glycosides, sugars, fatty acids and inorganic constituents.

Terpenes: The common chemical characteristic of terpenes is their composition of isopropene units. The terpenes are subdivided into monoterpenes (2 units), sesquiterpenes (3 units), diterpenes (4 units), sesterterpenes (5 units), and triterpenes (6 units). In general, the terpenes are pre hydrocarbons, while terpenoids are terpenes bearing radical functional groups (Fengel and Wegener 1984). The most common terpenes are alpha pinene and beta pinene (Kollman and Cote 1984). The relative proportion and distribution of each of these terpenes vary within the tree. For example, a high shift in terpene quantity has been found in slash pine oleoresins as a result of induced wounds on the tree (Koch 1972). However, oleoresin in softwoods is always rich in diterpenes and diterpenoidic acids (Fengel and Wegener 1984).

Fat and waxes: Fats are defined as esters of high carbonic acids and glycerol. Waxes are esters of fatty acids with higher alcohols. Softwoods contain less than 1% fat and waxes (Fengel and Wegener 1984).

Phenolic compounds: Most wood species contain a large number of phenolic compounds, usually resulting from the biosynthesis of lignin (Fengel and Wegener 1984). For example, some of the simplest compounds found in spruce extractives include vanillin, p-hydroxyladehyde, and coniferyl aldehyde as well as coniferin and syringin (Fengel and Wegener 1984).

Another group of phenolic compounds is composed of lignans, consisting of two phenylpropane units. The most common lignans in softwoods are lariciresinol in larches,

pineresinol in spruce and pine and conidendrin in spruce and hemlock (Kollman and Cote 1984).

There is a great variety of polyphenols occurring in both softwoods and hardwoods. Among these, stilbenes are particularly common in the heartwood of pines. Polyphenols are usually species specific and have been used to create a chemical taxonomy for the genus *Pinus* (Kollman and Cote 1984). The most important polyphenol is pinosylvin, known to be strongly toxic and responsible for the heartwood decay resistance of some pine species (Kollman and Cote 1984). The tropolones found only in the Cupressales include alpha, beta and gamma thujaplicin (Kollman and Cote 1984). Among polyphenols, flavonoids are also well represented in softwoods. This group is comprised of flavone, flavanes, flavanones and isoflavones. The flavonoids identified in softwood include chrysin, taxifolin, pinocembrin and pinobanksin (Fengel and Wegener 1984).

2.2.2 Hardwood extractives

The bark and sapwood of hardwoods is reported to be rich in simple monomers and nutrients such as fats, starch, sucrose, simple sugars, inositols, simple glycosides, free esterified sterols, phenylpropanoids, and other simple phenolics (Rowe and Conner 1979). The heartwood has fewer nutrients, glycosides and metabolic intermediates, but is rich in hydrolysable and condensed tannins and many other alkaloids, resins, essential oils, and specialized compounds (Rowe and Conner 1979).

The specific chemical composition in hardwoods varies with species and possibly, even individuals within the species. The description of the chemical constituents of most northern hardwood extractives has been conducted by Rowe and Conner (1979).

Hardwoods sapwood contains leucoanthocyanins and pinoresinol. In addition, coumarin and lignans are usually present. Wood extractives from secondary metabolism tend to be especially abundant in some particular groups of hardwoods. For example Koch (1985) reported that alkaloids were particularly abundant in magnolias and yellow poplar, sesquiterpenes in yellow poplar and elms, acetogenins in hickories, complex coumarins in sugar maple, and lignans in magnolias, elms, and oaks.

2.2.3 Formation of wood extractives

Extractives are formed in wood tissues at different stages in the life of the tree. The biochemical processes leading to the formation of wood extractives are not clearly established. There are two conflicting theories on the formation of wood extractives; the translocation theory and the in situ formation theory of extractive formation.

The translocation theory of wood extractive formation postulates that the extractives in the heartwood are accumulated by translocation from other regions (Hillis 1987). It is suggested that the precursors to heartwood extractives are formed in the foliage and other parts of the tree and diffuse radially to the heartwood periphery. However, this theory is however not able to explain the variability in amount and components observed in wood extractives.

The in situ theory states that wood extractives, particularly polyphenols, are formed in situ and are not mobile beyond the cell in which they are formed (Chattaway 1952; Hillis 1987). Hemingway and Hillis (1970) showed that extractives from Douglas fir heartwood and those formed in the living stump after the stem had been removed had similar composition, supporting the fact that it was unlikely that they originated from the foliage as proposed by the translocation theory. Apparently, physiological conditions near

the sapwood-heartwood boundary have a great effect on the rate and duration of aromatic biosynthesis during formation of heartwood extractives (Nelson 1975). Extractives in injured tissues, knot wood, and heartwood at various height of the tree can have differences in composition. Hillis (1987) reported that extractives obtained from mistletoe contain extractives with different composition from those of the adjacent eucalyptus on which they grow parasitically. These findings support the view that extractives are formed in situ from translocated primary metabolites.

Starch and sugars stored in the xylem ray and parenchyma cells are reported to be the raw materials for extractive production (Bosshard 1968; Hillis 1968; Hemingway and Hillis 1970). Hillis (1987) proposed that the biosynthesis of polyphenols involves both the shikimic acid and tricarboxylic acid pathways and takes place in the transition zone between sapwood and heartwood.

The function of extractives in the living tree is not clearly defined. However, wood extractives are believed to provide blockage of tissue from translocation stream (Hillis 1987). They also provide trees with resistance to destructive agents.

2.2.4 Dimensional Stability and Specific Gravity

How wood extractives affect the dimensional stability of wood depends on their chemical composition and location in the wood structure.

In gymnosperms, the longitudinal elements consist mainly of radially arranged tracheids, which can make up to 90 percent of their structure (Haygreen and Bowyer 1996). In addition to tracheids, some softwoods also have longitudinal resin canals in which the tree exudates most of its oleoresin.

The only possible locations for softwood extractives are either in the lumen of the tracheids and/or as inclusions in the cell wall structure. In hardwoods, extractives can be contained in the vessel elements, in the lumen of fibers or included in the cell wall.

The chemical constitution of extractive components, their size and molecular weight, and their affinity with the ligno-cellulosic wood complex will dictate their location within the wood structure. Low molecular weight monomers will be found in voids in cell walls, while high molecular weight components will be mostly located in the lumen of vessels, tracheids, or fibers.

Aromatic compounds derived from glucose such as flavonoids and condensed tannins usually have free hydroxyl groups and are water-soluble. Consequently, they will be more susceptible to adsorb water and induce greater dimensional change. This also applies to terpenoids, which usually have a hydrophilic functional group attached to the hydrocarbon radical. In the contrary, pure hydrocarbons such as terpenes are volatile and will not affect dimensional stability.

Extractives are known to have a bulking effect in the wood structure (Hillis 1987). When located in the lumen, they have an additive effect, increasing the weight and specific gravity of wood. They also increase the apparent specific gravity of wood (DeZeeuw 1965).

There are numerous publications in the open literature demonstrating this effect. For example, Taras and Saucier (1967) referring to specific gravity, wrote that in practice specific gravity is measured without removing the extractives, resulting in an overestimate of the amount of wood substance. They noted that specific gravity is overestimated by 6 to 7.5% in southern pines due to the extractive content.

Taylor (1974) obtained increased tangential and longitudinal dimensions and reduced radial dimension in extracted hardwoods and softwoods, resulting in a lower specific gravity for extracted woods. Lee (1986) also obtained a significant correlation between alcohol-benzene extractives and specific gravity of red pine. In addition, after extraction, he also observed an increase in the tangential as well as in the longitudinal dimension and a decrease in the radial dimension, sufficient enough to induce a decrease in specific gravity. This phenomenon is explained by the fact that the volume increase is due to an expansion of wood substance caused by water molecules occupying sorption sites where extractives have been removed (Taylor 1974).

Extractives within the cell wall structure would likely affect some mechanical properties of wood (Ajuong and Breese 1997). Hillis (1987) revealed that the hydrated S2 layers of tracheids in red pine contained 25% free space having cross sections of 16 to 60Å, large enough to contain molecules of extractives (A monomer of flavonoid is 6.3Å). This results in molecules of wood extractives maintaining the wood structure in a semi-swollen condition, and hindering the number of available sites for the formation of intermolecular lignin-cellulose and/or lignin-lignin bonds (Ajuong and Breese 1997).

2.2.5 Shrinkage and Wettability

There is evidence in the literature linking extractive content to checking and collapse when drying at high temperatures. Erikson (1968) obtained a highly significant positive correlation between hot-water soluble extractives and shrinkage in redwood implying a greater susceptibility to drying checks. Meyer and Barton (1971) looked at the extractives content of boards after drying and found collapsed boards to average 18.8% acetone soluble extractives while un-collapsed boards averaged 12.6%. Demaree and

Erickson (1976) investigated the relationship between extractive content and volumetric shrinkage for wood samples dried at various dry bulb temperatures. They found that at temperatures of lower than 190°F, the quantity of extractives was directly related to shrinkage. They hypothesized that at low drying temperatures, the extractives were acting as bulking agents, but at higher temperatures they become heat sensitive and made wood cell susceptible to collapse during apparent free water loss.

Wood extractives are also reported to affect the wettability of wood surfaces. Polar and hydrophilic extractives might increase wetting and non-polar extractives might decrease wetting. Chen (1970) obtained improved wettability and increased pH in all tropical woods used in his study. Jordan and Wellons (1977) also attributed the poor wettability found in keruing (*Dipterocarp* spp.) to extractives present in the veneer samples tested. Maldas and Kamdem (1999) observed the opposite effect. In their experiment, wood extracted with an ethanol-toluene solvent exhibited a higher contact angle (lower wettability) compared to un-extracted samples. They suggested that the higher contact angle was due to the hydrophobic nature of the extracted wood surface promoted by the migration of hydrophobic extractives to the wood surface. They suggested that the more hydrophobic extractives such as waxes and long chain hydrocarbons are present in wood, the less water this species will absorb.

Furthermore, wood extractives are reported to reduce wood permeability (Bosshard 1968; Bailey and Preston 1969).

2.2.6 Mechanical Properties

There is some controversy regarding the influence of wood extractives on mechanical properties. Brown et al. (1952), observed an appreciable effect from wood

extractives on compression parallel to grain, but there was no significant effect on shock resistance. Kellogg and Ifju (1962) argued that the effect of the removal of extractives could be positive or negative depending upon the mechanical properties under consideration and the location of extractives in the wood structure. Ajuong and Breese (1997) investigated the creep behavior of extracted and un-extracted blocks of Pai wood (*Afzelia africana* Smith) and concluded that the extractive fractions located in the lumen have no significant effect on short term creep, while the removal of cell wall-resident components permitted significant and accelerated creep development.

2.3 Factors Affecting the Weathering of Wood Surfaces

2.3.1 Factors Inherent to Wood

2.3.1.1 Density Variation

Density is one of the most studied properties of wood and is the primary factor influencing the properties of wood surfaces. Density is defined as the ratio of mass per unit volume at a given moisture content (Kollman and Cote 1984). The density of the solid wood substance is about 1.5g/cm^3 and is similar for most timber species. The relative proportion of the main constituents of wood affects wood density. Kollman and Cote (1984) estimated that the specific gravity of cellulose from spruce wood was about 1.58, while that of lignin was about 1.38 to 1.41. This explains why the proportion of cellulose to lignin will certainly influence density. Variations in densities are also due to the proportional amounts of different tissue types such as fibers, tracheids, vessels, resin ducts, wood rays, and their dimensions, especially the thickness of the cell wall.

The density across a wood section is affected by the width of the annual ring and the percentage of summerwood. However, there are variations between species. For

example, in spruce, the wood of lowest specific gravity is always produced near the pith of the tree where wide rings are usually formed. In pine and larch trees, the density increases outward from the center of the stem and reaches a maximum correlated with an optimum width of the growth rings; later, with the formation of narrow rings, the density decreases. Wood density and structural properties play an important role in the weathering behavior of wood surfaces (Sell and Feist 1986). For example, Yalinkilic et al. (1999) revealed that wood density and extractive content were the key wood properties interacting with varnish and wood preservatives in outdoor exposure of chestnut (*Castanea sativa* Mill.) and Scotch pine (*Pinus sylvestris* L.). Anderson et al. (1961) exposed four hardwood species (yellow poplar, quaking aspen, white oak and hard maple) to artificial weathering conditions, and observed a degradation pattern from poplar and aspen similar to that of softwoods. They explained this result by differences in the density of species used in their experiment. Feist (1994) also reported results showing that aspen had finishing and weathering characteristics similar to those of softwoods like ponderosa pine, fir, hemlock, and spruce.

Williams et al. (2001-a), reporting results of a 14 year outdoors weathering tests on lodgepole pine, Engelmann spruce, ponderosa pine and western hemlock, revealed that large differences exist between earlywood and latewood erosion rates during weathering. Erosion rates varied from 33μm/year for lodgepole pine latewood to 58 mm/year for western hemlock and red alder earlywood. This was in contrast with another project on tropical species with no clear delimitation between earlywood and latewood with uniform density distribution across the diameter of the trunk, which showed that

erosion rates were less variable and more uniform across the surface (Williams et al. 2001-c).

The orientation of the annual rings is an important factor for outdoor exposure. Cracks usually develop along rays. A board with a high proportion of horizontal annual rings (flat sawn) has rays oriented face to face and cracks can easily develop. A board with a high proportion of vertical annual rings oriented from the edge to the center of the board (quarter sawn) may show less cracks, because rays will reinforce parts of the board and prevent face to face cracks to force through. Williams et al. (2001-b) reported that for Douglas fir, loblolly pine, southern pine, western red cedar, red oak, and yellow poplar, the erosion rate increased as the angle of exposure decreased from 90 to 0 degrees. However, they noticed a notable exception to this for western red cedar, which had the fastest erosion rate at a 45 degrees exposure. For some species, particularly western red cedar and southern pine (earlywood), erosion rates differed for tangential and radial surfaces. Little difference was observed between erosion rates of tangential and radial surfaces for the other species.

The mechanism through which density affects wood shrinkage and ultimately the development of cracks and checks on the wood surface is still the subject of investigation. Some of the hypotheses proposed summarized by Quirk (1984) include: alternation of latewood and earlywood layers within the annual ring, effects of ray tissue, differing fibril angle in radial and tangential walls, presence of extractives, differences in number of transverse walls per unit of planar direction, and the degree of lignifications in the radial or tangential cell wall.

2.3.1.2. Juvenile wood, pith, and growth ring orientation

The pattern of weathering degradation from pith to bark is also variable due to the occurrence of juvenile wood. Juvenile wood can be defined as the portion of the xylem surrounding the pith in a cylindrical column whose cells were formed by a young cambium (Smith and Briggs 1986). Another definition provided by Rendle (1960) considers juvenile wood as secondary xylem produced by cambial regions that are influenced by activity in the apical meristem. Juvenile wood is also referred to as core, inner or pith wood as opposed to outer or mature wood (Panshin and DeZeeuw 1980; Zobel and Sprague 1998). The occurrence of juvenile wood is explained by the prolonged influence of the apical meristem in the region of active crown growth during the growing season (Panshin and DeZeeuw 1980). As the tree crown growths upward, the cambium at a lower height becomes less subject to the direct influences of the elongating crown region and adult wood is formed (Panshin and DeZeeuw 1980).

Compared to mature wood, juvenile wood of conifers is known to possess lower quality compared to mature wood. It usually has lower specific gravity, shorter tracheids length, larger fibril angle, lower transverse shrinkage, lower percentage latewood, more compression wood and higher equilibrium moisture content (Bendtsen 1978; Haygreen and Bowyer 1996). Large fibril angles and high amounts of reaction wood in juvenile wood cause excessive longitudinal shrinkage and instability in service (Bendtsen and Senft 1986). Short fibers, high fibril angles, thin cell walls, and low percentages of latewood in the annual ring contribute to lower bending strength and cause unusual warping problems (Zobel and Sprague 1998).

Chemical characteristics also differ between juvenile and mature wood. For example, Zobel and Sprague (1998) reported a higher proportion of cellulose to lignin in radiata pine (*Pinus radiata*) mature wood and higher hollocellulose and alpha cellulose proportions in juvenile wood in short leaf pine (*Pinus echinata*).

A juvenile core is also present in most hardwood species (Maeglin 1987), where it is characterized by excessive amounts of tension wood. This has been observed on *Populus* species (Isebrands and Bensend 1972) and ash (White and Robards 1965) when rapidly grown. Like compression wood, tension wood shrinks more than normal wood, frequently causes dimensional instability in lumber during seasoning and is more prone to collapse (Bendtsen 1978). The juvenile core in hardwoods is also known to possess poor physical properties, low specific gravity, low strength, and high shrinkage (Fukazawa 1984; Smith and Briggs 1986).

Based on the above difference in properties, it is reasonable to expect that wood located near the pith would show high instability resulting in crack development, and low weathering degradation due to its low lignin content. Sandberg (1996, 1997) found that the distance between sawn timber in the log and the pith with the surrounding juvenile wood was of vital significance for cracking. Timber from nears the pith or distinctly containing the pith has a higher relative crack length compared to timber sawn away from and lacking the pith. In addition, he hypothesized that the proportion of cracks can be related to pith cracks, which were present before the log was sawn, or the reduction in the angle of annual rings near the pith. Stehr and Ostlund (2000) investigating the tendency of wood surfaces to develop cracks after machining operations concluded that there were greater risks for cracks on the pith side than on the bark side. However, Flaete (2000)

observed the opposite effect and hypothesized that despite the fact that juvenile wood induces more crack formation; its straight grain direction may prevent cracks from propagating. The influence of juvenile wood and variation from pith to bark therefore needs to be further investigated.

2.3.1.3 Knots

A knot is a branch base that is embedded in the wood of a tree trunk or of larger limb or branch (Panshin and DeZeeuw 1980). The presence of knots in wood is detrimental and causes a loss in value and properties. The influence of knots depends upon their size, location, shape, and soundness. The orientation of the grain is usually distorted around the knot. The presence of knots in lumber affects its mechanical and physical properties. The knot itself is harder, more dense, often more resinous, and shrinks in a different manner that the surrounding wood tissue (Panshin and DeZeeuw 1980). These characteristics lead to uneven wear, higher susceptibility to checking, and difficulty in painting.

2.3.2 External Factors of Weathering

Environmental and biological factors such as light, temperature, moisture changes, wind, and microorganisms affect the weathering of wood surfaces. Among these, light, moisture, oxygen are the most important.

2.3.2.1 Light

Sunlight induces photochemical reactions leading to the discoloration of wood surfaces (Hon and Ifju 1978). Wavelengths of sunlight reaching to earth range from the ultraviolet region (200nm) to infrared (2300nm) (Bird et al. 1982).

Color is defined as a sensation evoked as a response to the stimulation of the eye by the radiation of certain wavelengths and intensities (Wengert 1966). The human eye generally responds to wavelengths from 400 to 700 nm, the visible range. Shorter wavelengths, from 200 to 400 nm are the UV range, and longer wavelengths from 700 to 50,000nm are the infrared range (Wengert 1966). The most common form of radiation used by the eye to determine color is that emitted from the sun or from artificial sources. When radiation strikes an object, it is absorbed, reflected or transmitted. The reflected wavelength received by the eye indicates the color of the object. For example, a white color would reflect nearly 100% at all wavelengths, while reflection from a black color is nearly zero.

The UV component of light (200nm-400nm) representing about 6% of the total solar irradiation has been reported to be the fraction inducing photochemical reactions in wood (Browne and Simonsen 1957; Sandermann and Schlumbom 1962; Hon and Ifju 1978; Feist and Hon 1984; Grelier et al. 2000). The initial color change of wood exposed to sunlight is a yellowing or browning, later followed by graying of the wood surface. These changes are superficial, occurring only to a depth of 0.05 to 0.5 mm, and are caused by ultraviolet (UV) light, which initiates the photodegradation by changing the chemical composition of the wood surface especially lignin. However, Browne and Simonson (1957) found that infrared light penetrated deeper in wood than visible light, while penetration by UV light was negligible, no more than a few millimeters. They also reached the conclusion that light turns wood brown in color, and browning occurred more rapidly in UV light than in visible or infrared light. Stout (1958) showed that absorption of UV light in wood is primarily due to lignin and lignin like substances. In his study,

pine cellulose exhibited a high reflectance, whereas the reflectance curve for lignin substances approximated that for wood.

Wengert (1966) reported that atmospheric gases were an important factor in the color change of wood exposed outdoors. In his project, air, oxygen, nitrogen, and argon each had a different effect on wood subjected to intense UV light. Redwood and birch samples showed rapid darkening during the first hours of exposure to air, oxygen, nitrogen, and argon. After initial darkening, samples exposed in oxygen and air stopped darkening and became lighter, while samples exposed to nitrogen continued to darken throughout the exposure period.

2.3.2.2 Moisture changes

Wood normally shrinks as it dries and swells as it absorbs moisture. The forces exerted in shrinking and swelling are great and have a marked effect on the permanence and serviceability of anything made of wood. As water leaves the spaces between wood strands during drying, they are drawn together, causing the fiber walls to be reduced in thickness and the fibers themselves to be reduced in girth. This contraction of the fibers causes the whole piece of wood to shrink. When green or wet wood dries, the water leaves the fiber lumens first; only when they are empty does continued drying remove the water from the fiber walls.

The weathering of unprotected woodwork exposed to the weather is due to same basic principles. When the surface layers of a dry board become damp, they try to swell but are restrained by the dry interior. As a result, the surface layers of fibers become somewhat crushed. As the surface dries out again, the crushed wood shrinks more than originally, causing fine cracks to open up. If this is repeated over and over again, as is the

case in unpainted wood, numerous little cracks develop that not only mar its appearance but also permit the deeper penetration of moisture. Although moisture will pass through protective paint, it does so slowly and, as a result, such large differences in moisture content between surface and interior layers do not develop, and serious compression set does not occur (Anon 1957). Visible cracks arise on the wood surface during outdoor exposure because of the growth of microcracks formed during the drying of the wood, photochemical reactions, or moisture induced stress field (Coupe and Watson, 1967).

Wood shrinks most in the direction of the annual growth rings (tangentially), somewhat less across these rings (radially), and very little, as a rule, along the grain (longitudinally). Sandberg (1999) measured the number and average lengths of cracks occurring on wood surfaces exposed outdoors for 33 months, and found that the radial surfaces had significantly smaller number of cracks than on tangential surfaces. On the radial surfaces, the cracks were primarily found in the annual ring border and the early wood, while on the tangential surface, they appeared in the latewood and across the whole exposed surface. The difference in crack susceptibility between radial and tangential surfaces is mainly the result of stresses, which arise in the wood as a consequence of anisotropic moisture movement of wood material and the moisture gradient between the surface of the test pieces and their internal regions (Sandberg, 1999). The shrinkage and swelling in the tangential direction are about twice as large as the radial movement. Stamm (1964) proposed that wood for outdoor use should have vertical annual rings (quarter sawn). This minimizes the risks of cracks as a consequence of anisotropic moisture movement (Browne 1960; Stamm 1964). Sandberg (1996 and 1997) researching the influence of annual ring orientation on crack formation in pine and

spruce found that timber exposed to cycles of wetting and drying developed increasing crack length irrespective of their prior cross sectional location on the stem.

Flaete et al. (2000) investigated cracks formation in solid wood sidings of aspen and Norway spruce exposed to accelerated weathering. They observed a high number of short cracks in aspen and a fewer but more injurious number of cracks in spruce. They explained this result as a consequence of the more asymmetrical cross sectional pattern in aspen, eventually preventing cracks from propagating.

Severity of shrinkage varies between species, but is particularly high in refractory woods such as oak, which contains up to 32% of its wood volume as ray tissue (Gaby, 1963). It is well known that tangential shrinkage is greater than radial shrinkage. Consequently, shrinkage is more severe in flat sawn boards. Since the long axis of the wood rays is at a right angle to annual rings, they are subjected to a sawing action that differs from longitudinal elements. The combination of ray orientation and the sawing action may be compounding factors leading to localized drying stresses that result in increased surface checking of oak boards.

Shrinkage not only differs with the three directions of grain, but also differs amongst species. It varies widely in material cut from the same species and even in material cut from the same tree. In general, heavier species of wood shrink more across the grain (transversely) than lighter ones. The overall, or volumetric, shrinkage of wood also generally increases with an increase in specific gravity. This relationship holds not only within a species, but also fairly well for a large number of species of both softwoods and hardwoods. Deviations from this relationship are usually caused by stresses, such as those set up in drying, and by water-soluble extractives (Anon 1999), which reduce

shrinkage because of their bulking effect when held between the strands within the fiber walls.

When a piece of wood of high moisture content dries, stresses are set up in various parts of the structure resulting in the phenomena which are normally referred to as checking, shaking, warping and twisting (Coupe and Watson 1967). Although seasoning and weathering are different processes (the former resulting from a single drying cycle and the latter from many), they appear to manifest themselves in a similar way. Both involve dimensional changes due to moisture changes in wood cells.

Many researchers have studied seasoning checks. Schniewind (1959) stated that seasoning checks normally occur as a result of setting up of moisture gradients leading to high tensile stresses on the faces of drying boards. This results in the formation of checks, which often occur in the rays and extend radically into the boards. The assumption has been made that this problem resulted from the low tensile strength of the ray tissue in the tangential direction. However, work on black oak by Schniewind (1959) showed that the rays in this species exhibited considerably higher tensile strength than found in longitudinally oriented cells.

The microscopic structure of wood has a major influence on the development of cracks and checks. Booker (1998) suggested that most of the resistance to crack development and propagation occur in S_2 layers, which are the thickest of the cell wall layers. In a single cell wall, a crack would propagate by cutting through the matrix material in the same direction as the microfibrils since the energy required to cut microfibrils is much larger than that to cut the matrix material. Consequently, the cracks propagate at an angle to the axis similar to the microfibrils angle. This suggests that the

position and properties of the specimen from the pith will influence the extent and pattern or crack formation.

2.3.2.3 Angle of Exposure

The angle of exposure of samples in the field can affect the performance of wood exposed to weathering. This was confirmed by Evans and Banks (1986), who investigated the influence of the season and angle of exposure on the weathering of wood samples in Australia. Williams et al. (2001-b) reported that for Douglas fir, loblolly pine, southern pine, western red cedar, red oak and yellow poplar, the erosion rate increases as the angle of exposure decreased from 90 degrees to 0 degrees from the horizontal. However, they noticed a notable exception to this for western red cedar, which had the fastest erosion at 45 degrees.

2.3.2.4 Temperature

The role of temperature in the natural weathering process is generally felt to be of less importance than that of light or water (Rowell 1984). However, Derbyshire et al. (1997) investigated the influence of temperature on photodegradation rates in wood exposed to up to 400 hours of artificial weathering. Their results confirmed that photodegradation rates for the different species were temperature dependent and increased with rising temperature.

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Chapter 3

Fourier Transformed Infrared and X-ray Photoelectron Spectroscopy Analysis of Red Oak (*Quercus rubra*), Black Cherry (*Prunus serotina*) and Red Pine (*Pinus resinosa*) Extractives and Wood Surfaces

ABSTRACT

The Fourier Transformed Infrared (FTIR) analysis of extractives removed from black cherry (*Prunus serotina*), red oak (*Quercus rubra*), and red pine (*Pinus resinosa*) wood samples using ethanol, ethanol-toluene, and water was conducted to obtain basic understanding of the nature of the components removed using those solvents.

Results indicated that substances removed from black cherry and red oak with ethanol and ethanol-toluene are made up of fatty acids and their esters as well as aromatic compounds probably from flavonoids. Water extraction predominantly removed low molecular weight carbohydrates, sugars, and condensed tannins. The FTIR spectra of surfaces revealed no major difference between extracted and non-extracted wood surfaces. However, there were signs of increased exposure of cellulose and hemicelluloses on extracted wood surfaces. X-ray Photoelectron Spectroscopy (XPS) indicated a rise in the oxygen to carbon (O/C) values following extraction treatments due to the partial removal of extractives including fatty acids, esters, sterols, terpenes, and phenolic compounds such as lignans. The C1s peaks indicated a decrease in the area of the C1 peak following extraction. The C2 peak increased as a result of increased exposure of cellulose components on the wood surface. The O1s peaks showed an increase in the O1 peak originating from cellulose.

3.1 Introduction

Wood extractives include several classes of organic compounds ranging from relatively simple molecules such as phenols and sugars to highly complex flavonoids, tannins, and resins (Hillis 1987). Extractives are soluble in different organic solvents, and polar and non-polar organic solvents are used to remove extractives without any great alteration in either their structure or that of the wood.

Extractives have different solubility characteristics, which enable their selective removal through the use of various organic solvents (Laks 1991). Toluene is a non-polar solvent, traditionally used to remove the extractable non-polar compounds located within the cell lumen (Ajuong and Breese 1998). Previous reports indicate that such substances are long chain fatty acids, fats, resins, waxes, terpenes, and phytosterols with relatively high molecular weights (Hillis 1987; Anon 1999). It is reported that ethanol solvent can penetrate the cell wall and swell the wood structure (Laks 1991; Ajuong and Breese 1998). Thus, ethanol would be expected to remove materials from within the wall structure, including condensed tannins, flavonoids and phenolics (Laks 1991). Hot water extraction recovers condensed tannins and water soluble, low molecular weight carbohydrates (Ajuong and Breese 1998).

Conventional methods based on the oven dry extractive-free weight have been developed for determination of the total extractive content of wood. They include ASTM standards D1105-96, D1107-96, D1108-96, and D1110-84 (ASTM 1999), TAPPI standards T204 OM-88, T207 OM-88, and T264 OM-88 (TAPPI 1993). These methods are based on the reflux of hot organic solvents into wood and provide satisfactory information for the determination of the total extractive content of a given species. Fine

analytical methods are needed to identify the chemical components of the extractives and characterize their structure. These include solid, liquid, and gas chromatography, mass spectrometry, X-rays photoelectron Spectroscopy (XPS), Infrared Spectroscopy (IR), and Hydrogen and Carbon Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR).

Infrared spectrometry has been widely used to investigate various aspects of wood and its chemical structure. It has been successfully used to monitor chemical changes occurring on the surface of weathered wood (Owen et al. 1993; Dawson and Torr 1992; Cui et al. 2003). Diffuse Reflectance Infrared Fourier Transformed (DRIFT) spectroscopy was used to determine the klaxon lignin and the polyflavonoid content of *Pinus pinaster* bark (Vasquez 2000). Fourier Transformed Infrared Reflectance (FTIR) was also used to indirectly measure the lignin content in Sitka spruce (*Picea sitchensis* (Bong.) Carr.) wood (Costa e Silva et al. 1999).

FTIR has been employed to study pulp (Berben et al. 1987), chemically modified wood (Schultz 1985), and treated wood (Liu 1994; Zhang and Kamdem 2000). DRIFT was also used to characterize and identify the major functional groups of extractives recovered from Pai wood (*Afzelia Africana* Smith) using various organic solvents (Ajuong and Breese 1998). The FTIR technique was combined with Phosphorous-31 NMR, Carbon-13 NMR, and GC/MS to characterize the polyphenolic compounds related to the color of western red cedar (*Thuja plicata* Donn) heartwood (Johansson 2000).

Another spectroscopic solid-state non-destructive technique used to monitor chemical changes on the surface of wood samples is X-ray Photoelectron Spectroscopy (XPS). XPS is based on a direct analysis of the kinetic energy of electrons which are excited by high energy X-rays and ejected (Kamdem et al. 1991). XPS has been used in

several applications in wood science for surface characterization. XPS has been used to study the chemical interaction between waterborne copper naphthenate and wood surfaces (Cracium and Kamdem 1997). XPS was used to analyze changes occurring during the fixation of CCA on the surface of treated wood, and to estimate the amount of cuprous oxide formed after post steam treatment (Ruddick et al. 1993; Maldas and Kamdem 1998; Kamdem et al. 1998). Other applications of XPS include surface analysis of different wood species (Sinn et al. 2001), surface characterization of chemically modified pulp and wood (Chtourou et al. 1995; Torr et al. 1996), evaluation of surface lignin on cellulose fibers (Kamdem et al. 1991; Johansson et al. 1999), and weathering of wood and wood-plastic composites (Owen et al. 1993; Matuana and Kamdem 2002).

The goals of this study were to use solid-state non-destructive tools such as FTIR and XPS to characterize the surface of wood before and after extraction using several organic solvents, and the extractives removed in order to understand the role of extractives in the durability of wood.

3.2 Materials and Methods

3.2.1 Materials

Three wood species were selected for this study: black cherry (*Prunus serotina),* red oak (*Quercus rubra*) and red pine *(Pinus resinosa).* All three species are largely available resources in the Northeastern United States. Oak and red pines are largely used in outdoor applications where wood is susceptible to variations in moisture content. Black cherry is mainly used in indoor applications. However, due to its specific color (due to its extractive content), it was a potentially interesting hardwood species for comparison with red oak.

Black cherry and red oak logs measuring 1.2m (4 feet) with top diameters larger than 35cm were randomly selected from the lumberyard at the Devereaux sawmill in Pewamo, Michigan. Red pine logs measuring 35cm in diameter and 2.4m (8 feet) in length were obtained from the Kellogg Forest in Augusta, Michigan.

The logs were sawn in a traditional flat sawn scheme to obtain exterior boards with the main face in tangential direction and boards closer to the pith in radial direction. The thickness of each cut was set at 2.5cm (1inch), and 14 to 16 boards were obtained from each log, with approximately seven to eight boards for each half of the cross section. Care was taken to keep track of the position of each board from pith to bark. From each half section, the first two to three boards were flat sawn and the last four to five boards were quarter-sawn.

All boards were dried in a laboratory kiln following drying schedules recommended by the Forest Products Laboratory (Anon 1999). Drying schedule T8-B4 was used for black cherry, T4-C2 for red oak and T12-B4 for red pine. The final moisture content was between 6 and 8%. The boards were then stored until further use.

The density of samples at 12% moisture content from each log, determined according to ASTM standard D2395-93 were 393kg/m^3 for red pine, 624kg/m^3 for red oak, and 540kg/m^3 for black cherry.

Boards numbers 4 and 5 (heartwood), measuring 2.5cm x 40cm x 120cm from areas of the log at least 30mm away from the pith, and 50mm from the bark, therefore not including any sapwood material, were selected to prepare the samples.

The samples measured 4mm x 44mm x 80mm (T x W x L). Care was taken to keep the radial face as the main surface to be exposed.

The samples were then planed and successively sanded with 60, 100, 150, and 220mm grit sanding paper. Sanded specimens were conditioned to equilibrium moisture content of 10 ± 2 % before extraction.

3.2.2 Extraction

The samples were extracted with various combinations of solvents including ethanol, toluene, and water according to modified ASTM and TAPPI standards.

Water extraction was conducted according to ASTM 1110-96 (ASTM 1999) and TAPPI T207 OM-88 (TAPPI 1993). Solvent extractions were conducted according to TAPPI T204 om-88 (TAPPI 1993) and ASTM D1107-96 (ASTM 1999). The main modification was related to the fact that solid wood samples were used in the extraction process instead of grinded wood (powder) as recommended in the standards. The extraction time was consequently increased to remove more extractives from the specimens. Preliminary tests to determine the appropriate extraction time suggested that an extraction cycle of 72hours was sufficient.

Conditioned samples were divided into five groups. The first group was extracted with a mixture of ethanol: toluene (1:2 by volume) (Eth-Tol), the second group was extracted with ethanol: toluene for 72 hours and then extracted with water for 72 hours (Eth-Tol + Water), the third group was extracted with ethanol (Eth), the fourth group was extracted with ethanol for 72 hours and water for 72 hours (Eth + Water), and the fifth group was kept un-extracted as a reference (control). Twenty-four samples were extracted for each treatment from each species.

The total amount of extractives removed (Table 3.1) was calculated by the weight difference of the moisture free samples before and after extraction as recommended by

the standard (ASTM 1999; TAPPI 1993). Extracted specimens were stored under dark in the conditioning room until further tests.

3.2.3 Sample Preparation for FTIR and XPS

Extractives collected from the extraction process as well as extracted wood samples were characterized with FTIR and XPS to monitor the modifications that occurred.

Extractives solution was concentrated by using roto-evaporation under 25 inches vacuum at 40°C. Two milligrams of extractives were thoroughly mixed with 200mg of dry potassium bromide (KBr). About 10mg of the mix was subjected to FTIR analysis. For solid wood samples, specimens measuring 4mm x 12mm x 12mm were used for the FTIR and XPS.

Table 3.1: Extractives Removed[1] as a percentage of wood dry weight

	Eth-Tol	Eth-Tol +Water	Eth	Eth + Water	Water
Red Pine	2.67 (0.52)[2]	3.54 (0.39)	3.32 (0.67)	4.6 (0.64)	1.80(0.25)
Black Cherry	2.02 (0.54)	3.1 (1.17)	3.21 (0.97)	4.79 (0.53)	3.46(0.44)
Red Oak	2.03 (0.59)	2.76 (0.12)	1.59 (0.08)	4.07 (0.41)	3.44(0.10)

[1] Mean of four replicas

[2] Numbers in parenthesis are standard deviation

3.2.4 FTIR

FTIR was performed on a Nicolet Protégé 460 spectrometer equipped with Spectra-Tech diffuse reflectance accessory. The Diffuse Reflectance Infrared Fourier Transform (DRIFT) technique was used for solid samples. A total of 64 scans were collected from 400 to 4000cm^{-1} wavenumbers at a resolution of 4cm^{-1}.

3.2.5 X-ray Photoelectron Spectroscopy Analysis

XPS analysis was performed on a PHI 5400 ESCA System from Physical Electronics with a base pressure of less than 10^{-8} Torr, equipped with a non-monochromatized Mg anode X-ray source. Kinetic energy measurements were made using a hemispherical electrostatic analyzer with a 150-mm radius working at a constant-pass energy mode.

Samples were mounted on a stainless steel sample holder with stainless steel rings and screws. Care was taken to obtain a flat surface and to avoid contamination of the sample. Data was collected using a MgK (1253.6 eV) anode source at 300 watts. For each sample, the spectral data for C_{1s} and O_{1s} were collected.

3.3 Results And Discussion

3.3.1 FTIR of Wood Extractives

FTIR spectra of components extracted by ethanol, ethanol-toluene, and water are presented in Figure 3.1 (black cherry), Figure 3.2 (red oak), and Figure 3.3 (red pine).

3.3.1.1 Black Cherry Extractives

FTIR spectra of black cherry (BC) extractives (Figure 3.1) indicate the removal of several functional groups with both ethanol and ethanol-toluene extractions.

Table 3.2: Peak assignment for FTIR spectra

Range (Wavenumbers in cm^{-1})	**Peak Assignment**
1738-1709	C=O stretch in unconjugated ketone, carbonyl and ester groups
1675-1655	C=O stretch on conjugated p-substituted aryl ketones
1605-1593	Aromatic skeletal vibration plus C=O stretch
1515-1505	Aromatic Skeletal vibration
1470-1460	C-H deformation in CH_3 and CH_2
1430-1422	Aromatic skeletal vibration combined with C-H in-plane deformation
1370-1365	Aliphatic in CH stretch in CH_3
1330-1325	S-ring plus G-ring condensed
1270-1266	C=O stretching
1230-1221	C-C plus C-O plus C=O stretch
1166	C=O in ester group

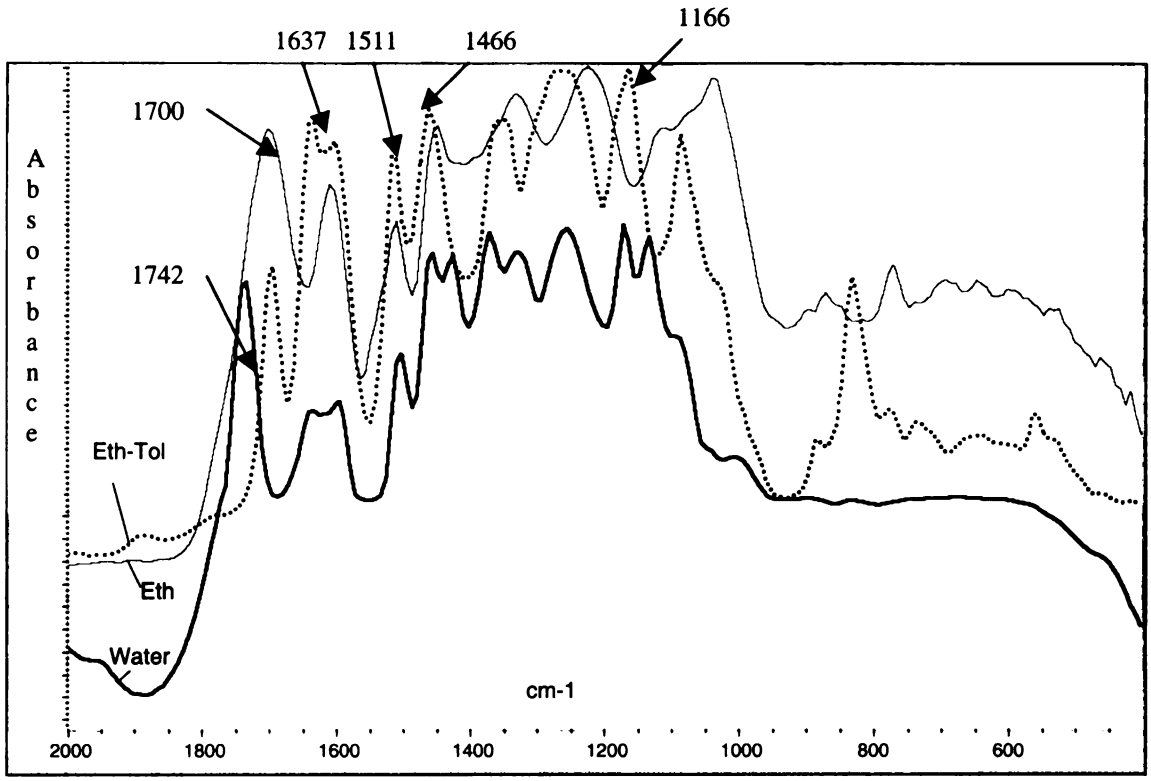

Figure 3.1: FTIR spectra of black cherry extractives removed with Ethanol-Toluene (Eth-Tol), Ethanol (Eth) and Water

Peak assignments reveal similar strong absorption bands at 1705cm^{-1}, 1608cm^{-1} and 1511cm^{-1}, originating from carbonyl vibrations (C=O), carboxylic stretching and weak skeletal carbon-to-carbon single bonded vibration respectively. It has been suggested that carbonyl stretching at 1705cm^{-1} arises from dimerized saturated aliphatic acids (Ajuong and Breese 1998). Ethanol-Toluene and Ethanol extraction systems also revealed strong peaks at 1466cm^{-1}, which were attributed to methylene vibration. Next to the methylene peak appeared a broad band at 1364 cm^{-1} attributed to methyl symmetrical bending. This band was coupled with a band at 1260 cm^{-1}, which was attributed to a carbon bonded to single oxygen. Ethanol-toluene spectra revealed a strong band at 1166cm^{-1} that arose from saturated esters. This band was not present in the spectra of components removed with ethanol. Ethanol and ethanol-toluene substances both had broad bands at 1079 cm^{-1} and 1042cm^{-1} arising from aryl alkyl ether, which normally absorbs between 1070-1020cm^{-1} (Ajuong and Breese 1998). The peak at 833cm^{-1} from the ethanol-toluene component's spectra was probably due to an out of ring carbon single bonded hydrogen vibration. Previous reports indicate that ethanol-toluene removes waxes, fats, some resins, and portions of wood gums. Hot water extracts are made up of tannins, gums, sugars, starches and coloring matter (Anon 1999). Consequently, it can be hypothesized that the carbonyl and carboxylic group peaks detected indicate the presence of fatty acids and their esters. It can also be inferred that the strong carbon-to-carbon absorption bands are an indication of aromatic - predominantly ethanol soluble compounds.

The spectra of extractive components removed with water displayed a shifted carboxylic absorption band at 1742cm^{-1}. Absorption bands at 1615cm^{-1} were due to

carbonyl stretching and the 1505cm^{-1} bands were due to skeletal carbon-to-carbon ring vibration. Both bands were weak, probably due to the low content in substances with aromatic structure. However, absorption bands at 1371cm^{-1} (methyl asymmetrical bending), 1269cm^{-1} (carbon bonded to a single oxygen) and 1166cm^{-1} (carboxylic double bond) were all relatively strong and probably originated from low molecular weight carbohydrates (Anon 1999).

3.3.1.2 Red oak Extractives

The red oak extractives spectra presented in Figure 3.2 also showed similar absorption peaks for ethanol and ethanol-toluene. Both spectra showed strong absorption peaks at 1703cm^{-1} attributed to carbonyl stretching; 1615cm^{-1} attributed to carboxylic vibrations; 1515cm^{-1} caused by within ring skeletal carbon-to-carbon single bonded stretching. Absorption bands at 1459cm^{-1} (due to methylene vibrations), 1372cm^{-1} (due to methyl asymmetrical bending) and 1238cm^{-1} (from an unknown origin) were also present. The absorption band at 1166 cm^{-1} - due to carboxylic stretching from saturated esters was not present as was the case for black cherry. The water extraction components showed similar patterns to that observed in cherry with a shifted absorption band for carboxyl vibrations at 1744cm^{-1}, a weak carboxylic shoulder and within ring carbon to carbon vibration at 1615cm^{-1} and 1515cm^{-1} respectively. The conclusion derived for red oak is similar to that obtained for cherry. It is believed that ethanol and ethanol-toluene removes fatty acids and their esters, and components removed by water extractions are probably made up of low molecular weight carbohydrates, sugars, and condensed tannins.

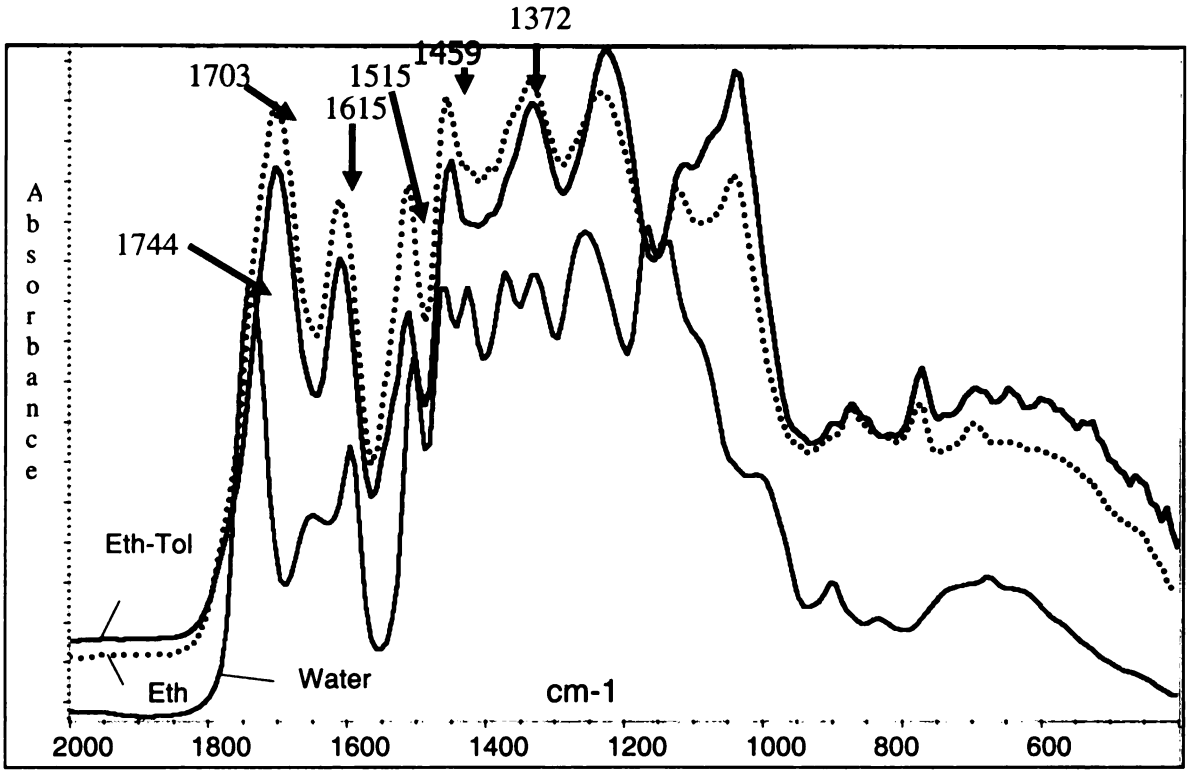

Figure 3.2: FTIR spectra of red oak extractives removed with Ethanol-Toluene (Eth-Tol), Ethanol (Eth) and Water

3.3.1.3 Red pine Extractives

The FTIR spectra of red pine extractives are presented in Figure 3.3. The most characteristic peaks for ethanol and ethanol-toluene extracts were 1738cm^{-1} for C=O in unconjugated ketones, carbonyls, and in esters groups; 1596cm^{-1} for aromatic carbon to carbon (C=C) skeletal vibrations, 1454cm^{-1} for C-H vibrations in methylene; 1372cm^{-1} for methyl asymmetrical bending; 1155cm^{-1} for C=C from saturated esters. For water extraction a weak C=O peak occurred at 1738cm^{-1}, followed by a weak skeletal C-C vibration at 1567cm^{-1}. There was also a broad absorption band at 1169 cm^{-1} due to C-O-C asymmetric stretch vibration.

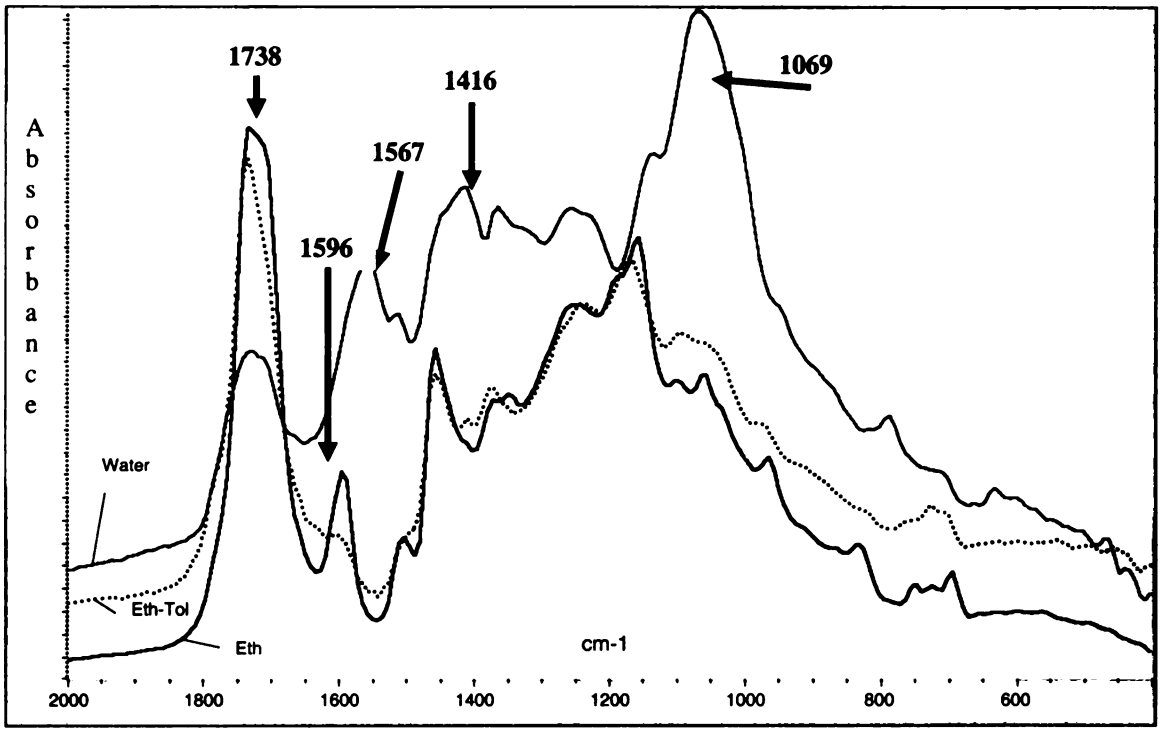

Figure 3.3: FTIR spectra of red pine extractives removed with ethanol-toluene (Eth-Tol), Ethanol (Eth) and Water

3.3.2 FTIR Spectra of Extracted Wood Surfaces

The FTIR spectra of extracted and non-extracted wood surfaces are presented in Figure 3.4 (black cherry), Figure 3.5 (red oak), and Figure 3.6 (red pine). The three figures show similar spectral characteristics between extraction treatments for all species. The characteristic peaks are bands at 1735cm^{-1} from C=O stretching in COOH, a broad band at 1650 cm^{-1} from C=O vibrations in α-ketone groups, and 1505cm^{-1} caused by aromatic skeletal vibrations. There are also C-H deformations at 1465cm^{-1}, aromatic skeletal vibrations at 1425cm^{-1}, symmetric C-H deformations at 1370cm^{-1}, C-O-C asymmetric stretching at 1230cm^{-1}, as well as C-O deformation at 1150cm^{-1}. The main difference between the un-extracted and extracted wood spectra was the low peak expression in the wavenumbers region below 1500cm^{-1} in un-extracted samples compared to extracted samples. It has been previously reported that the 1742cm^{-1} carbonyl peaks and the 1505cm^{-1} peaks originate from lignin molecules, while major peaks below 1500cm^{-1} - especially C-H deformations at 1465cm^{-1} and 1370cm^{-1} and asymmetric C-O-C deformations at 1265cm^{-1} and 1230cm^{-1} mainly originate from wood carbohydrates (Owen et al. 1993; Schultz et al. 1985). Consequently, the stronger expression of these peaks from extracted wood surfaces can be interpreted as a sign of increased exposure of cellulose and hemicelluloses on the wood surface.

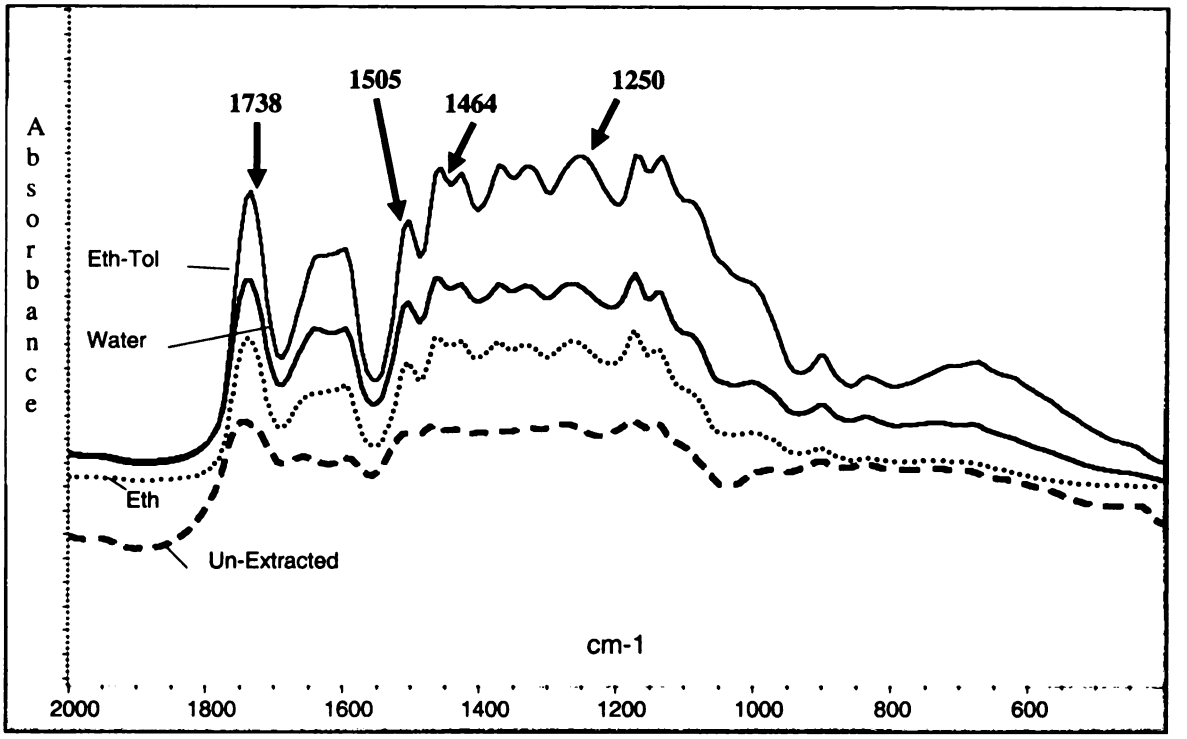

Figure 3.4: FTIR Spectra of black cherry extracted wood surfaces

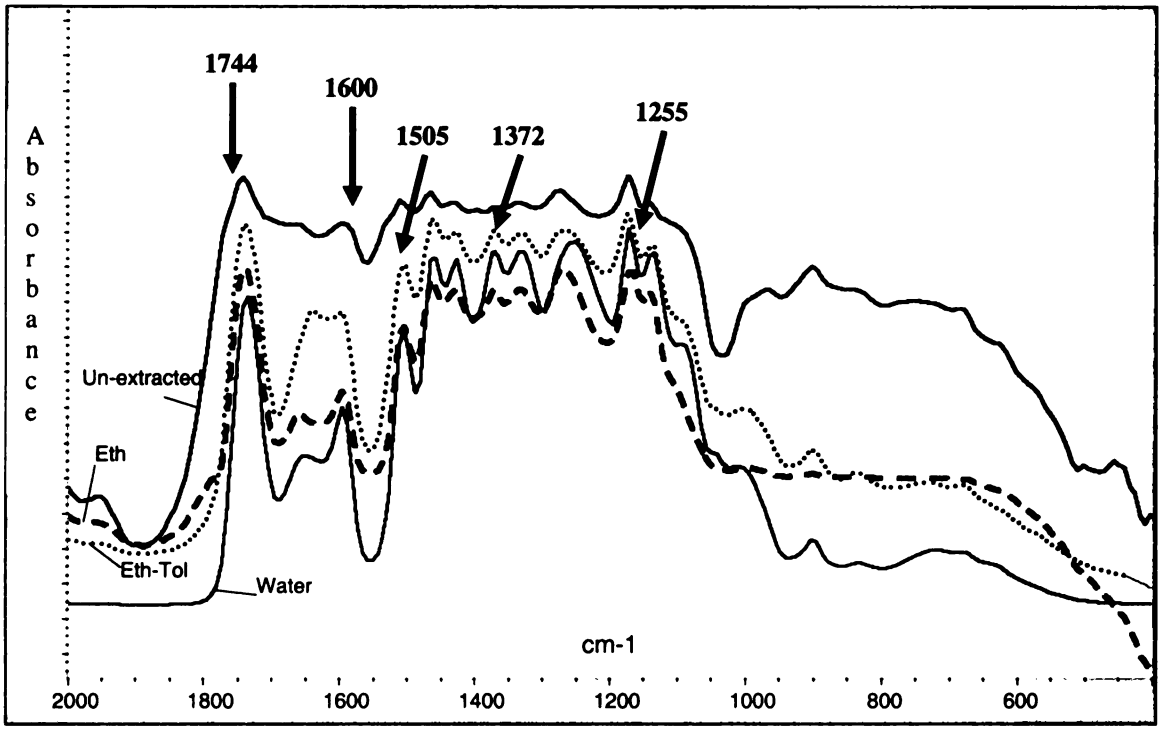

Figure 3.5: FTIR spectra of red oak extracted wood surfaces

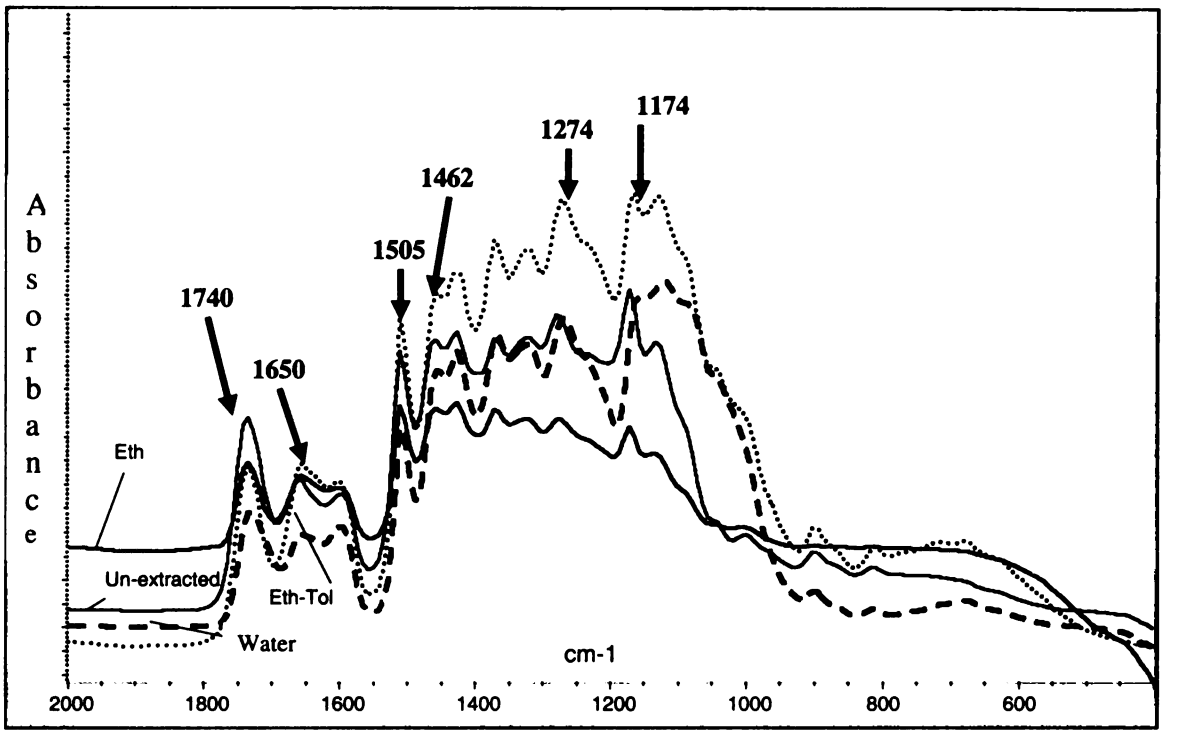

Figure 3.6: FTIR spectra of red pine extracted wood

3.3.3 XPS Surface Characterization of Extracted Wood Surfaces

It has been previously reported that the degradation of cellulosic materials and polymers can be detected by a change in the C_{1s} spectra and by a change in the O/C atomic ratio (Kamdem et al. 1991).

XPS spectra revealed the presence of O, C, N, and traces of Si (on untreated red oak). The relative composition of O and C atoms and the calculated oxygen to carbon (O/C) ratio for all species and extraction treatments are listed in Table 3.3.

The data presented shows that for red oak, the percentage of oxygen detected increased from 25.35% to 33.95% following ethanol-toluene extraction. The percentage rose to 34.05% when ethanol-toluene extraction was followed by water extraction, resulting in an increased O/C ratio (0.34 to 0.51). A similar trend was observed with specimens extracted with ethanol and ethanol followed by water, where the percentage oxygen detected increased from 25.35 to 29.45% and 31.12% respectively, resulting in the O/C ratio increasing from 0.34 to 0.42 and 0.46.

For black cherry, the total oxygen from the wood surface also increased, raising the O/C ratio from 0.32 (un-extracted samples) to around 0.50 for extracted samples. This effect was somehow less pronounced in red pine where the O/C rose from 0.29 to 0.35 for ethanol-toluene based extractions and 0.38-0.43 for ethanol based extractions.

Table 3.3: Percent of C_{1s}, O_{1s} and O/C peak of red oak, black cherry and red pine wood surfaces

	Treatment	C_{1s}	O_{1s}	O/C
Red Oak	Control	73.74	25.35	0.34
	Eth –Tol	66.05	33.95	0.51
	Eth –Tol + W	65.95	34.05	0.51
	Eth	69.88	29.45	0.42
	Eth + W	67.07	31.12	0.46
Black cherry	Control	75.19	24.81	0.32
	Eth –Tol	66.35	33.65	0.50
	Eth –Tol + W	67.62	32.38	0.47
	Eth	64.36	35.64	0.55
	Eth + W	68.49	31.51	0.46
Red pine	Control	77.36	22.64	0.29
	Eth –Tol	74.73	25.27	0.35
	Eth –Tol + W	74.05	25.95	0.35
	Eth	69.70	30.30	0.43
	Eth + W	72.29	27.71	0.38

The O/C ratios observed in control samples for all three species were lower or very close to the theoretical value of O/C for lignin (0.33) and significantly lower than that of pure cellulose (0.83) (Kamdem et al. 1991; Barry and Zoran 1990). The high carbon content in wood samples has been reported to be an indication of the presence of lignin and extractives on the wood surface (Kamdem et al. 1991; Barry and Zoran 1990). The increase in O/C following extraction treatments is due to the partial removal of carbon rich extractives such as resin, fatty acids, esters, sterols, terpenes, and phenolic materials.

C_{1s} Peaks

There is general agreement in the literature on the assignment of deconvoluted peaks C_{1s} for lignocellulosic materials (Kamdem et al. 1991; Barry and Zoran 1990; Liu et al. 1998; Kamdem et al. 2001; Briggs 1990). C1s deconvoluted in 4 components, C_1, C_2, C_3 and C_4. The assignment of deconvoluted carbon peaks is presented in Table 3.4 The C_1 peak corresponds to a carbon atom bound only to other carbon atoms and/or hydrogen atoms. It is established that this component arises mainly from lignin and wood extractives (Kamdem et al 1991). The C_2 component is due to a carbon bound to a single non-carbonyl oxygen atom, which has been shown to mainly derive from cellulose (Kamdem et al. 1991). The C_3 represents a carbon atom bound to one carbonyl oxygen or to two non-carbonyl oxygen atoms. The C_4 represents a carbon atom linked to one carbonyl oxygen and one non-carbonyl oxygen. The area of the C_1 peak (from lignin and extractives) logically decreased following extraction treatments for all three species. However, differences in magnitude were observed between the two hardwood species and the softwood species.

Table 3.4: Classification of carbon and oxygen peak components, C1s and O1s for woody materials.

Group	Chemical shift ΔE (eV)	Symbol	Carbon Atom or Oxygen Atom Binding
Carbon			
I	0.0 ± 0.4	C_1	C-C or/and C-H
II	1.5 ± 0.4	C_2	C-O
III	3.0 ± 0.4	C_3	C=O or/and O-C-O
IV	4.5 ± 0.4	C_4	O-C=O
Oxygen			
I	0.0 ± 0.4	O_1	O-C=O
II	1.5± 0.4	O_2	C-O

Source: Kamdem et al. 1991

Table 3.5: Summary of XPS Spectral Parameters in red oak

	Peak	Control	Eth-Tol	Eth-Tol+ W	Eth	Eth + W
C_1	BE (eV)	284.67	284.41	284.68	284.45	284.51
	Area (%)	53.98	34.32	30.07	43.87	42.21
C_2	BE (eV)	286.28	286.26	286.39	286.27	286.25
	Area (%)	37.00	53.60	58.13	45.72	49.08
C_3	BE (eV)	287.95	287.95	287.95	287.95	287.95
	Area (%)	7.01	10.16	9.87	8.18	8.40
C_4	BE (eV)	289.16	289.16	289.16	289.16	289.16
	Area (%)	2.01	1.93	1.93	2.23	0.31
O_1	BE (eV)	531.43	530.91	531.09	531.37	531.15
	Area (%)	11.02	2.91	4.49	10.55	7.55
O_2	BE (eV)	532.75	532.72	532.88	532.91	532.71
	Area (%)	88.98	97.09	95.51	89.45	92.45

In red oak, C_1 decreased from 53.9% to 34.6% (36% decrease) following ethanol-toluene extraction (Table 3.5) and a similar decrease was observed in black cherry (Table 3.6). For red pine however, the C_1 changed from 62.8% to 58.6% (Table 3.7) representing a decrease of only 4%. These differences are due to the nature of extractives contained in each species. A previous study reported a two-dimensional paper chromatogram of the sapwood and heartwood red oak extractives removed with a mixture of acetone and water (95:5) (Rowe and Conner 1979). They reported that hydrolyzable gallotannins such as hamamelitannin [5-galloyl-2-(galloylhydroxy- methyl)-ribofuranose] and ellagitannins were the predominant compounds. The characteristic compounds found in the black cherry family (Rosaceae) include cyanogenetic glycosides (Prunasin) and polyphenols (Rowe and Conner 1979). The wood of *Prunus* species has been also reported to contain up to 4.5 percent tannins (Rowe and Conner 1979). These are all simple phenols known to be present in heartwood either as free acids or esterified with glucose, polyols, and other phenols (Hillis 1987). Their removal would consequently cause significant variation to the C_1 peak. Pines known to be richer in less branched terpenes and terpenes derivatives had less variation in the C_1 peak.

The C_2 peak increased with extraction treatment as result of increased exposure of cellulose components on the wood surface. The effect was higher with ethanol extractions than with ethanol-toluene. Black cherry (72% increase) and red pine (93% increase) increased more than red oak (23% increase). A possible explanation is that the ethanol extractions were more effective at removing extractives associated with the cell wall, wood fibers and tracheids, which resulted in more cellulose components being exposed after extraction. The differences observed between black cherry, red pine, and

red oak are probably due to the amount of extractable material present in the wood structure before the treatment.

A slight increase in the C_3 peak was observed for red oak and black cherry and no significant difference was observed in red pine.

The C_4 peak representing a carbon atom linked to a carbonyl and a non-carbonyl oxygen was insignificant in all three species (only about 2%). This could be explained by a possible low concentration of carboxylic groups at the wood fiber surface (Kamdem et al. 1991).

O_{1s} Spectra

The assignment of O_{1s} peaks of wood materials have been previously discussed by several researchers (Kamdem et al. 1998; Liu et al. 1998; Hua et al. 1993). There is common agreement that the O1 peak originates from an oxygen atom linked to a carbon atom by a double bond, and the O2 peak with higher binding energy represents an oxygen atom linked by a single bond to a carbon atom. It has been previously shown that the O1 fraction can be associated with lignin and extractives, the elimination of which decreases the O1 fraction and increases the O2 fraction (Barry and Zoran 1990; Hua et al. 1993). Results obtained (Tables 3.5, 3.6, and 3.7) showed a decrease in the O1 peak with extractives in agreement with previous findings. At the same time the O2 peaks originating from cellulose and hemicelluloses increased as a result of more cellulose being exposed to the wood surface.

Table 3.6: Summary of XPS Spectral Parameters in black cherry

	Peak	Control	Eth-Tol	Eth-Tol+ W	Eth	Eth + W
C_1	BE (eV)	284.65	284.51	284.51	284.51	284.60
	Area (%)	58.00	36.02	39.29	29.94	41.37
C_2	BE (eV)	286.26	286.26	286.22	286.20	286.32
	Area (%)	31.96	53.85	48.84	55.17	48.36
C_3	BE (eV)	287.78	287.94	287.69	287.76	288.01
	Area (%)	7.26	9.40	9.26	11.96	9.19
C_4	BE (eV)	288.93	289.19	288.79	289.06	289.53
	Area (%)	2.78	0.74	2.61	2.93	1.08
O_1	BE (eV)	531.48	530.90	531.11	531.29	531.05
	Area (%)	7.25	2.34	8.25	5.91	5.23
O_2	BE (eV)	532.71	532.66	532.72	532.70	532.78
	Area (%)	92.75	97.66	91.75	94.09	94.77

Table 3.7: Summary of XPS Spectral Parameters in red pine

	Peak	Control	Eth-Tol	Eth-Tol+ W	Eth	Eth + W
C_1	BE (eV)	284.78	284.73	284.73	284.46	284.73
	Area (%)	62.85	58.68	57.01	41.90	49.50
C_2	BE (eV)	286.32	286.25	286.26	285.97	286.32
	Area (%)	23.72	30.34	32.76	45.87	39.88
C_3	BE (eV)	287.55	287.77	287.94	287.56	287.94
	Area (%)	6.14	6.71	7.25	9.76	8.60
C_4	BE (eV)	288.96	289.01	289.23	289.01	289.23
	Area (%)	7.29	4.27	2.98	2.47	2.02
O_1	BE (eV)	531.72	531.49	531.49	531.44	531.69
	Area (%)	18.94	4.69	4.75	11.59	14.59
O_2	BE (eV)	532.82	532.66	532.66	532.53	532.82
	Area (%)	81.06	95.31	95.25	88.41	85.41

3.4 CONCLUSION

FTIR and XPS were successfully used to characterize extractives removed with organic solvents and to analyze wood surfaces after extraction. The FTIR spectra showed that components removed by ethanol and ethanol-toluene are made up of fatty acids, saturated esters, and cyclic polyphenolic compounds. The water extracts mainly consisted of colorific matter, condensed tannins, and low molecular weight carbohydrates. The spectra obtained from extracted wood surfaces were very similar to that of un-extracted samples. However, absorption peaks related to polysaccharides were enhanced in extracted samples, as a result of hemicelluloses and cellulose becoming more exposed on the surface. This was confirmed by the XPS analysis that showed a decrease in the O/C ratio and a decrease in the C1 peak resulting from the removal of higher carbon content compounds from the wood surface. Therefore, the O2 spectra originating from cellulose increased considerably.

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Chapter 4

Influence of Wood Extractives on Moisture Sorption and Wettability of Red Oak (*Quercus rubra*), Black Cherry (*Prunus serotina*) and Red Pine (*Pinus resinosa*)

Abstract

Red oak, black cherry, and red pine wood samples were soxhlet extracted with various combinations of organic solvents including ethanol, toluene and water according to ASTM 1110-96, ASTM D1107-96, TAPPI T207 om-88 and TAPPI T204 om-88 standards.

Contact angle and sorption isotherms with distilled water of extracted and un-extracted specimens were determined to evaluate the role of wood extractives on the wettability and sorption properties of these wood species.

Extracted specimens adsorbed more water than un-extracted specimens at high relative humidities in agreement with the literature. The contact angle decreased with increased extraction due to the removal of hydrophobic extractives. However, the absorption rate of water measured as the decrease in contact angle over time suggests a physical/chemical modification of the wood surface and structure by solvent extraction due to the migration and redistribution of hydrophobic extractives.

4.1 Introduction

Extractives are heterogeneous chemical compounds naturally occurring in woody plants (Panshin and DeZeeuw 1980). Hillis (1970) defined extractives as non-structural constituents of plants. They have lower molecular weights than other polymeric constituents of wood and are distributed in the lumen or other specific tissues in plants. The term extractive covers a large number of compounds of different classes, which can be extracted from wood with polar and non-polar solvents (Hillis 1987).

According to Koch (1972), softwood extractives comprise a heterogeneous group of compounds present in low concentrations. Among the most important are terpenes and wood resins, both of which are composed of isopropene units, polyphenols such as flavonols, anthocyanins, quinones, stilbenes, lignans and tannins, tropolones, glycosides, sugars, fatty acids, and inorganic constituents (Kollman and Cote 1984).

The description of the chemical composition of most northern hardwood extractives has been conducted (Rowe and Conner 1979). In most hardwoods, hydrolyzable gallotannins and ellagitannins are the predominant compounds. The sapwood also contains leucoanthocyanins and possibly pinoresinol. In addition, coumarin and lignans are usually present. How extractives affect water properties and the dimensional stability of wood depends upon their chemical composition and location in the wood structure. The chemical constitution of extractive components, their size and molecular weight, and their affinity to the ligno-cellulosic wood complex will dictate their location within the wood structure. Low molecular weight monomers are found in voids in cell walls, while high molecular weight components will be mostly located in the lumen of vessels, tracheids, or fibers.

Aromatic compounds derived from glucose such as flavonoids and condensed tannins, usually have free hydroxyl groups and are water-soluble. Consequently, they will be more susceptible to absorbing water and inducing greater dimensional change. This can also be applied to terpenoids, which usually have hydrophilic functional groups attached to the hydrocarbon radical. To the contrary, pure hydrocarbons such as terpenes are volatile and will not affect dimensional stability.

The dimensional stability of wood when exposed to various humidity conditions is the main obstacle for its efficient use. It has been reported that wood-water relationships are affected by the type and total extractive content in the wood. For example, Nearn (1955) reported early work that concluded that the increased shrinkage samples of *Acacia melanoxylon* was due to the increase of the fiber saturation point (fsp) of that species caused by the presence of water-soluble extractives. This was later confirmed by Wangaard and Granados (1967), when they showed that one of the principal effects of extractives is to depress the sigmoid isotherm in the upper range of relative humidity.

Recent publications are in line with these views (Choong and Achmadi 1991; Chen and Chong 1994). Stamm (1952) investigated the anti-shrink efficiency of wood treated with organic salts, sugars, and water-soluble phenol-formaldehyde resinoids. He observed that extractives rich species do not conform to the usual shrinkage-specific gravity relationship and concluded that water-soluble extractive solutes reduce the shrinkage of wood in proportion to the fraction of transient cell wall capillary structure that is occupied by the solute.

Nearn (1955) focused on the effect of extractives on the volumetric shrinkage of 15 tropical and temperate species. He found that wood with low fiber saturation points have lower than normal equilibrium moisture contents at high relative humidity due to the bulking action of extractives. The removal of extractives caused an increase in equilibrium moisture content at higher relative humidities. Chong (1969) observed wide variations in hygroscopic properties related to extractive content in ten southern pine woods samples. Cooper (1974), working on black walnut, also observed a lower fiber saturation point on extracted samples. He obtained higher swelling at low relative humidities, attributed to the fact that some of the sites formerly blocked by extractives were made available for water which is consistent with the theory of extractives functioning as bulking agents in the cell wall.

Wood extractives are also known to affect the wettability of wood surfaces (Maldas and Kamdem 1999). Polar and hydrophilic extractives might increase wetting, and non-polar extractives might decrease wetting. Chen (1970) observed increased wettability with distilled water in all 70 tropical woods used in his study. To the contrary, Jordan and Wellons (1977) observed lower wettability with keruing wood and attributed that finding to extractives present in veneer samples tested. Maldas and Kamdem (1999) also observed decreased wettability. In their experiment, wood extracted with an ethanol-toluene solvent exhibited higher contact angle (lower wettability) compared to un-extracted samples. They suggested that the high contact angle was due to the hydrophobic nature of the extracted wood surface promoted by the migration of hydrophobic extractives from the wood surface. They also concluded that the more hydrophobic

extractives such as waxes and long chain hydrocarbons are present in a wood species, the less water this species will absorb.

From measurement of the contact angle and moisture adsorption properties, the surface free energy of the wood surface can be calculated. The surface free energy of solids is known to govern their wettability and coatability by liquids. It controls their propensity to absorb species from adjacent fluid phases, and influences their catalytic activity (Sun and Berg 2002).

Most studies on sorption and wettability properties have been focused on tropical woods known for their high extractive content. Several temperate woods possess limited amount of extractives compared to tropical woods (Spalt 1957). I am hypothesizing that they would affect in a similar way most water properties of wood surfaces. How significant is the influence of wood extractives on sorption and equilibrium constant? How is the free energy change and contact angle affected? What are implications of these property changes on the dimensional stability of some temperate woods are all areas that need to be further investigated.

The goal of this study is to investigate the influence of wood extractives on the sorption and wettability behavior of northern red oak, black cherry, and red pine.

4.2 Materials and Methods

4.2.1 Materials

Black cherry (*Prunus serotina),* red oak (*Quercus rubra*) and red pine *(Pinus resinosa)* samples were prepared and extracted according to the procedure described in Chapter 3, section 3.2.1 and 3.2.2.

4.2.2 Sorption Test

From each treatment four samples were selected for the sorption test. Specimens were divided into two matching halves measuring 4x22x40mm each (tangential, radial, longitudinal). One half was used in adsorption and the matching half was used in desorption. Four specimens from each extraction type were exposed at various relative humidity conditions in saturated salt solutions (Table 4.1) in a conditioning room maintained at 20°C according to ASTM E104-85 (ASTM 2000).

Samples were considered to have reached equilibrium at any given humidity when the daily weight changes were less than 0.1mg. The equilibrium moisture contents (MC) were calculated on the basis of the oven-dried weight of the samples.

4.2.3 Contact angle

The left and right contact angle between each specimen's surface and a drop of distilled water was measured using a VCA 2000 system from AST Inc. Wood specimens were set on a stage and a droplet of 5μl of water was placed on the specimen with a syringe. The mean value of the contact angles of 8 measurements for left and right contact angles (CA) between the droplet and wood surface at 1-second intervals were collected. The initial contact angle (t_o) was described as the point where the regression line of contact angle values over time crossed the Y-axis (Maldas and Kamdem 1999; Nzokou and Kamdem 2002).

The rate of decrease of the contact angle was computed as an indication of the absorption rate of the water on the wood surface (Maldas and Kamdem 1999). The following equation was used to calculate the rate:

$$R = \frac{d\Theta}{dt}$$

Where:

R = Rate of decrease of the contact angle

$d\Theta$ = Variation of the contact angle

dt = variation of the time

4.2.4 Data Analysis

Adsorption and desorption moisture contents were plotted against the various relative humidities and the hysteresis ratio (A/D) was calculated at each condition. The Hailwood-Horrobin (1946) equation was applied to the data and the free energy was calculated. The statistical significance of the difference between the various extraction types and control specimens was evaluated using the one-way analysis of variance procedure in SigmaStat version 2.0 for Windows (SPSS Inc. 1997). Tukey's multiple comparisons test (95% confidence) was employed to determine differences between average CA values for the various extractions.

Table 4.1: Relative Humidity Values for Selected Saturated Salt Solutions (ASTM E104-85)

Salt	**Relative Humidity (%) at 20°C**
Lithium Chloride ($LiCl.H_2O$)	11±0.3
Magnesium Chloride ($MgCl_2.6H_2O$)	33±0.2
Magnesium Nitrate ($Mg(NO_3).6H_2O$)	54±0.2
Sodium Chloride (NaCl)	75±0.1
Potassium Chloride (KCl)	85±0.3
Potassium Nitrate (KNO_3)	94±0.7
Distilled Water	100

4.3 Results and Discussion

4.3.1 Sorption

Adsorption and desorption EMC for each species and extraction type are summarized in Table 4.2. Desorption EMC, were consistently higher than adsorption EMC as result of hysteresis. Hysteresis ratio data (Table 4.3), calculated by dividing adsorption EMC to the desorption EMC showed that ethanol extracted samples had higher hysteresis than control samples. According to the Urquhart theory, hysteresis is believed to be caused by the development of hydrogen bonds between hydroxyl groups on adjacent cellulose molecules upon initial drying (Spalt 1957). Consequently, higher hysteresis in ethanol-extracted samples is an indication that extractives removed by ethanol prevent some of the Urquhart type hydrogen bonding reactions from occurring.

Adsorption data comparing extracted and un-extracted specimens for each species are presented in Figures 4.1, 4.2 and 4.3.

Table 4.2: Adsorption and Desorption EMC (% average of four specimens) of Extracted and Un-Extracted Specimens

	Black cherry									
	Control		Eth-Tol		Eth-Tol + Water		Eth		Eth + Water	
RH	Ads	Des	Ads	Des	Ads	Des	Ads	Des	Ads	Des
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11.0	2.5(0.05)*	4.9(0.09)	2.3(0.03)	4.8(0.03)	2.7(0.02)	4.8(0.01)	2.9(0.05)	5.0(0.08)	2.9(0.02)	4.8(0.17)
33.1	5.3(0.10)	6.1(0.02)	5.1(0.04)	6.4(0.09)	5.5(0.03)	6.4(0.07)	5.7(0.07)	6.9(0.04)	5.7(0.08)	6.5(0.03)
54.0	8.3(0.02)	9.1(0.10)	8.1(0.07)	9.4(0.01)	8.5(0.03)	9.4(0.01)	8.7(0.03)	9.9(0.06)	8.7(0.08)	9.5(0.02)
75.5	11.2(0.06)	14.3(0.02)	11.1(0.06)	15.4(0.02)	11.8(0.03)	15.8(0.01)	12.1(0.10)	15.3(0.02)	12.1(0.01)	15.6(0.02)
85.1	12.8(0.02)	15.1(0.03)	12.5(0.02)	16.4(0.01)	13.6(0.03)	17.0(0.02)	13.9(0.01)	16.4(0.02)	14.1(0.02)	16.8(0.09)
94.6	16.1(0.02)	18.7(0.03)	16.6(0.08)	20.0(0.02)	18.5(0.07)	20.6(0.02)	18.2(0.02)	19.9(0.03)	18.7(0.01)	20.5(0.07)
100.0	23.8(0.01)	24.5(0.03	23.3(0.06)	25.3(0.05)	26.1(0.06)	26.9(0.03)	25.7(0.03)	25.5(0.03)	26.6(0.03)	26.8(0.03)
	Red oak									
	Control		Eth-Tol		Eth-Tol + Water		Eth		Eth + Water	
RH	Ads	Des	Ads	Des	Ads	Des	Ads	Des	Ads	Des
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11.0	2.1(0.06)	4.5(0.06)	2.0(0.14)	4.2(0.14)	2.2(0.05)	4.4(0.10)	2.3(0.03)	4.2(0.11)	2.4(0.11)	4.4(0.01)
33.1	4.5(0.05)	5.6(0.04	4.3(0.14)	5.7(0.10)	4.4(0.14)	5.7(0.07)	4.6(0.05)	5.6(0.09)	4.8(0.06)	5.8(0.12)
54.0	7.5(0.07)	9.6(0.06)	7.2(0.09)	9.7(0.02)	7.5(0.04)	9.7(0.04)	7.6(013)	9.6(0.02)	7.8(0.16)	9.7(0.01)
75.5	10.5(0.10)	15.2(0.01)	10.5(0.25)	16.1(0.02)	10.7(0.16)	15.9(0.02)	11.2(0.08)	16.1(0.01)	11.5(0.21)	16.0(0.03
85.1	12.3(0.10)	18.0(0.01)	12.3(0.06)	19.1(0.06)	12.5(0.04)	18.9(0.02)	13.2(0.15)	18.9(0.01)	13.8(0.12)	19.2(0.02)
94.6	16.3(0.08)	20.5(0.01)	16.5(0.07)	21.4(0.03)	16.2(0.12)	21.7(0.04)	17.5(0.09)	21.9(0.02)	18.4(0.07)	22.3(0.02)
100.0	21.2(0.1)	26.4(0.12)	22.1(0.07)	26.6(0.06)	23.0(0.01)	27.2(0.04)	23.7(0.09)	27.1(0.11)	24.2(0.09)	27.3(0.03
	Red pine									
	Control		Eth-Tol		Eth-Tol + Water		Eth		Eth + Water	
RH	Ads	Des	Ads	Des	Ads	Des	Ads	Des	Ads	Des
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11.0	2.5(0.06)	4.8(0.08)	2.7(0.05)	4.9(0.09)	2.7(0.08)	4.7(0.01)	2.6(0.04)	4.9(0.03)	2.7(0.04)	4.7(0.08)
33.1	5.3(0.02)	7.6(0.02)	5.5(0.01)	7.7(0.06)	5.5(0.02)	7.5(0.05)	5.5(0.02)	7.6(0.03)	5.5(0.03)	7.3(0.06)
54.0	8.3(0.09)	9.5(0.02)	8.5(0.05)	9.8(0.02)	8.5(0.04)	9.4(0.02)	8.5(0.06)	9.5(0.03)	8.5(0.03)	9.3(0.01)
75.5	12.4(0.01)	16.3(0.09)	13.1(0.09)	16.8(0.01)	13.2(0.01)	16.4(0.02)	12.9(0.01)	16.6(0.03)	13.1(0.06)	16.4(0.04)
85.1	14.4(0.03)	17.3(0.02)	15.1(0.04)	17.7(0.06)	15.2(0.03)	17.3(0.03)	14.9(0.01)	17.3(0.02)	15.4(0.02)	17.2(0.01)
94.6	17.7(0.07)	18.0(0.02)	19.1(0.03)	18.7(0.01)	18.7(0.07)	18.3(0.03)	18.7(0.04)	18.4(0.04)	19.1(0.04)	18.3(0.01)
100.0	26.8(0.03)	27.6(0.06)	28.0(0.05)	27.9(0.03)	29.7(0.03)	29.3(0.06)	28.8(0.05)	29.0(0.08)	30.4(0.03)	29.6(0.05)

* Numbers in parenthesis are standard deviation

Ads: Adsorption

Des: Desorption

Eth: Ethanol

Eth + Water: Ethanol + Water

Eth-Tol: Ethanol-Toluene

Eth-Tol + Water: Ethanol-Toluene + Water

Note: Adsorption EMC higher than Desorption EMC for all treatments.

Table 4.3: Hysteresis Ratio of Specimens at Various Relative Humidities

	Black cherry				
	Control	Eth-Tol	Eth-Tol + Water	Eth	Eth + Water
11.0%	0.51	0.48	0.56	0.59	0.60
33.1%	0.87	0.79	0.86	0.82	0.87
54.0%	0.92	0.86	0.90	0.87	0.91
75.5%	0.78	0.72	0.75	0.79	0.78
85.1%	0.85	0.76	0.80	0.85	0.84
94.6%	0.86	0.83	0.89	0.92	0.91
100.0%	0.97	0.92	0.97	1.01	0.99
	Red oak				
11.0%	0.48	0.48	0.49	0.54	0.54
33.1%	0.80	0.75	0.77	0.82	0.84
54.0%	0.78	0.75	0.77	0.80	0.80
75.5%	0.69	0.65	0.67	0.70	0.72
85.1%	0.68	0.64	0.66	0.70	0.72
94.6%	0.80	0.77	0.75	0.80	0.82
100.0%	0.80	0.83	0.85	0.87	0.89
	Red pine				
11.0%	0.52	0.54	0.57	0.53	0.57
33.1%	0.68	0.71	0.74	0.72	0.75
54.0%	0.86	0.86	0.91	0.89	0.92
75.5%	0.76	0.78	0.80	0.78	0.80
85.1%	0.84	0.86	0.88	0.86	0.89
94.6%	0.98	1.02	1.02	1.02	1.04
100.0%	0.97	1.00	1.02	0.99	1.02

Eth: Ethanol

Eth-Tol: Ethanol-Toluene

Eth + Water: Ethanol + Water

Eth-Tol + Water: Ethanol-Toluene + Water

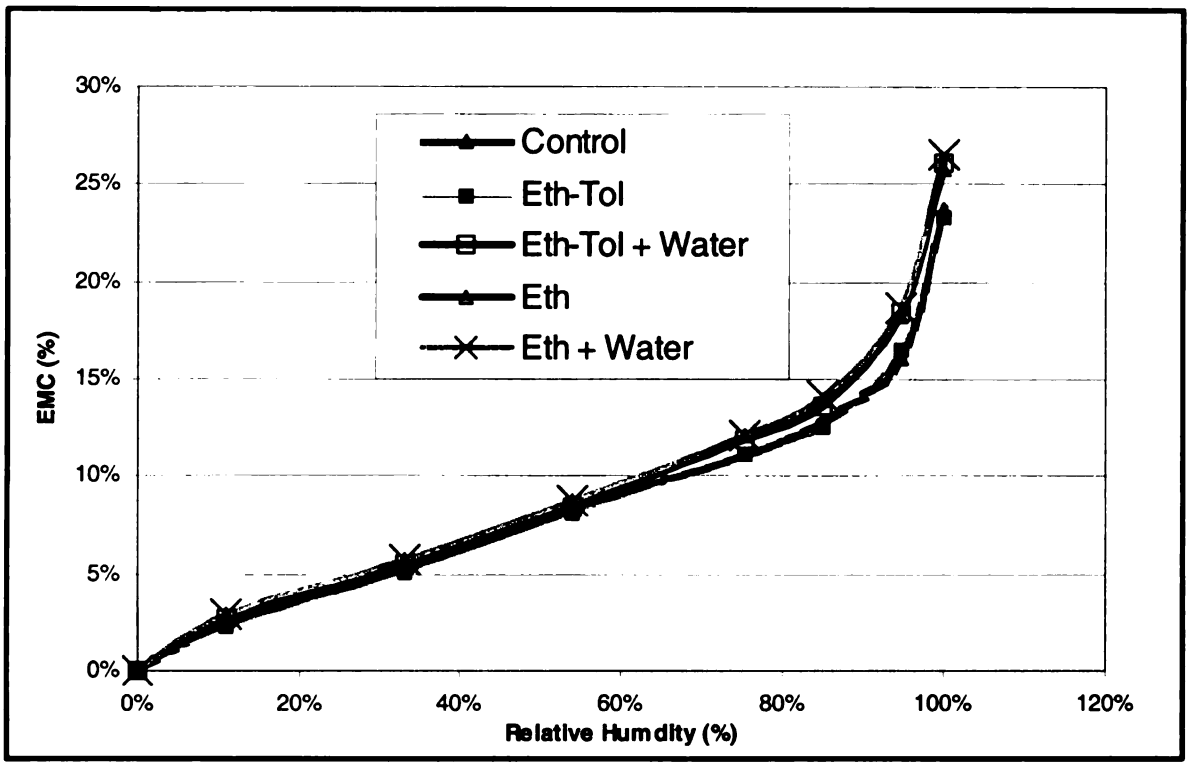

Figure 4.1: Adsorption Curves of Extracted and Non Extracted Black Cherry specimens

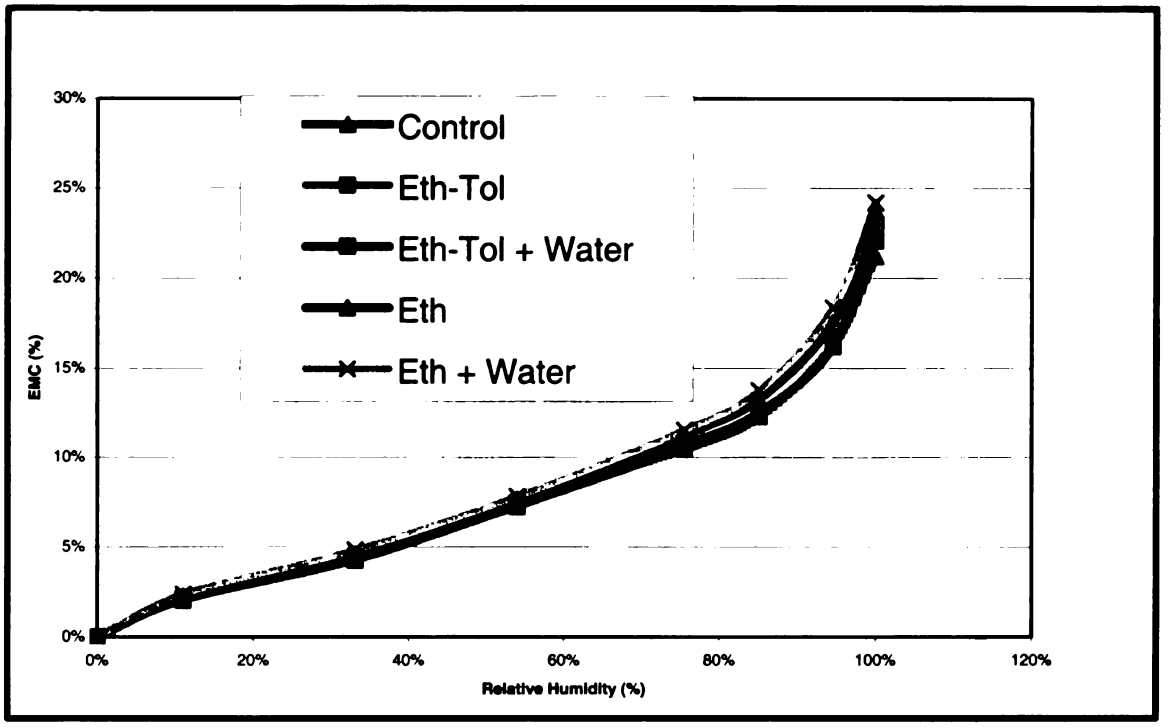

Figure 4.2: Adsorption Curves of Extracted and Non Extracted Red Oak Specimens

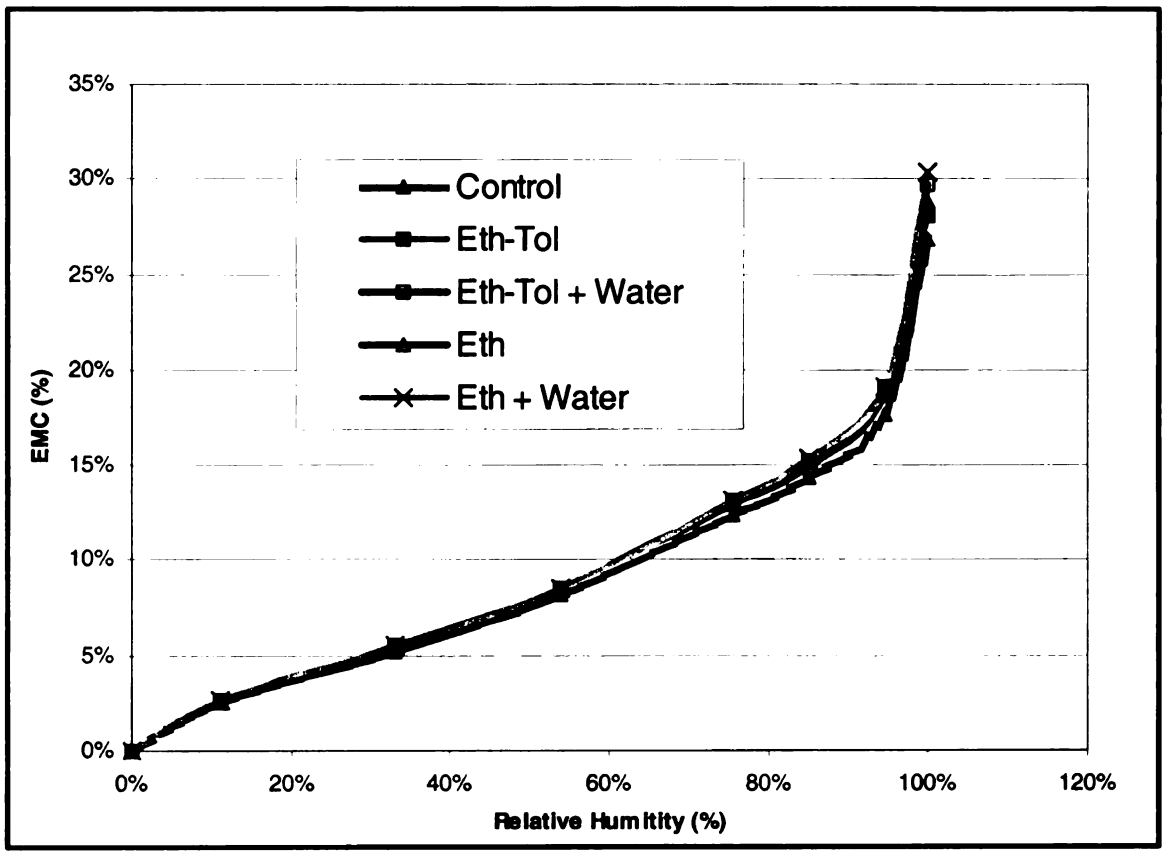

Figure 4.3: Adsorption Curves of Extracted and Non Extracted Red Pine Specimens

For black cherry, ethanol-toluene extracted samples had an adsorption curve similar to that of control samples (Figure 4.1). However, when ethanol-toluene extraction was subsequently followed by water extraction, the adsorption curve for extracted samples was higher than the curve for un-extracted specimens, especially in the higher range of the relative humidity values. Samples extracted with ethanol and ethanol + water had consistently slightly higher EMC than control samples. A similar trend was observed in red oak (Figure 4.2). For red pine (Figure 4.3), the adsorption curves for all extraction treatments were consistently higher than the curve for un-extracted specimens. From these observations, it can be concluded that extracted samples generally adsorbed more water than un-extracted samples at high relative humidity. This conclusion is in agreement with previously published data on tropical and domestic hardwoods by Spalt (1957), Wangaard and Granados (1967) and Chong and Achmadi (1991). The higher EMC in extracted samples is explained by the increased availability of moisture sites previously occupied by extractives, which became available to water once extractives were removed (Nearn 1955; Spalt 1979).

Analysis of Adsorption Data by the Hailwood-Horrobin Sorption Model

The Hailwood-Horrobin (1946) model considers that part of the sorbed water forms a hydrate with wood, and the balance forms a solid solution in the cell wall (Spalt 1958; Spalt 1979; Cao and Kamdem 2003). Water therefore exists in two states, hydrated water and dissolved water. The sorption equation of the Hailwood-Horrobin model is expressed as:

$$h/m = A + bh - Ch^2 \qquad (1)$$

Where h is the relative vapor pressure

m is the equilibrium moisture content,

A, B, and C are empirical constants.

A, B, and C are obtained by fitting the h/M values to equation (1) by the least square method, and the physical constants α, β, and W can be calculated using equation (2), equation (3), and equation (4) (Spalt 1958).

$$\beta = \frac{\left(2+\frac{B^2}{AC}\right)+\sqrt{\left(2+\frac{B^2}{AC}\right)^2-4}}{2} \qquad (2)$$

$$\alpha = B/A(\beta-1) \qquad (3)$$

$$\frac{W}{1800} = A(\beta+1)\alpha \qquad (4)$$

α is the equilibrium constant between free dissolved water and the hydrated water,

β is the equilibrium constant between dissolved water and the external vapor pressure,

W is the molecular weight of wood substance necessary to be associated with one molecular weight of water molecules (mol/mol).

From the above constants, the free energy change for hydrated water can be calculated using equation (5).

$$\Delta G_h = -RT\ln(\beta) \qquad (5)$$

Table 4.4: Parameters of the Hailwood-Horrobin Sorption Model

		A	B	C	R^2	β	α	W	ΔG_h
Red pine	**Control**	0.07	0.08	0.11	0.92	2.48	0.81	347.1	526.7
	Eth-Tol	0.06	0.09	0.12	0.91	2.94	0.83	347.5	490.5
	Eth-Tol + Water	0.06	0.09	0.12	0.90	2.88	0.83	346.1	486.6
	Eth	0.06	0.08	0.11	0.92	2.63	0.81	341.2	503.1
	Eth+Water	0.06	0.09	0.12	0.92	2.84	0.83	350.1	467.0
Red oak	**Control**	0.03	0.17	0.16	0.96	7.32	0.78	405.4	578.0
	Eth-Tol	0.038	0.16	0.16	0.94	6.57	0.79	411.2	549.9
	Eth-Tol + Water	0.03	0.17	0.16	0.91	7.34	0.79	408.7	547.7
	Eth	0.032	0.16	0.15	0.95	7.45	0.79	387.6	548.3
	Eth + Water	0.03	0.16	0.15	0.97	7.74	0.80	377.2	544.7
Black cherry	**Control**	0.027	0.17	0.15	0.87	9.23	0.77	379.0	643.1
	Eth-Tol	0.025	0.17	0.14	0.85	9.96	0.76	381.6	663.7
	Eth-Tol + Water	0.024	0.17	0.15	0.88	10.16	0.78	372.5	588.4
	Cherry Eth	0.021	0.16	0.14	0.87	11.37	0.77	354.7	637.9
	Eth + Water	0.021	0.17	0.14	0.88	11.11	0.78	361.1	601.4

A, B, and C are empirical constants.

α: Equilibrium constant between free dissolved water and the hydrated water

β: Equilibrium constant between dissolved water and the external vapor pressure

W: Molecular weight of wood substance necessary to be associated with one molecular weight of water molecules (mol/mol).

ΔG: Free energy change for hydrated water

Parameters from the Hailwood-Horrobin model are listed in Table 4.4 From that table, it can be observed that adsorption data for all three species had a good fit with the model with R^2 values above 80% for all the treatments. The data also shows that α and β equilibrium constants were consistently higher for all red pine extracted samples resulting in lower values for W and ΔG_h. ΔG_h is the energy required to swell the wood structure, and lower values of ΔG_h mean less energy is required to swell the wood structure. Therefore, lower values obtained for extracted red pine specimens are indications that the wood structure requires less energy to swell due to the increase of hydrophilic sites. Similar trends were observed for red oak specimens (Table 4.4) and for black cherry samples extracted with ethanol. The ΔG_h value for black cherry samples extracted with ethanol-toluene (663.7 j/mol) was higher than that of control samples (643.1 j/mol). However, this value decreased to 588j/mol when ethanol-toluene extraction was followed by water extraction. The reason for the variation is unknown, however it could be hypothesized that this is the result of the migration and relocation of some hydrophobic extractives not removed by the extraction process, but washed out by the subsequent water extraction.

4.3.2 Contact Angle

The average contact angle values and standard deviations of eight replicates for each treatment are reported in Table 4.5 Extracted samples had contact angle values consistently lower than control samples for all three species, and the difference analyzed by one-way ANOVA (95% confidence level) was statically significant between all extraction types and control samples. In addition, the results also show that following organic solvent (ethanol or ethanol-toluene) extraction by water extraction resulted in slightly lower contact angle values. Lower contact angles for extracted samples confirms

observations of the sorption experiment and reinforces the hypothesis of a removal of hydrophobic compounds during the extraction process. This result is in agreement with results from Chen (1970) and Maldas and Kamdem (1999) who also obtained increased wettability in eight tropical woods and southern yellow pine following extraction. However, Nussbaum and Sterley (2002) obtained a more complex relationship between the contact angle, total extractives, and storage time. They explained the variability in their results by the migration of extractives spreading on the wood surface and causing chemical changes to the surface.

Computed values of the water absorption rate estimated as the decrease in contact angle of the water drop overtime are summarized in Table 4.6. Results presented show a tendency to a lower absorption rate of the water drop after initial solvent extraction. However, subsequent water extraction induced a higher absorption rate, similar or higher to the values for control samples. This is explained by the migration phenomenon suggested by Nussbaum and Sterley (2002) during the first solvent extraction. Migrates are subsequently washed out during the following water extractions, resulting in wood surfaces with more affinity for water.

Table 4.5: Average (Left and Right) Advancing Contact Angle (Degrees)*

	Red oak	Black cherry	Red pine
Control	88.1 (7.2)**	89.2 (4.1)	116.2 (6.5)
Eth-Tol	49.4 (7.5)	50.1 (6.2)	103.3 (6.9)
Eth-Tol + Water	48.3 (9.2)	42.4 (6.3)	45.6 (7.9)
Eth	62.1 (9.1)	57.6 (11.0)	80.4 (17.3)
Eth + Water	50.8 (9.2)	54.6 (6.6)	53.1 (6.5)

* Control samples were statistically different from extracted samples. Details of the one-way ANOVA are presented in Appendix 1.

** Numbers in parenthesis are standard deviation.

Eth: Ethanol

Eth-Tol: Ethanol-Toluene

Eth + Water: Ethanol + Water

Eth-Tol + Water: Ethanol-Toluene + Water

Table 4.6: Rate of Change in Contact Angle (R) over time between distilled water and wood surface (Degrees/Second)*

	Contol	Eth-Tol	Eth-Tol + Water	Eth	Eth + Water
Oak	2.75 (0.64)**	1.44 (0.38)	2.34 (0.75)	2.54 (0.65)	2.77 (0.84)
Cherry	1.62 (0.81)	0.82 (0.18)	2.82 (0.71)	0.69 (0.25)	3.16 (0.96)
Pine	5.19 (0.91)	6.95 (1.45)	3.66 (1.02)	2.78 (0.73)	3.31 (0.86)

* The difference between the various groups was statistically significant. Details of the one-way ANOVA procedure are presented in Appendix 2.

** Numbers in parenthesis are standard deviations.

Eth: Ethanol

Eth-Tol: Ethanol-Toluene

Eth + Water: Ethanol + Water

Eth-Tol + Water: Ethanol-Toluene + Water

4.4 Conclusion

The influence of wood extractives on sorption and wettability of two hardwoods and one softwood species was investigated in this project. Results showed that wood extractives lowered the equilibrium moisture content of wood at high relative humidities. The difference between extracted and un-extracted specimens was less pronounced when toluene was included in the solvent system. This was explained as a result of the migration and redistribution of hydrophobic extractives following the extraction resulting in lower hysteresis.

Analysis of data using the Hailwood-Horrrobin sorption model showed that extracted red pine and ethanol extracted cherry and oak had more adsorption sites available and needed lower energy to absorb water. However, this trend was not verified for black cherry samples extracted with ethanol-toluene mixture. This observation is probably due to the migration of some extractives to the wood surface following ethanol-toluene extraction.

The contact angle was found to decreases with increased extraction. The absorption rate after an initial increase, due to the modification of the wood surface caused by extractive migration, decreased following water extraction.

These results suggest that the increased ability of wood surfaces to absorb water due to their extractive content could lead to increased dimensional instability and eventually lead to more cracks and checks in extracted wood.

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Chapter 5

The Influence of Wood Extractives on the Physical Degradation of Wood Surfaces Exposed to Artificial Weathering

Abstract

Organic solvents were used to remove extractives from red pine (*Pinus resinosa*), red oak (*Quercus rubra*), and black cherry (*Prunus serotina*) wood samples before exposure to artificial weathering. Surface roughness, weight loss, and scanning electron microscopy were used to assess the damages caused to the wood surface by the weathering process and to evaluate the influence of wood extractives on the physical degradation of these wood species.

As expected, the average roughness and maximum peak to valley increased with exposure time for all species and extraction treatments. However, comparison between the various extraction treatments and un-extracted specimens showed no statistically significant differences.

All three species had considerable weight loss after weathering; 8-10% for red pine, 13.1-15% for black cherry, and 16.2-19% for red oak; but there was no significant difference between extractive treatments within each species.

Scanning Electron Microscopic observations showed severe roughening, cracking, breakage of wood fibers and erosion of wood structures, but revealed no distinguishable trend due to extractive treatments.

These results suggest no detectable effect of extractives on the roughening, weight loss, and microscopic degradation of wood surfaces.

5.1 Introduction

Wood is one of the most efficient natural materials and exhibits major technical, economic, and environmental advantages over other construction materials: It is a renewable resource and sustainable and sound forestry can ensures its continuous supply and ecological advantage. It is generally cheaper, lighter, and more versatile compared to its competitors. However, like other biological materials wood is susceptible to degradation.

Exposed board surfaces become rough as the grain surface becomes eroded, develops cracks, and ultimately warps (Feist 1982). The process also leads to formation of microscopic inter and intra-laminar checks or cracks. The wood color quickly changes towards a brown color, and later to whitish gray (Browne 1960; Feist & Hon 1984, Nzokou and Kamdem 2002).

However, the effects of weathering on wood surfaces vary between and within species and even in material cut from the same tree. The reasons for this variability are often attributed to wood variability, which itself is partly caused by its extractive content.

Several authors have investigated the influence of species variation and wood structure on the weathering of wood surfaces. Flaete et al. (2000) investigated cracks formation in solid wood sidings of aspen and Norway spruce exposed to accelerated weathering. They observed a high number of short cracks in aspen and a fewer but more injurious number of cracks in spruce. They explained this result as a consequence of the more asymmetrical cross sectional pattern in wood of aspen, eventually preventing cracks from propagating. Kamdem and Zhang (2000) used a surface profilometer to measure

several surface roughness parameters and correlated those to the number and size of checks on the wood surface after weathering.

The amount of such cracking differs considerably with species. For example, Gaby (1963) found particularly high shrinkage in refractory wood such as oak, which contains up to 32% of its wood volume as ray tissue.

The influence of extractives on physical properties of wood has been reported to result from the bulking effect of extractives on wood, which suggests that large molecules of wood extractives keep the wood structure in a semi-swollen condition and hinders the number of available sites for the formation of intermolecular lignin-cellulose and/or lignin-lignin bonds (Ajuong and Breese 1998). Therefore, the removal of extractives should make available additional moisture sorption sites, and induce higher dimensional change leading to increased roughening, weight loss, and cracks on the wood surface when exposed to weathering.

The goal of this project was to investigate the influence of wood extractives on physical changes occurring on wood surfaces after artificial weathering.

5.2 Materials and Methods

Samples were selected, prepared and extracted according to methods presented in Chapter 3, section 3.2.1 and 3.2.2.

5.2.1 Artificial weathering

Artificial weathering was conducted in a QUV weathering tester (Q-Panel Ltd., Ohio, USA) fitted with UV fluorescent lamps. The samples were subjected to a repeated weathering cycle comprised of 2hours of UV light and 18 minutes of water spray.

The average irradiance was set at about 0.85 W/m^2 at 340 nm wavelengths with a chamber temperature set at 50°C during the UV irradiation. The spray temperature was set at a constant value of 25°C. It is essential to use both UV irradiance and water spray to accelerate the weathering rate of the specimens' surfaces. This was confirmed by the work of Horn et al. (1994) who found that changes on the surface of western red cedar and southern pine after artificial weathering were considerably greater when irradiation and water were used together, compared to water or irradiation only. Specimens were removed for roughness measurement after 100, 200, 400, 800, 1600, and 2400h. Specimens were removed for SEM imagery after 400, 800, 1600, and 2400h exposure.

5.2.2 Surface Roughness

A stylus model RC-4000 system manufactured by Hommel America was used to evaluate and monitor the modification of the wood surface roughness after weathering. The roughness-measuring device consists of a main unit, a pick-up unit, and a drive unit. The pick-up unit has a skidless-type diamond stylus with 196-micro-inch (5-micro meters) radius and a 90 degrees tip angle. The stylus traverses the surface and its vertical displacement is converted into an electrical signal. The signal is later amplified before it is converted into digital information. The digital information is transmitted to the computer and the surface roughness parameters are automatically calculated from this information (Mummery, 1992).

The stylus travels at a speed of 0.50 mm/sec across the wood grain within a span of 25.6 mm. The peak-to-valley maximum was set at 800 μm, and an average of 5 measurements were taken from each specimen.

Several surface-texture parameters can be obtained from this method: R_a, R_z, R_{max}, R_k, R_{pk}, and R_{vk} (Kamdem and Zhang 2000; Nzokou and Kamdem 2002). R_a is the average surface roughness, and it represents the deviation from the mean peak. R_a is often used to define surface roughness, but it does not differentiate between the peaks and valleys of a surface profile (Maldas and Kamdem 1998; Nzokou and Kamdem 2002). R_{max} is the maximum of the peak-to-valley height. R_a, and R_{max} were selected to characterize the physical changes of the wood surface.

5.2.3 Weight Loss

Before weathering exposure the MC of a subset of specimens was determined by the oven-dried method and recorded. After 2400h exposure, specimens were oven-dried and their weight loss determined using the following equation (1).

$$\text{Weight loss, } \% = [(W_1-W_2)/W_1] \times 100 \qquad (1)$$

Where: W_1 is the initial oven-dried weight (calculated by adjusting with the MC values from the subset of specimens)

W_2 is the final oven-dried weight of the specimen (measured after oven drying the samples).

5.2.4 SEM Observations

Samples measuring 1"x1" (length and width) were cut and mounted on aluminum stubs with epoxy resin and oven dried at 60° C. After drying, they were kept in vacuum desiccators to prevent moisture pick up. Immediately before the SEM observation, the samples were sputter coated with a 35nm layer of gold to avoid charging. The SEM to be used was a JEOL JSM 6400 located at the Center for Advanced Microscopy at MSU.

5.2.4 Statistical Analysis

Statistical analysis based on non-parametric one-way ANOVA was used to compare the difference in average values of the various parameters considered between extraction treatments at the 95% significance level.

5.3 Results and Discussion

5.3.1 Surface Roughness

The changes in roughness (Ra) and maximum peak to valley (Rmax) before weathering exposure for extracted and un-extracted samples are presented in Figures 5.1 and 5.2. Ra for red pine increased from 0.97μm to 3.9μm and 4.7μm following ethanol-toluene and ethanol-toluene + water extractions respectively. Similar increases were found for ethanol (2.8μm) and ethanol + water (5.8μm) extractions (Figure 5.1). Figure 5.1 also shows that red oak and black cherry also had higher Ra values following extraction treatments. Similar results were obtained for Rmax for all three species (Figure 5.2). These results clearly show that the extraction process increased the roughness and created small valleys on the surface even before specimens were exposed to artificial weathering. Based on this observation, in order to compare the various extraction treatments after artificial weathering, it was necessary to define new parameters that take into account these original variations in Ra and Rmax.

Two parameters named Roughening Index (RI) and Microcracking Index (MCI) were defined according to equations 2 and 3.

$$RI = \frac{Ra_w - Ra_i}{Ra_i} \qquad (2)$$

$$MCI = \frac{R\max_w - R\max_i}{R\max_i} \qquad (3)$$

Where: Ra_w is the Average roughness after artificial weathering

Ra_i is the Average roughness before weathering exposure

$Rmax_w$ is the maximum peak to valley after artificial weathering

$Rmax_i$ is the maximum peak to valley before weathering exposure

RI and MCI are estimates of the change in roughness and microscopic cracking following weathering exposure. They take into consideration the variation in initial Ra and Rmax of the sample. The higher the RI, the higher is the roughening of the sample. Similarly, the higher the MCI, the deeper is the cracking of the wood surface.

Average RI and MCI values for all three species and extractives treatments are presented in Table 5.1.

For red pine, control samples had a RI of 39 and a MCI of 17, significantly higher than values for all extracted specimens (RI 4-9 and MCI 2-6). This indicates that un-extracted red pine samples exhibited rougher surfaces and developed more injurious microcracks than extracted wood samples. This result was unexpected as our hypothesis was that the removal of extractives would lead to increased roughening in extracted samples. For red oak and black cherry, RI and MCI for control samples were also higher than those of extracted specimens, but the differences were not statistically significant at 95% confidence level. These results suggest that there is no statistical difference in roughening and microcracking due to extractive removal and disproves our hypothesis. The significant difference in RI and MCI values between un-extracted and extracted samples obtained in red pine could be explained by irreversible damages caused to the wood structure by the extraction process.

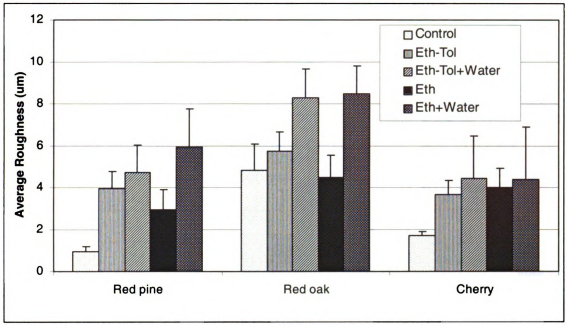

Figure 5.1: Change in surface roughness (Ra) after extraction

* Bar represents the standard deviation

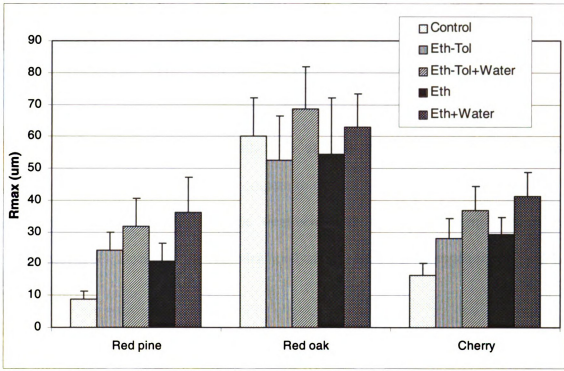

Figure 5.2: Changes in maximum peak to valley (Rmax) after extraction

* Bar represents the standard deviation

Table 5.1: Calculated Indexes of Roughening and Microcracking after 2400h weathering

	Red pine		Red oak		Black cherry	
	RI	MCI	RI	MCI	RI	MCI
Control	39.8a	17.2a	5.7a	1.6a	2.8a	1.9a
Eth-Tol	8.1b	5.2b	4.3b	2.5b	0.9b	0.9b
Eth-Tol+Water	5.5b	3.2b	3.3b	1.7a	0.7b	0.6b
Eth	9.9b	6.1b	5.2a	2.2a	1.1b	1.3b
Eth+Water	4.3b	2.9b	2.6b	1.8a	0.6b	0.4b

The letter indicates statistical significance at 95% confidence level. Similar letter indicates no statistical significance compare to control. Different letters indicate that the difference between control and the treatment was statistically significant at 95% confidence level. Details of the statistical analysis are presented in appendixes 3 and 4.

5.3.2 Weight Loss

The weight loss of un-extracted and extracted specimens after artificial weathering exposure is presented in Figure 5.3. The weight loss of red pine specimens varied from 8.1% to 10%. Black cherry specimens had weight losses of 13.1% to 15% and red oak had higher weight losses ranging from 16.2% to 19% (Figure 5.3). The variation in weight loss values for all three species were well within the standard deviation values, and there were no statistically significant differences between un-extracted and extracted specimens. This is further evidence that there is no difference in physical degradation due to the removal of extractives.

5.3.3 SEM observations

A wide range of microscopic observations was conducted to visualize the physical damages caused by the weathering process. Low magnification images of wood surfaces after 2400h exposure are presented in Figures 5.4a-e(red pine), Figures 5.5a-e(red oak) and Figures 5.6a-e(black cherry). There was no observable difference between the different extractives treatments, and all surfaces displayed similar patterns of degradation within each species. All wood surfaces showed severe erosion and degradation of wood structures. Wood fibers and tracheids were broken at several points, and there were signs that some broken pieces of had been washed away during exposure to water spray. The surface appeared brittle and there were large longitudinal cracks, usually along the rays. Close observation of the cross section of a broken black cherry fiber showed early degradation of pits, which are enlarged and developed radial cracks that propagated through the cell wall (Figures 5.7a and 5.7b).

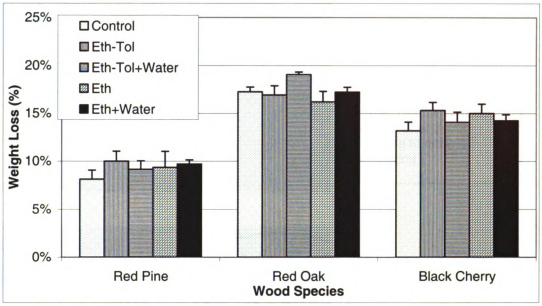

Figure 5.3: Weight loss of wood samples after 2400h exposure to artificial weathering

* Bar represents the standard deviation

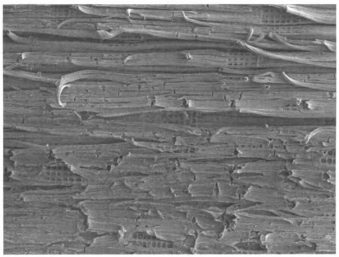

Figure 5.4a: Un-extracted red pine after 2400h exposure to artificial weathering

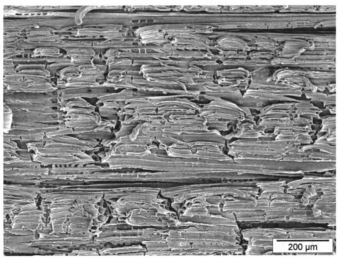

Figure 5.4b: Ethanol-Toluene extracted red pine surface after 2400h exposure to artificial weathering

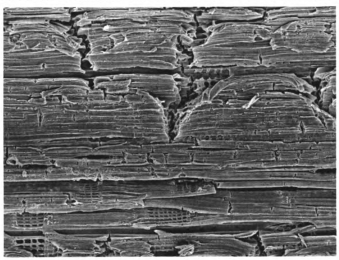

Figure 5.4c: Ethanol-Toluene + Water extracted red pine surface after 2400h exposure to artificial weathering

Figure 5.4d: Ethanol extracted red pine surface after 2400h exposure to artificial weathering

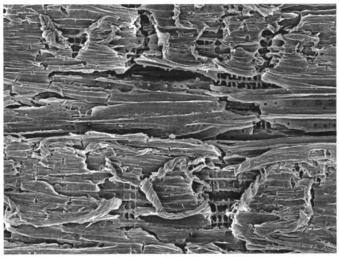

Figure 5.4e: Ethanol + Water extracted red pine surface after 2400h exposure to artificial weathering

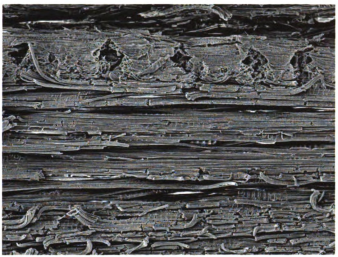

Figure 5.5a: SEM image of un-extracted red oak surface after 2400h exposure to artificial weathering

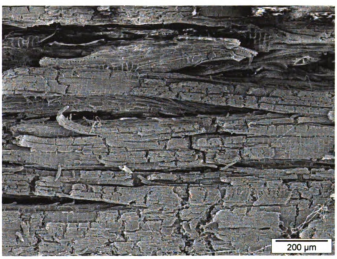

Figure 5.5b : SEM image of Ethanol-Toluene extracted red oak surface after 2400h exposure to artificial weathering

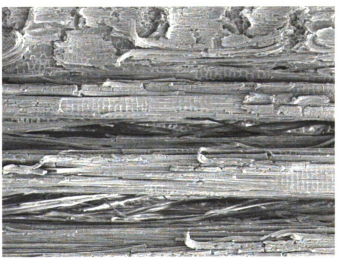

Figure 5.5c : SEM image of Ethanol-Toluene + Water extracted red oak surface after 2400h exposure to artificial

Figure 5.5d: SEM image of Ethanol extracted red oak wood surfaces after artificial weathering

Figure 5.5e: SEM image of Ethanol + Water extracted red oak wood surface after artificial weathering

Figure 5.6a: Un-extracted black cherry surface after 2400h exposure to artificial weathering

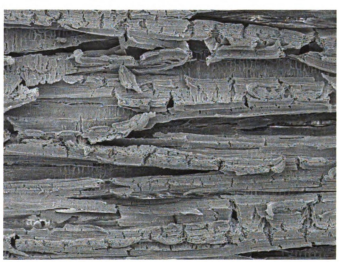

Figure 5.6b: Ethanol-Toluene extracted black cherry surface after 2400h exposure to artificial weathering

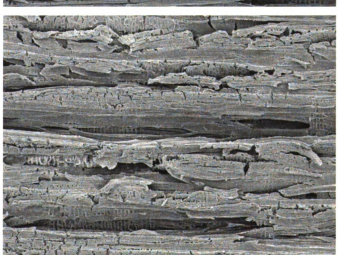

Figure 5.6c: Ethanol-Toluene + Water extracted black cherry surface after 2400h exposure to artificial weathering

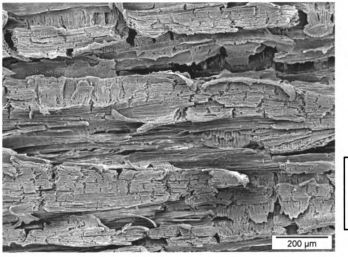

Figure 5.6d: Ethanol extracted black cherry surface after 2400h exposure to artificial

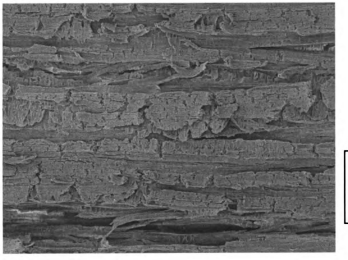

Figure 5.6e: Ethanol + Water extracted black cherry surface after 2400h exposure to artificial weathering

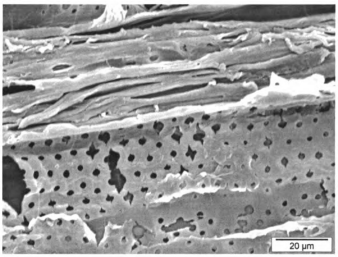

Figure 5.7a: Ethanol-Toluene extracted black cherry surface after 400h exposure to artificial weathering

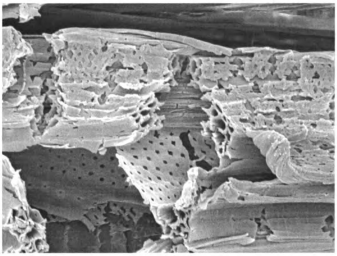

Figure 5.7b: Ethanol-Toluene extracted black cherry surface after 2400h exposure to artificial weathering

The radial cracks have been reported to be consequences of stresses that develop in the pit chambers during drying and wetting (Turkulin and Sell 1997; Sandberg 1999). In red oak and black cherry, rays were enlarged, and exhibited deformations and delamination. This was expected as it has been previously reported that rays tissues are tender and porous and susceptible to deteriorate quickly when exposed to adverse conditions (Minuitti 1970; Turkulin and Sell 1997). Similarly, the larger cracks in red pine can be associated with resin canals, rays and ring boundaries (Borgin 1971; Turkulin and Sell 1997). The extent of degradation appears to be much more severe in red oak and black cherry than that in red pine. This can be explained by the structure and density of red pine, red oak and black cherry. It has been reported that the overall performance of exterior wood structures is heavily affected by its water uptake (Turkulin and Sell 1997). Consequently red oak and cherry, which are porous and multiseriate woods, have more conducting tissues than red pine where water conduction occurs by tracheids.

5.4 Conclusion

The influence of wood extractives on the physical degradation of hardwood and softwood surfaces exposed to artificial weathering was investigated in this project.

As expected, the Average Roughness (Ra) and the Maximum Peak to Valley (Rmax) increased with time of exposure to artificial weathering. However evaluation of the difference between the various extraction treatments through a roughening index (RI) and a Microcracking index (MCI) showed no statistically significant variation between un-extracted and extracted samples. Measurements of the weight loss due to artificial weathering also showed no significant difference between extractive treatments, but

weight loss values for the softwood (red pine) were lower than those of hardwood species.

SEM observations revealed multiple breaking, brittleness, cracking, loosening and erosion of wood structures, however there were no observable differences between extraction types.

These results suggest no specific influence of wood extractives on the roughening, weight loss, and microscopic degradation of red pine, red oak, and black cherry following exposure to artificial weathering.

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Chapter 6

The Influence of Wood Extractives on the Photo-discoloration of Wood Surfaces Exposed to Artificial Weathering

Abstract

Extracted and un-extracted black cherry (*Prunus serotina*), red oak (*Quercus rubra*), and red pine (*Pinus resinosa*) wood specimens were exposed to artificial weathering and their discoloration process investigated to obtain basic understanding on the role of wood extractives in the weathering of hardwoods and softwoods. Color measurements were made using a spectrometer according to ISO 2470 standards using the CIELAB system.

Results obtained showed that the rate of whiteness was not significantly affected by extractives removed with organic solvents, but were significantly affected when organic solvent extraction was followed by water extraction. The total discoloration rate had the same pattern, and chromaticity coordinates were less affected by wood extractives. These results confirm the hypothesis that some extractives contained in wood act as anti-oxidants and are able to provide some protection to wood surfaces against weathering degradation.

However, more work is needed to understand the chemistry and mechanism of action of these extractives in order to develop any practical use for this property.

6.1 Introduction

The term photodegradation refers to the photochemical deterioration wood surfaces exposed to light (Feist and Hon 1984). When wood is exposed outdoors, a complex combination of chemical, mechanical, and light energy factors contribute to what is described as weathering. The weathering of wood depends on many environmental factors such as solar radiation, (ultraviolet, visible, and infrared), moisture (dew, rain, snow, and humidity), temperature, oxygen and air pollutants, and it is well accepted that the ultraviolet portion of the electromagnetic spectrum of sunlight is responsible for the primary photochemical process (Hon 1991)

Wood is an excellent light absorber. It is capable of absorbing several different wavelengths of electromagnetic radiation to initiate photochemical reactions leading to wood discoloration. The wood polymer blend contains cellulose, hemicellulose, lignin, and extractives. These wood components contain internal chemical labile entities such as carbonyl, carboxyl, aldehyde, phenolic hydroxyl, unsaturated double bonds, and external entities such as waxes, fats, and metal ions. All the chemical constituents of wood (cellulose, hemicellulose, lignin, and extractives) are sensitive to ultraviolet radiation.

According to Kuo and Hu (1991), lignin contributes 80-95%, carbohydrates 5-20%, and extractives about 2% to the total UV absorption of wood. Hon and Chang (1984) reported that after 40 days exposure to UV, the lignin content of southern pine wood samples was reduced from 28% to 14.5%. Infrared studies revealed that, during UV irradiation of wood, absorption due to carbonyl groups at 1720 cm^{-1} and 1735 cm^{-1} increased, whereas the absorption for lignin at 1265 cm^{-1} and 1510 cm^{-1} gradually decreased. The increment of carbonyl groups was the result of oxidation of cellulose and

lignin, and the reduction in the amount of lignin was due to its degradation by light (Feist and Hon 1984).

Cellulose absorbs little UV radiation in terrestrial sunlight and hemicellulose has an absorption pattern similar to that of cellulose (Kalnins and Tarkow 1966; Kuo and Hu 1991). An increase in cellulose content of the weathered wood surface has been reported (Feist and Hon 1984). Data on white pine wood weathered outdoors for 20 years showed that weathering degraded and solubilized lignin, and cellulose appeared to be affected considerably less, except for the top surface layer of the wood. Similar results were obtained with wood exposed on a test fence for 30 years. On those specimens, the top gray layer consistently exhibited very low lignin content, while the brown layer immediately under the outer gray layer had lignin content 40 to 60% more than the level found for fresh unexposed wood (Feist and Hon 1984).

The role of extractives is not well defined. However, Kalnins and Tarkow (1966) suggested that they possibly act as antioxidants exerting protective effects on photodegradation. It has been reported that extractives are the cause of wood color, and have a plasticizing effect in wood. Substances such as flavonoids, lignans, and tannins are polyphenolic substances with the natural tendency to greasiness (Ajuong and Breese 1998). They can act as antioxidants capable of protecting wood surface against photooxidation (Maldas and Kamdem 1999). Hon and Minemura (2000) reported that many woods absorb light beyond 500nm due to the presence of phenolic substances such as flavonoids, stilbene, lignan, tannin and quinone. In addition, the intrinsic and extrinsic color of wood is reported to possess functional chromophoric groups such as phenoxyl hydroxyl groups, double bonds, carbonyl groups, etc., which absorb light and control the

course of photoreactions by acting as donors or acceptors in the energy transfer processes (Hon and Feist 1992).

The discoloration of wood during exposure to weathering is somehow correlated to the type and content of extractives. Our expectation is that extracted wood samples will be more prone to discoloration and roughening after weathering compared to un-extracted wood samples due to the loss or reduction of its antioxidant protection.

The aim of the project is to investigate the influence of wood extractives on the discoloration of wood surfaces exposed to artificial weathering.

6.2 Material and Methods

6.2.1 Materials

Samples were selected, prepared and extracted according to methods presented in Chapter 3, sections 3.2.1 and 3.2.2.

6.2.2 Artificial weathering test

Artificial weathering was conducted as described in Chapter 5, Section 5.2.1.

Specimens were removed for color measurement after 2h, 6h, 12h, and 24h during the first 24hours, then at 48, 96, 200, 400, 800, 1600, and 2400h. Special attention was made to always remove the sample for color measurement at 1h and 55mn into the UV exposure cycle to ensure similar moisture and temperature conditions for the specimens.

6.2.3 Color measurement

The surface color of wood was determined according to ISO 2470 Standard using a Microflash model 200 Reflectometer from DataColor. The color in the CIELAB system is characterized by three parameters, L^*, a^*, and b^* (Figure 6.1). The L^* axis represents the lightness, a^* and b^* are the chromaticity coordinates. In the CIELAB coordinates, $+a^*$

is for the red, -a* for green, +b* for yellow, -b* for blue, and L* varies from 100 (white) to zero (black). L*, a* and b* color coordinates of each group of samples were measured after exposure to UV irradiation. These values were then used to calculate the color change ΔE* as a function of the UV-irradiation duration according to equations 1, 2, 3 and 4.

$$\Delta L^* = L_f^* - L_i^* \qquad (1)$$

$$\Delta a^* = a_f^* - a_i^* \qquad (2)$$

$$\Delta b^* = b_f^* - b_i^* \qquad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (4)$$

Where, ΔL*, Δa* and Δb* are the change between the initial (i) and the final (f) values. L*, a* and b* contribute to the color change ΔE*. A low ΔE* corresponds to a low color change or a stable color.

6.2.4 Statistical Analysis

Statistical analysis using F-test on a generalized linear model (GLM) on SAS version 8.0 (SAS Institute 2000) was used to test the effect of extraction treatments on the discoloration property of wood surface. The GLM procedure uses the least square to fit general linear model. The contrast procedure was used to compare control and the various extraction treatments.

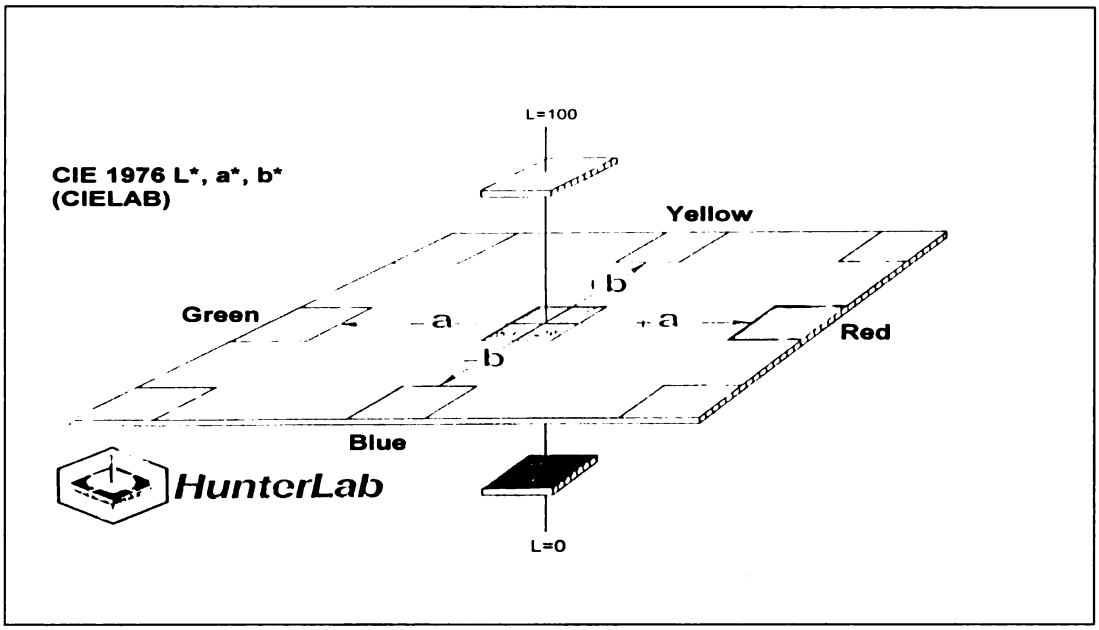


Figure 6.1 Color L*, a*, b* of solid in the CIELAB system (CIE 1976)

6.3 Results and Discussion

6.3.1 Changes in lightness (L)*

The lightness values for red pine, red oak, and black cherry during the weathering process are presented in Table 1. The initial L* value for un-extracted red pine specimens was 85. Extraction with organic solvents (ethanol or ethanol-toluene) did not induce any significant change in L* values, measured at 85.95 and 86.6 respectively. However when organic solvent extractions were followed by water extraction, the L* values were significantly lower, measured at 81.4 for Eth-Tol + Water and 81.06 for Eth +Water, indicating that subsequent extraction with water induced some darkening of the wood surface. Similar trends were observed in red oak and black cherry. The initial lightness values of red pine samples (80-85) were higher than those of red oak (68-72) and black cherry (58-64). This trend is expected because the wood surface of red pine is noticeably lighter than that of red oak and black cherry.

The lightness values for all three species and all extraction types decreased during the first 48h and increased afterwards to values comparable or higher than the initial L* values (Table 6.1). Weathering generally induces a rapid darkening of wood surfaces due to the degradation of lignin and extractives into quinones (darker in color), which are progressively washed out leaving the cellulose rich wood surface lighter in color as the process progresses (Feist and Hon 1984; Nzokou and Kamdem 2002). After 2400h exposure to artificial weathering, all three wood species had similar lightness values (83-90), indicating that their final whitish colors were of the same intensities.

Table 6.1: Lightness of wood specimens after artificial weathering (Average of 6 samples, and 3 measurement for each sample)

	Red Pine Lightness After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	85.1	71.0	69.8	69.8	72.2	75.2	79.3	83.3	86.8	88.9
Eth-Tol	85.9	70.6	68.3	69.9	73.5	76.8	81.7	85.2	88.5	89.9
Eth-Tol+Water	81.4	72.2	72.2	71.4	73.6	74.8	80.6	84.2	87.5	89.4
Eth	86.7	71.4	69.3	70.2	73.7	78.1	82.1	85.8	88.9	90.4
Eth+Water	81.1	66.5	65.1	66.2	69.8	74.4	81.2	84.4	87.9	89.8
Water	79.5	67.3	65.2	67.9	69.1	73.9	79.5	84.7	87.5	89.8
	Red Oak Lightness After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	72.0	64.9	64.9	64.6	67.7	72.1	76.9	80.7	86.4	87.2
Eth-Tol	73.4	67.7	67.5	67.8	70.6	73.3	77.8	82.8	86.4	88.1
Eth-Tol+Water	70.6	67.9	68.5	69.1	70.9	74.6	79.6	83.6	87.2	88.1
Eth	73.9	68.5	68.1	68.2	69.9	72.9	77.4	81.6	85.8	87.2
Eth+Water	68.4	66.6	67.1	67.8	70.8	74.2	77.8	82.2	85.6	87.4
Water	65.0	64.3	65.7	66.8	69.6	73.4	77.9	82.7	86.5	87.6
	Black Cherry Lightness After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	64.8	57.3	56.9	56.5	59.8	65.1	70.2	75.5	80.5	83.5
Eth-Tol	67.9	57.0	56.8	56.7	60.3	65.9	70.4	75.4	81.7	84.9
Eth-Tol+Water	58.3	47.5	49.1	52.1	60.1	68.1	76.1	81.5	85.5	87.2
Eth	69.9	53.9	55.1	58.7	65.1	71.9	78.8	82.9	86.7	88.3
Eth+Water	58.7	46.7	48.7	53.9	60.8	67.9	76.8	82.6	86.5	87.0
Water	56.2	47.4	49.5	52.9	61.9	70.0	77.3	81.7	85.6	87.6

Note: SAS "General Linear Model" analysis showed that the differences between treatments were not due to chance. The SAS "Contrast" procedure showed no significant differences between Control and extraction treatment for lightness over exposure time. The detail of the statistical output is presented in appendix 5.

Table 6.2: Lowering index of whiteness for red pine, red oak and black cherry after artificial weathering

	Lowering Index of Whiteness (ΔL/L%) for Red Oak After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	0.00	-9.9	-9.8	-10.2	-6.0	0.1	6.9	12.1	20.0	21.0
Eth-Tol	0.00	-7.9	-8.1	-7.6	-3.9	-0.3	5.9	12.8	17.7	19.9
Eth-Tol+Water	0.00	-3.8	-2.9	-2.1	0.6	5.8	12.7	18.4	23.5	24.8
Eth	0.00	-7.3	-7.9	-7.8	-5.4	-1.3	4.8	10.4	16.0	17.9
Eth+Water	0.00	-2.7	-1.9	-0.9	3.5	8.5	13.7	20.2	25.2	27.8
Water	0.00	-1.1	1.0	2.8	7.0	12.9	19.9	27.2	33.1	34.8
	Lowering Index of Whiteness (ΔL/L%) for Red Pine After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	0.00	-16.5	-17.91	-17.9	-15.1	-11.6	-6.8	-2.1	2.0	4.6
Eth-Tol	0.00	-17.9	-20.50	-18.7	-14.5	-10.6	-4.9	-0.9	3.0	4.6
Eth-Tol+Water	0.00	-11.4	-11.29	-12.3	-9.6	-8.1	-0.9	3.4	7.5	9.8
Eth	0.00	-17.6	-19.99	-19.0	-14.9	-9.9	-5.3	-0.9	2.5	4.3
Eth+Water	0.00	-17.9	-19.72	-18.3	-13.9	-8.2	0.2	4.1	8.4	10.8
Water	0.00	-9.3	-17.94	-14.6	-13.1	-7.0	-0.1	6.6	10.1	12.9
	Lowering Index of Whiteness (ΔL/L%) for Black Cherry After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	0.00	-11.6	-12.2	-12.8	-7.7	0.6	8.4	16.5	24.3	28.9
Eth-Tol	0.00	-16.0	-16.3	-16.5	-11.1	-2.9	3.7	11.1	20.4	25.2
Eth-Tol+Water	0.00	-18.5	-15.9	-10.6	3.1	16.7	30.6	39.8	46.8	49.6
Eth	0.00	-22.9	-21.2	-16.1	-6.9	2.8	12.6	18.5	23.9	26.2
Eth+Water	0.00	-20.5	-17.2	-8.1	3.5	15.7	30.8	40.6	47.3	48.1
Water	0.00	-15.6	-11.9	-5.9	10.3	24.7	37.7	45.4	52.4	55.9

Note: SAS "General Linear Model" analysis showed that the differences between treatments were not due to chance. The SAS "Contrast" procedure showed significant differences between Control and Eth-Tol+Water, Control and Eth+Water, and Control and Water for all three species. The detail of the statistical output is presented in appendix 6.

To compare the different extraction types, the measured lightness values were used to calculate the "Lowering Rate of Whiteness" (LIW) estimated by dividing the difference in lightness after irradiation by the original lightness before the weathering procedure (equation 5) (Hon 1991). An increase in the LIW indicates lightening, a decrease in the LIW indicates darkening.

$$LIW = \frac{L_f - L_i}{L_i} \qquad (5)$$

Where: L_f is the lightness after weathering exposure,

L_i is the lightness before weathering exposure.

The Lowering Index of Whiteness data presented in Table 6.2 show that control specimens had similar indexes of whiteness with eth-tol and eth extractions across the range of weathering exposure time. However, the LIW values were consistently higher for Ethanol-Toluene + Water and Ethanol + Water extractions, indicating that further extraction with water after organic solvent extraction increased the rate of whiteness for all three species. Statistical analysis (General Linear Model on SAS version 8) of the LIW values revealed no significant difference between control specimens, Ethanol-Toluene, and Ethanol specimens. However the differences were statistically significant with 95% confidence between control specimens and samples extracted with the above organic solvents and further extracted with water.

6.3.2 Chromaticity Coordinates

The chromaticity coordinates a* and b* over the weathering period for the three species are presented in Tables 6.3 and 6.4. As for lightness, observation of the values of a* at time 0 (initial a*) reveals that extraction with solvent systems that include water (Eth-Tol + Water and Eth + Water) resulted in higher a* (5.21 and 5.15) compared to

control samples (3.89), which had similar values to those of solvent only extracted samples (Eth-Tol and Eth). The same phenomenon was observed for the initial b* values, and similar trends were found in black cherry. There was no significant difference in initial chromaticity coordinated for red oak specimens.

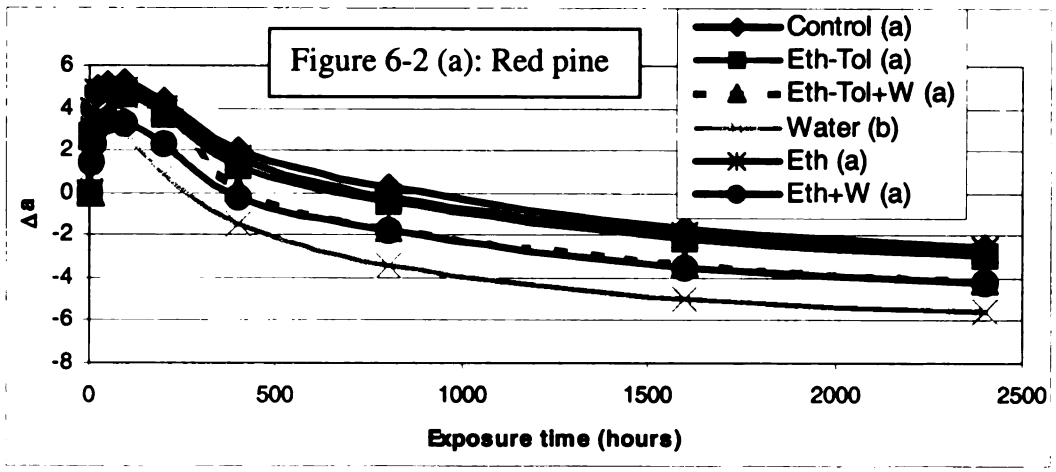
Red oak and black cherry had higher initial a* values (redder) than red pine, and their final a* values after 2400h artificial weathering were slightly lower, indicating that they were slightly bluer than red pine.

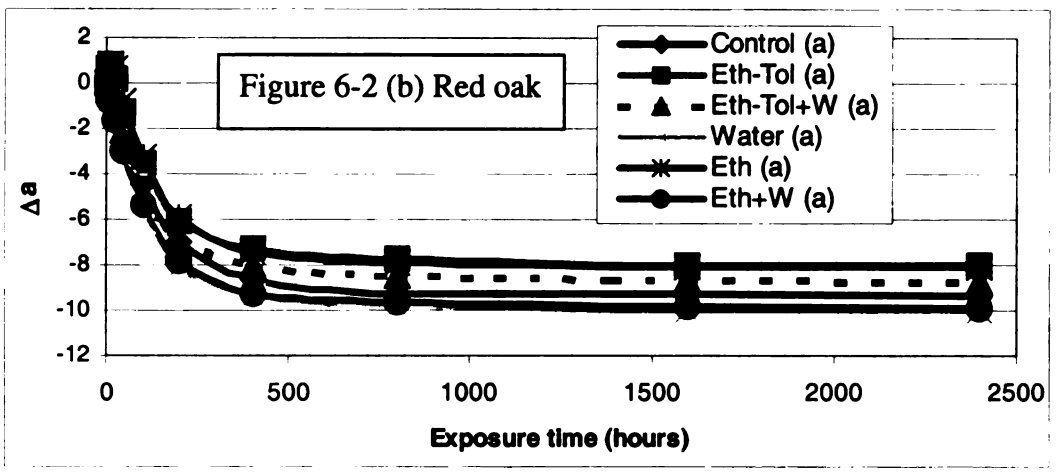
The change in chromaticity coordinates Δa^* and Δb^* (Figure 6-2 and 6-3) shows an increase during the first 100 hours and a decrease afterwards for all three species and extraction treatments. This is due to the sample surface becoming reddish and yellowish during the first phase of the weathering process, and progressively greenish and bluish with extended exposure to artificial weathering. Similar trends were observed for red oak and black cherry. It is important to note that the initial color parameters for the three wood species were quite different.

Chromaticity coordinates a* and b* were plotted in pairwise plots to evaluate the direction of the color change. For red pine (Figure 6.4), the figure shows a clear two phases process. During the first phase, the specimens are becoming increasingly reddish and yellowish. This is followed by a second phase where the samples are changing towards green and blue. In red oak (Figure 6.5) and black cherry (Figure 6.6), the first phase is absent, and the samples just changed to a more bluish-green color. There is no noticeable difference between the various extraction treatments.

Table 6.3: Chromaticity coordinate a* of wood specimens after artificial weathering

	Red Pine Chromaticity Coordinate (a*) After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	3.9	8.1	8.9	8.9	9.1	8.2	5.9	4.2	2.3	1.4
Eth-Tol	3.9	7.5	8.3	8.5	8.6	7.6	5.2	3.5	1.8	1.0
Eth-Tol+Water	5.2	8.5	10.0	10.2	10.3	9.1	5.4	3.5	1.9	1.1
Eth	3.5	7.3	8.2	8.3	8.3	7.4	5.1	3.2	1.5	0.8
Eth+Water	5.2	7.5	8.4	8.5	8.5	7.4	4.9	3.4	1.7	0.9
	Red Oak Chromaticity Coordinate (a*) After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	9.3	10.1	9.5	7.4	4.8	2.3	0.6	0.01	-0.1	-0.1
Eth-Tol	7.9	8.7	8.1	6.6	4.3	1.8	0.6	0.1	-0.1	-0.1
Eth-Tol+Water	8.6	8.4	7.9	6.5	3.7	1.7	0.6	0.1	-0.0	-0.1
Eth	7.9	8.8	8.6	7.2	4.7	2.0	0.5	0.01	-0.1	-0.1
Eth+Water	9.8	8.9	8.21	6.8	4.4	2.0	0.5	0.1	-0.1	-0.1
	Black Cherry Chromaticity Coordinate (a*) After Artificial Weathering									
	0	**12h**	**24h**	**48h**	**100h**	**200h**	**400h**	**800h**	**1600**	**2400h**
Control	10.6	14.2	13.7	10.8	6.8	2.7	0.9	0.4	0.1	0.01
Eth-Tol	10.7	14.5	13.6	11.2	9.9	6.4	1.9	0.5	0.1	0.01
Eth-Tol+Water	15.7	12.7	12.9	11.2	8.8	5.3	2.7	1.6	0.7	0.3
Eth	10.8	10.0	10.3	8.7	6.4	3.9	2.2	1.2	0.5	0.2
Eth+Water	18.7	11.2	11.5	10.0	7.4	4.3	2.3	1.3	0.5	-0.0





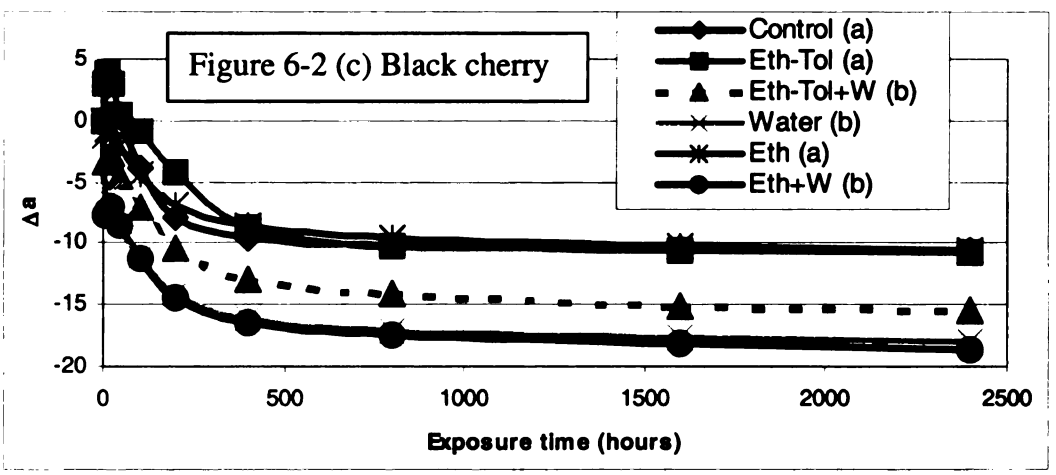
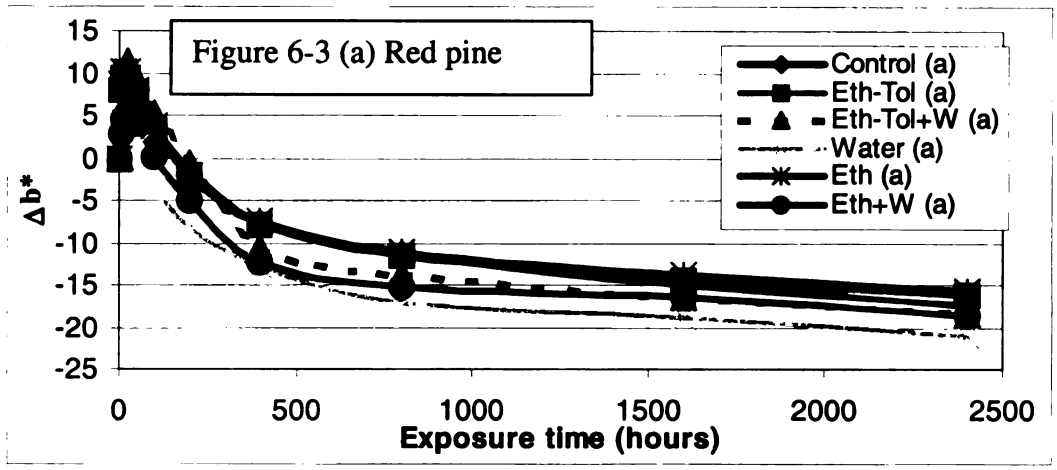


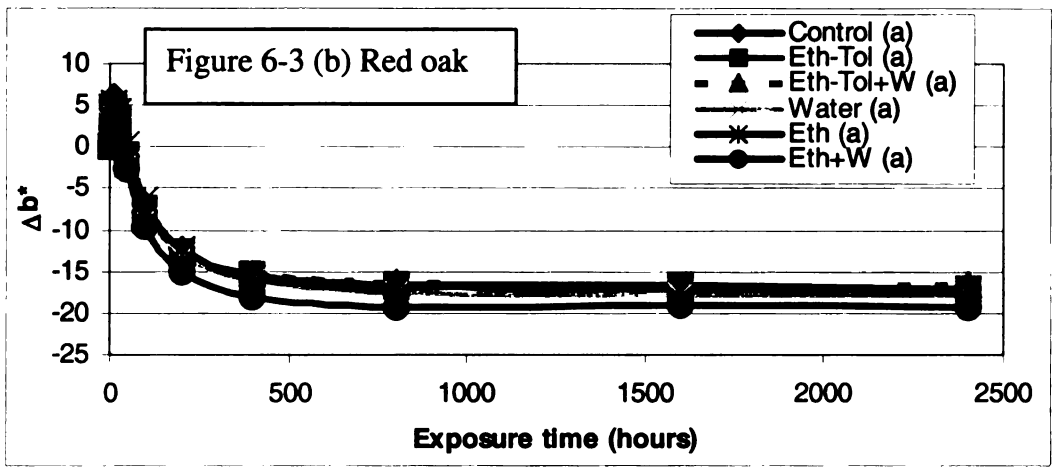
Figure 6-2: Change in chromaticity coordinate a (Δa*) over the exposure time.

Note: Letters in parenthesis in the legend indicate statistical significance compared to control. Similar letter mean no statistical difference with control. Different letters mean statistical significant 95% confidence level. Details of the statistical analysis are presented in appendix 7.

Table 6.4: Chromaticity coordinate b* of wood specimens after artificial weathering

	Red Pine Chromaticity Coordinate (b*) After Artificial Weathering									
	0	12h	24h	48h	100h	200h	400h	800h	1600	2400h
Control	21.5	30.9	31.2	29.6	25.2	20.2	13.7	10.2	6.6	4.1
Eth-Tol	19.9	29.3	29.3	27.6	23.3	17.9	12.1	8.2	5.5	3.8
Eth-Tol+Water	22.0	32.0	33.5	31.3	27.2	21.4	11.5	8.2	5.5	3.6
Eth	19.3	29.3	29.4	27.2	23.1	17.2	11.9	8.1	5.4	3.6
Eth+Water	22.6	27.0	27.8	26.6	22.7	17.5	10.2	7.4	6.0	3.9
	Red Oak Chromaticity Coordinate (b*) After Artificial Weathering									
	0	12h	24h	48h	100h	200h	400h	800h	1600	2400h
Control	19.6	25.8	24.1	19.1	12.8	7.3	3.9	3.1	2.1	2.5
Eth-Tol	19.3	24.2	22.6	18.3	12.0	6.6	4.0	2.8	2.7	2.3
Eth-Tol+Water	19.3	23.8	22.3	18.0	10.9	6.3	3.9	2.9	2.4	2.6
Eth	19.4	24.8	23.7	19.7	12.9	7.0	3.7	2.6	2.2	2.4
Eth+Water	21.8	24.5	22.9	19.0	12.2	6.6	3.7	2.6	2.7	2.5
	Black Cherry Chromaticity Coordinate (b*) After Artificial Weathering									
	0	12h	24h	48h	100h	200h	400h	800h	1600	2400h
Control	19.6	26.3	25.6	21.1	13.9	6.5	3.5	2.0	1.8	2.3
Eth-Tol	19.9	25.8	24.5	20.3	16.8	10.8	4.8	2.3	1.6	1.5
Eth-Tol+Water	21.6	21.3	21.9	19.4	14.6	9.1	5.5	4.6	3.6	2.6
Eth	20.2	21.2	21.3	17.7	12.4	7.9	4.9	4.6	3.5	3.1
Eth+Water	22.2	18.7	19.3	17.5	12.6	7.5	4.8	4.1	3.8	2.6





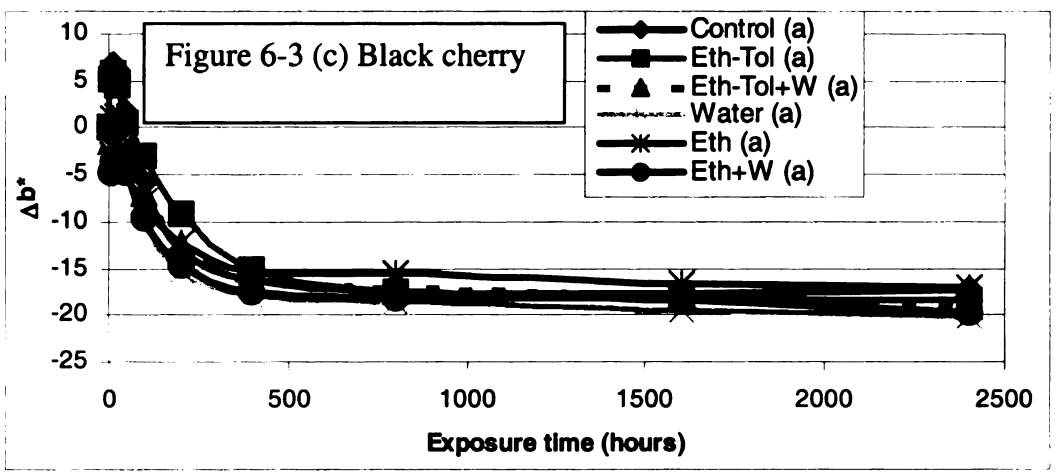


Figure 6-3: Change in chromaticity coordinate b (Δb*) over the exposure time.

Note: Letters in parenthesis in the legend indicate statistical significance compared to control. Similar letter mean no statistical difference with control. Different letters mean statistical significant 95% confidence level. Details of the statistical analysis are presented in appendix 8.

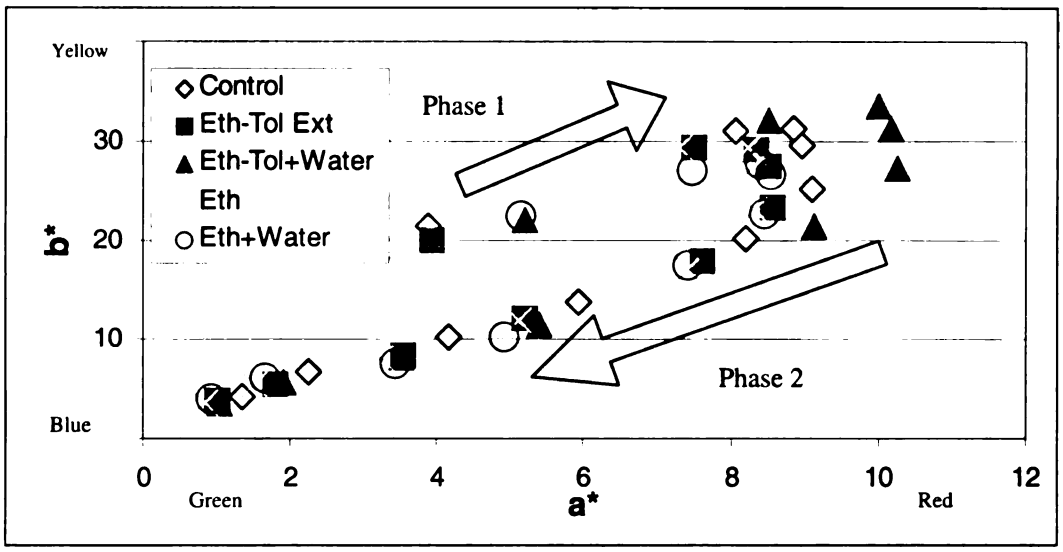


Figure 6.4: Relation between chromaticity coordinates a* and b* for red pine after artificial weathering

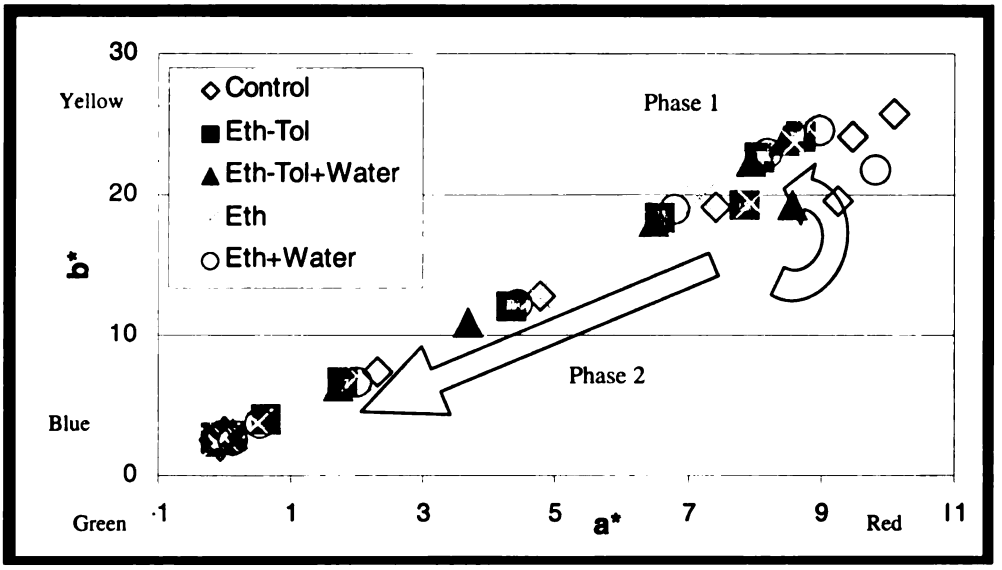


Figure 6.5: Relation between chromaticity coordinates a* and b* for red oak after artificial weathering

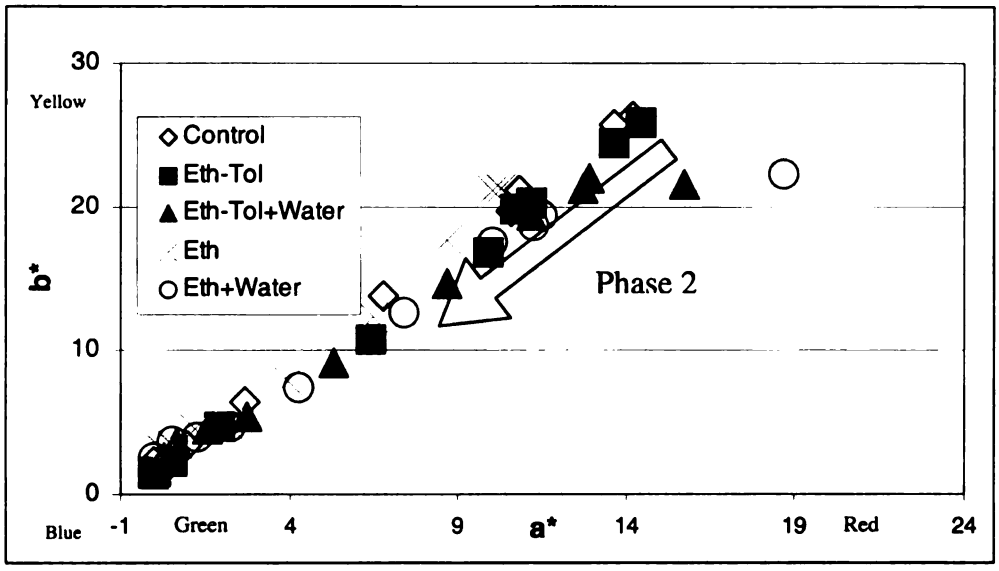


Figure 6.6: Relation between chromaticity coordinates a* and b* for black cherry after artificial weathering

6.3.3 Color Change (ΔE)

The overall color change (ΔE) values after 2400h in relation to the total extractives removed from the wood specimens are presented in Table 6.5. For red pine samples, the color change for un-extracted samples was 18.01. The color change value was 16.91 for ethanol-toluene extracted samples and 16.32 (2.62% extractives) for ethanol-extracted samples (3.32% extractives). Water extraction of red pine samples following these solvent extractions induced higher color change; 20.51 and 21.02 for ethanol-toluene + water (3.54% extractives) and ethanol + water respectively (4.6% extractives). Similar trends were observed with red oak and black cherry specimens. These are all observable and very important discolorations according to the scale proposed by Dirckx et al (1992) and presented in Table 6.6. The variability between the total amount of extractives removed and the color change suggests the quantity removed is of less importance, and the nature and chemical composition more critical in relation to discoloration. FTIR spectra of wood extractives reported Chapter 3 showed that extractives removed by ethanol and ethanol-toluene were made up of fatty acids, saturated esters and cyclic polyphenolic compounds. Water extracts were mainly made of colorific matter, condensed tannins, and low molecular weight carbohydrates. This explains the observed enhanced discoloration when solvent extractions were followed by water extraction.

The total discoloration over the weathering duration is presented Table 6.7 and Figure 6.7(a-c). The general pattern for all species and treatments show a rapid increase during the first 12 hours, followed by a steep decrease in ΔE extending to about 48 hours of exposure. This stage is immediately followed by a continuous increase in the value of

ΔE as the sample surface becomes increasingly whiter. Visual observation of ΔE figures for all three species beyond the first 48 to 100 hours of rapid change shows a clear separation between the control curve, the curve for solvent extracted samples (Eth-Tol and Eth), and the curves for samples extracted with solvents and water (Eth-Tol + Water, and Eth + Water). The discoloration curves for samples extracted with water included in the system were consistently higher than the control curves, which remained similar to those of specimens extracted with organic solvents. Analysis of variance using the SAS version general linear model of ΔE showed no statistical difference at 95% confidence level between control, Eth-Tol and Eth. However, there was significant difference between the above treatments and Eth-Tol + Water and Eth + Water. These lower rates of discoloration for control and solvent extracted samples can only be explained by some level of weathering protection provided by extractives contained in control samples and not removed by organic solvents. Such extractives, which could be polyphenolic water extractable compounds were removed when water extraction was included in the system. These effects were less marked in red oak where there was no statistical difference between control, Eth-Tol, Eth, Eth-Tol+Water, and the Eth + Water was the only group significantly different from the other treatments.

Wood weathering is caused by the absorption of light energy by active wood components, which bring them to an excited triplet state that transfers the energy to triplet ground state oxygen molecules to create singlet oxygen (Feist and Hon 1984). These radicals rapidly interact with oxygen to produce hydroperoxide impurities that are decomposed easily to produce chromophoric groups such as carbonyl and carboxyl groups (Feist and Hon 1984). Free radical chain reactions in the presence of oxygen and

light are responsible for the discoloration and deterioration of wood surfaces. Results obtained in this project suggest that the presence of extractives slow this process, with polyphenolic water extractives acting as anti-oxidant protecting the wood surface against photodegradation.

Table 6.5: Extractives removed and color change after artificial weathering

Red Pine		
	Extractives %	**ΔE**
Control	0	18.01
Eth-Tol	2.67	16.91
Eth-Tol+Water	3.54	20.51
Eth	3.32	16.32
Eth+Water	4.6	21.02
Water	1.8	24.12
Red Oak		
	Extractives %	ΔE
Control	0	24.73
Eth-Tol	2.03	23.78
Eth-Tol+Water	2.76	25.71
Eth	1.59	23.04
Eth+Water	4.07	28.84
Water	3.44	30.44
Black Cherry		
	Extractives %	ΔE
Control	0	27.63
Eth-Tol	2.02	27.30
Eth-Tol+Water	3.1	37.90
Eth	3.21	27.18
Eth+Water	4.79	39.16
Water	3.46	41.44

Table 6.6: Correspondence between ΔE and visual observation in the CIELAB system (Dirckx et al. 1992)

Visual change	ΔE
Trace	0-0.5
Light	0.5-1.5
Noticeable	1.5-3
Considerable	3-6
Important	6-12
Very Important	> 12

Table 6.7: Color change after artificial weathering

	Color Change (ΔE) of Red Pine After Artificial Weathering									
	0	**12**	**24**	**48**	**100**	**200**	**400**	**800**	**1600**	**2400**
Control	0.00	17.44	18.76	18.03	14.37	10.87	9.91	11.42	15.08	18.01
Eth-Tol	0.00	18.32	20.41	18.37	13.71	10.04	9.05	11.74	14.86	16.91
Eth-Tol+Water	0.00	14.02	15.45	14.52	10.64	7.72	10.53	14.20	17.88	20.51
Eth	0.00	18.71	20.62	18.89	14.32	9.67	8.84	11.16	14.20	16.32
Eth + Water	0.00	15.38	17.12	15.76	11.75	8.66	12.37	15.60	18.24	21.02
Water	0.00	13.25	15.17	12.06	11.26	9.82	12.87	19.19	21.09	24.12
	Color Change (ΔE) of Red Oak After Artificial Weathering									
	0	**12**	**24**	**48**	**100**	**200**	**400**	**800**	**1600**	**2400**
Control	0.00	9.43	8.37	7.59	9.26	14.14	18.59	20.83	24.51	24.73
Eth-Tol	0.00	7.62	6.82	5.83	8.59	14.05	17.48	20.50	22.55	23.78
Eth-Tol+Water	0.00	5.24	3.75	2.87	9.70	15.21	19.48	22.56	25.18	25.71
Eth	0.00	7.69	7.27	5.79	8.23	13.76	17.77	20.06	22.36	23.04
Eth + Water	0.00	3.40	2.36	4.11	11.26	18.01	22.39	25.56	27.54	28.84
Water	0.00	3.61	2.67	4.41	11.76	17.64	22.63	26.72	29.66	20.44
	Color Change (ΔE) of Black Cherry After Artificial Weathering									
	0	**12**	**24**	**48**	**100**	**200**	**400**	**800**	**1600**	**2400**
Control	0.00	10.66	10.41	8.41	8.52	15.32	19.54	22.99	25.96	27.63
Eth-Tol	0.00	12.92	12.35	11.18	8.15	10.23	17.65	21.67	25.26	27.30
Eth-Tol+Water	0.00	11.19	9.65	7.97	10.06	18.94	27.33	32.03	36.00	37.90
Eth	0.00	16.12	14.89	11.71	10.13	14.22	19.64	22.37	25.79	27.18
Eth + Water	0.00	14.58	12.68	10.92	15.00	22.57	30.01	34.67	37.97	39.16
Water	0.00	12.34	9.30	10.10	16.06	24.97	32.03	35.90	39.51	41.44

Note: SAS "General Linear Model" analysis showed that the differences between treatments were not due to chance. The SAS "Contrast" procedure showed significant differences between Control and Eth-Tol+Water, Control and Eth+Water, and Control and Water for black cherry. There was no significant difference between control and ethanol-toluene and control and ethanol for any of the three species. The detail of the statistical output is presented in appendix 9.

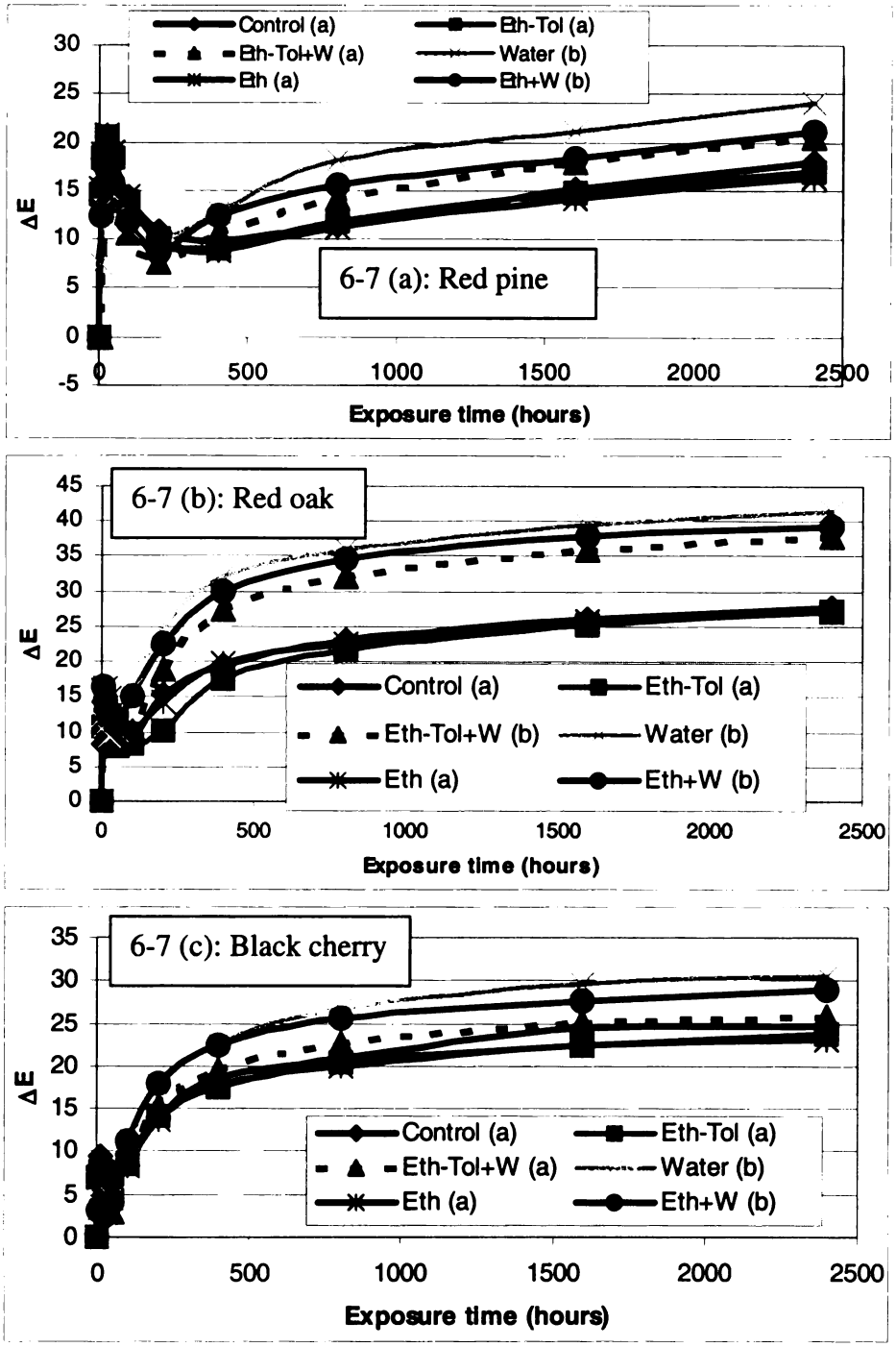


Figure 6.7: Color change ΔE of wood samples after artificial weathering

Note: Letters in parenthesis in the legend indicate statistical significance compared to control. Similar letter mean no statistical difference with control. Different letters mean statistical significant 95% confidence level.

6.4 Conclusions

This study investigated the influence of wood extractives on the discoloration behavior of red pine, red oak, and black cherry. Results obtained showed that the rate of whitening and the total discoloration rate of wood specimens were significantly affected by the removal of water extractable compounds from wood. Chromaticity coordinates were less affected by the removal of wood extractives. These extractives, which are known to be polyphenolic in nature, act as anti-oxidants and provide some level of protection to wood against photodegradation.

However, more work is required to understand the chemistry of photo-protection of wood surface by extractives, before any practical and economically viable of use of this property could be developed.

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Based on observations made in this study, extractives removed by ethanol and ethanol-toluene from red oak, black cherry, and red pine were made up of fatty acids, saturated esters, and cyclic polyphenolic compounds. The water extracts were mainly colorific matter, condensed tannins, and low molecular weight carbohydrates. FTIR and XPS analysis of wood surfaces showed that extraction results in hemicelluloses and cellulose becoming more exposed on the wood surface.

Further investigations showed that these wood extractives lowered the equilibrium moisture content of wood at a high relative humidity. Application of the Hailwood-Horrrobin Sorption Theory to our data demonstrated that extracted wood had more adsorption sites available and needed lower energy to absorb water.

The contact angle of extracted wood surface and distilled water decreased with increased extraction, suggesting increased ability of wood surfaces to absorb water due to the removal of extractive. This could lead to increased dimensional instability and eventually lead to more severe physical damages on extracted wood.

However, monitoring of the physical degradation of specimens showed no specific influence of wood extractives on the roughening, weight loss and microscopic degradation of red pine, red oak, and black cherry following exposure to artificial weathering. This observation suggests that the structure of wood, its density and internal stresses developed during drying, and wetting are, as largely published in the literature, the main factors of the erosion, weight loss and cracking of wood during weathering, with extractives having only a limited and undetectable effect.

Investigation of the discoloration behavior of specimens showed that the rate of whitening and the total discoloration rate of wood specimens were significantly affected by the removal of water extractable compounds from wood. This confirms that extractives, which are known to be polyphenolic in nature, act as anti-oxidants, and provide some level of protection to wood against photodegradation.

However, more work is required to understand the chemistry of photo-protection of wood surface by extractives, before any practical and economically viable use of this property could be developed.

Recommendations for further study can be summed up as the followings:

(1) These results need to be confirmed by conducting a similar study with field test exposure.

(2) More studies are needed on the chemical nature of extractives and their mechanism of interaction with wood components.

APPENDIXES

Appendix 1: One Way Analysis of Variance of the contact angle values for wood specimens

Black Cherry

Normality Test: Passed (P = 0.019)

Equal Variance Test: Passed (P = 0.271)

Source of Variation	DF	SS	MS	F	P
Between Groups	11	30539.204	2776.291	58.203	<0.001
Residual	84	4006.817	47.700		
Total	95	34546.021			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth-Tol+Water	46.788	12	19.161	<0.001	Yes
Control vs. Eth-Tol	39.078	12	16.003	<0.001	Yes
Control vs. Eth+W	34.612	12	14.175	<0.001	Yes
Control vs. Eth	31.613	12	12.946	<0.001	Yes

Red Oak

Normality Test: Passed (P > 0.200)

Equal Variance Test: Passed (P = 0.805)

Source of Variation	DF	SS	MS	F	P
Between Groups	4	8994.801	2248.700	31.321	<0.001
Residual	35	2512.826	71.795		
Total	39	11507.628			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth-Tol+W	39.737	5	13.265	<0.001	Yes
Control vs. Eth-Tol	38.612	5	12.889	<0.001	Yes
Control vs. Eth+W	37.287	5	12.447	<0.001	Yes
Control vs. Eth	25.950	5	8.662	<0.001	Yes

One Way Analysis of Variance **Saturday, March 06, 2004, 16:09:02**

Red Pine

Normality Test: Passed (P > 0.200)

Equal Variance Test: Passed (P = 0.021)

Source of Variation	DF	SS	MS	F	P
Between Groups	4	30068.394	7517.099	76.317	<0.001
Residual	35	3447.442	98.498		
Total	39	33515.836			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth-Tol+W	70.632	5	20.130	<0.001	Yes
Control vs. Eth+W	63.114	5	17.987	<0.001	Yes
Control vs. Eth	35.796	5	10.202	<0.001	Yes
Control vs. Eth-Tol	12.995	5	3.703	0.089	No

Appendix 2: One-Way ANOVA Analysis of the change in contact over time

Black Cherry

Normality Test: Passed (P = 0.011)

Equal Variance Test: Passed (P = 0.206)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	8	0	1.622	0.816	0.289
Eth-Tol	8	0	0.827	0.187	0.0661
Eth-Tol+W	8	0	2.823	0.717	0.253
Eth	8	0	0.692	0.257	0.0907
Eth+W	8	0	3.164	0.967	0.342

Source of Variation	DF	SS	MS	F	P
Between Groups	4	40.885	10.221	23.060	<0.001
Residual	35	15.513	0.443		
Total	39	56.398			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Eth+W vs. Eth	2.472	5	10.503	<0.001	Yes
Eth+W vs. Eth-Tol	2.337	5	9.928	<0.001	Yes
Eth+W vs. Control	1.542	5	6.551	<0.001	Yes
Eth+W vs. Eth-Tol+W	0.341	5	1.448	0.843	No
Eth-Tol+W vs. Eth	2.131	5	9.055	<0.001	Yes
Eth-Tol+W vs. Eth-Tol	1.996	5	8.481	<0.001	Yes
Eth-Tol+W vs. Control	1.201	5	5.103	0.008	Yes
Control vs. Eth	0.930	5	3.952	0.060	No
Control vs. Eth-Tol	0.795	5	3.377	0.143	Do Not Test
Eth-Tol vs. Eth	0.135	5	0.575	0.994	Do Not Test

Red Oak

Normality Test: Passed (P > 0.200)

Equal Variance Test: Passed (P = 0.213)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	8	0	2.758	0.649	0.230
Eth-Tol	8	0	1.449	0.384	0.136
Eth-Tol+W	8	0	2.347	0.751	0.265
Eth	8	0	2.543	0.658	0.233
Eth+W	8	0	2.771	0.847	0.300

Source of Variation	DF	SS	MS	F	P
Between Groups	4	9.515	2.379	5.212	0.002
Residual	35	15.975	0.456		
Total	39	25.490			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.002).

Power of performed test with alpha = 0.050: 0.892

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Eth+W vs. Eth-Tol	1.322	5	5.533	0.004	Yes
Eth+W vs. Eth-Tol+W	0.424	5	1.773	0.720	No
Eth+W vs. Eth	0.227	5	0.952	0.961	Do Not Test
Eth+W vs. Control	0.0130	5	0.0544	1.000	Do Not Test
Control vs. Eth-Tol	1.309	5	5.479	0.004	Yes
Control vs. Eth-Tol+W	0.411	5	1.719	0.743	Do Not Test
Control vs. Eth	0.214	5	0.897	0.968	Do Not Test
Eth vs. Eth-Tol	1.094	5	4.581	0.021	Yes
Eth vs. Eth-Tol+W	0.196	5	0.821	0.977	Do Not Test
Eth-Tol+W vs. Eth-Tol	0.898	5	3.760	0.081	No

Red Pine

Normality Test: Passed (P > 0.200)

Equal Variance Test: Passed (P = 0.226)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	8	0	5.199	0.915	0.324
Eth-Tol	8	0	6.950	1.457	0.515

Eth-Tol+W	8	0	3.660	1.024	0.362
Eth	8	0	2.790	0.735	0.260
Eth+W	8	0	3.319	0.860	0.304

Source of Variation	**DF**	**SS**	**MS**	**F**	**P**
Between Groups	4	91.595	22.899	21.642	<0.001
Residual	35	37.032	1.058		
Total	39	128.628			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	**Diff of Means**	**p**	**q**	**P**	**P<0.050**
Eth-Tol vs. Eth	4.160	5	11.440	<0.001	Yes
Eth-Tol vs. Eth+W	3.632	5	9.986	<0.001	Yes
Eth-Tol vs. Eth-Tol+W	3.290	5	9.046	<0.001	Yes
Eth-Tol vs. Control	1.752	5	4.816	0.014	Yes
Control vs. Eth	2.409	5	6.623	<0.001	Yes
Control vs. Eth+W	1.880	5	5.170	0.007	Yes
Control vs. Eth-Tol+W	1.538	5	4.230	0.038	Yes
Eth-Tol+W vs. Eth	0.870	5	2.393	0.452	No
Eth-Tol+W vs. Eth+W	0.342	5	0.940	0.963	Do Not Test
Eth+W vs. Eth	0.529	5	1.453	0.841	Do Not Test

A result of "Do Not Test" occurs for a comparison when no significant difference is found between two means that enclose that comparison. For example, if you had four means sorted in order, and found no difference between means 4 vs. 2, then you would not test 4 vs. 3 and 3 vs. 2, but still test 4 vs. 1 and 3 vs. 1 (4 vs. 3 and 3 vs. 2 are enclosed by 4 vs. 2: 4 3 2 1). Note that not testing the enclosed means is a procedural rule, and a result of Do Not Test should be treated as if there is no significant difference between the means, even though one may appear to exist.

Appendix 3: One-Way ANOVA Analysis of the Roughness Index (RI)

Red Pine

Normality Test: Passed (P = <0.001)

Equal Variance Test: Failed (P = <0.001)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	25	0	39.857	7.757	1.551
Eth-Tol	25	0	8.106	1.032	0.206
Eth-Tol+Water	25	0	5.465	2.095	0.419
Eth	25	0	9.964	3.697	0.739
Eth+Water	25	0	4.284	0.934	0.187

Source of Variation	DF	SS	MS	F	P
Between Groups	4	22144.615	5536.154	345.308	<0.001
Residual	120	1923.903	16.033		
Total	124	24068.517			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth+Water	35.573	5	44.421	<0.001	Yes
Control vs. Eth-Tol+Water	34.392	5	42.946	<0.001	Yes
Control vs. Eth-Tol	31.752	5	39.649	<0.001	Yes
Control vs. Eth	29.893	5	37.329	<0.001	Yes

Red Oak

Normality Test: Passed (P = 0.075)
Equal Variance Test: Failed (P = <0.001)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	25	0	5.708	1.857	0.371
Eth-Tol	25	0	4.332	1.212	0.242
Eth-Tol+Water	25	0	3.316	1.397	0.279
Eth	25	0	5.179	1.475	0.295
Eth+Water	25	0	2.611	0.498	0.0996

Source of Variation	DF	SS	MS	F	P
Between Groups	4	163.785	40.946	22.028	<0.001
Residual	120	223.055	1.859		
Total	124	386.840			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth+Water	3.096	5	11.356	<0.001	Yes
Control vs. Eth-Tol+Water	2.392	5	8.772	<0.001	Yes
Control vs. Eth-Tol	1.375	5	5.044	0.005	Yes
Control vs. Eth	0.528	5	1.937	0.648	No

Black Cherry

Normality Test: Passed (P = 0.003)
Equal Variance Test: Passed (P = <0.001)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	24	0	2.814	0.439	0.0896
Eth-Tol	25	0	0.945	0.198	0.0396
Eth-Tol+Water	25	0	0.717	0.306	0.0612
Eth	25	0	1.084	0.688	0.138
Eth+Water	25	0	0.644	0.289	0.0578

Source of Variation	DF	SS	MS	F	P
Between Groups	4	77.907	19.477	110.476	<0.001
Residual	119	20.979	0.176		
Total	123	98.886			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	**Diff of Means**	**p**	**q**	**P**	**P<0.050**
Control vs. Eth+Water	2.169	5	25.569	<0.001	Yes
Control vs. Eth-Tol+Water	2.096	5	24.707	<0.001	Yes
Control vs. Eth-Tol	1.869	5	22.029	<0.001	Yes
Control vs. Eth	1.729	5	20.382	<0.001	Yes

Appendix 4: One-Way ANOVA Analysis of Microcracking index (MCI)

Red Pine

Normality Test: Passed (P = 0.024)

Equal Variance Test: Failed (P = <0.001)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	25	0	17.175	4.013	0.803
Eth-Tol	25	0	5.246	1.482	0.296
Eth-Tol+Water	25	0	3.236	1.773	0.355
Eth	25	0	6.064	2.708	0.542
Eth+Water	25	0	2.897	0.915	0.183

Source of Variation	DF	SS	MS	F	P
Between Groups	4	3461.287	865.322	146.093	<0.001
Residual	120	710.771	5.923		
Total	124	4172.058			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth+Water	14.278	5	29.334	<0.001	Yes
Control vs. Eth-Tol+Water	13.938	5	28.636	<0.001	Yes
Control vs. Eth-Tol	11.929	5	24.508	<0.001	Yes
Control vs. Eth	11.110	5	22.826	<0.001	Yes

Red Oak

Normality Test: Passed (P > 0.200)
Equal Variance Test: Passed (P = 0.078)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	25	0	1.616	0.768	0.154
Eth-Tol	25	0	2.455	0.997	0.199
Eth-Tol+Water	25	0	1.732	0.581	0.116
Eth	25	0	2.213	0.839	0.168
Eth+Water	25	0	1.809	0.559	0.112

Source of Variation	DF	SS	MS	F	P
Between Groups	4	12.535	3.134	5.330	<0.001
Residual	120	70.552	0.588		
Total	124	83.087			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 0.932

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Eth-Tol vs. Control	0.839	5	5.468	0.002	Yes
Eth-Tol vs. Eth-Tol+Water	0.722	5	4.710	0.010	Yes
Eth-Tol vs. Eth+Water	0.645	5	4.209	0.029	Yes
Eth-Tol vs. Eth	0.242	5	1.575	0.799	No
Eth vs. Control	0.597	5	3.893	0.052	No
Eth vs. Eth-Tol+Water	0.481	5	3.134	0.181	Do Not Test
Eth vs. Eth+Water	0.404	5	2.634	0.343	Do Not Test
Eth+Water vs. Control	0.193	5	1.259	0.900	Do Not Test
Eth+Water vs. Eth-Tol+Water	0.0768	5	0.501	0.997	Do Not Test
Eth-Tol+Water vs. Control	0.116	5	0.759	0.983	Do Not Test

A result of "Do Not Test" occurs for a comparison when no significant difference is found between two means that enclose that comparison. For example, if you had four means sorted in order, and found no difference between means 4 vs. 2, then you would not test 4 vs. 3 and 3 vs. 2, but still test 4 vs. 1 and 3 vs. 1 (4 vs. 3 and 3 vs. 2 are enclosed by 4 vs. 2: 4 3 2 1). Note that not testing the enclosed means is a procedural rule, and a result of Do Not Test should be treated as if there is no significant difference between the means, even though one may appear to exist.

Black Cherry

Normality Test: Passed (P = 0.001)
Equal Variance Test: Failed (P = <0.001)

Group Name	N	Missing	Mean	Std Dev	SEM
Control	25	0	1.864	0.623	0.125
Eth-Tol	25	0	0.915	0.289	0.0579
Eth-Tol+Water	25	0	0.640	0.328	0.0655
Eth	25	0	1.260	0.527	0.105
Eth+Water	25	0	0.393	0.211	0.0422

Source of Variation	DF	SS	MS	F	P
Between Groups	4	32.967	8.242	45.754	<0.001
Residual	120	21.615	0.180		
Total	124	54.582			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
Control vs. Eth+Water	1.471	5	17.334	<0.001	Yes
Control vs. Eth-Tol+Water	1.224	5	14.423	<0.001	Yes
Control vs. Eth-Tol	0.949	5	11.178	<0.001	Yes
Control vs. Eth	0.605	5	7.122	<0.001	Yes

Appendix 5: Results of SAS Statistical GLM analysis of the Lightness data (L)

Red Pine

Number of observations 60

Dependent Variable: y

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	368388.7713	30699.0643	1092.65	<.0001
Error	48	1348.6016	28.0959		
Uncorrected Total	60	369737.3729			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.72598477	0.72598477	0.03	0.8730
slope of Control vs Eth-Tol+W	1	0.00924161	0.00924161	0.00	0.9856
slope of Control vs Eth	1	14.23527164	14.23527164	0.51	0.4800
slope of Control vs Eth-W	1	14.23527164	14.23527164	0.51	0.4800
slope of Control vs water	1	14.07350123	14.07350123	0.50	0.4825

Red Oak

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	339659.9699	28304.9975	2055.74	<.0001
Error	48	660.9003	13.7688		
Uncorrected Total	60	340320.8702			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	2.08948435	2.08948435	0.15	0.6986
slope of Control vs Eth-Tol+W	1	1.71459606	1.71459606	0.12	0.7257
slope of Control vs Eth	1	1.30646772	1.30646772	0.09	0.7594
slope of Control vs Eth-W	1	1.30646772	1.30646772	0.09	0.7594
slope of Control vs water	1	0.62354435	0.62354435	0.05	0.8324

Black cherry

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	282297.1321	23524.7610	397.11	<.0001
Error	48	2843.5121	59.2398		
Uncorrected Total	60	285140.6442			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.26361542	0.26361542	0.00	0.9471
slope of Control vs Eth-Tol+W	1	59.11629405	59.11629405	1.00	**0.0228**
slope of Control vs Eth	1	58.89795477	58.89795477	0.99	0.3237
slope of Control vs Eth-W	1	58.89795477	58.89795477	0.99	**0.0323**
slope of Control vs water	1	57.97243644	57.97243644	0.98	**0.0275**

Appendix 6: Results of SAS Statistical GLM analysis of the Lowering Rate of Whiteness Index Lightness (LWI)

The GLM Procedure

Red pine

Dependent Variable: y

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	0.59187584	0.04932299	12.50	<.0001
Error	48	0.18934891	0.00394477		
Uncorrected Total	60	0.78122475			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.00007150	0.00007150	0.02	0.8935
slope of Control vs Eth-Tol+W	1	0.00005865	0.00005865	0.01	0.0903
slope of Control vs Eth	1	0.00288025	0.00288025	0.73	0.3971
slope of Control vs Eth-W	1	0.00288025	0.00288025	0.73	0.0497
slope of Control vs water	1	0.00232179	0.00232179	0.59	0.0446

Red oak

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	0.95722441	0.07976870	28.82	<.0001
Error	48	0.13286554	0.00276803		
Uncorrected Total	60	1.09008995			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.00058550	0.00058550	0.21	0.6477
slope of Control vs Eth-Tol+W	1	0.00019489	0.00019489	0.07	0.0799
slope of Control vs Eth	1	0.00002084	0.00002084	0.01	0.9312
slope of Control vs Eth-W	1	0.00002084	0.00002084	0.01	0.0932
slope of Control vs water	1	0.00111741	0.00111741	0.40	0.0582

Black cherry

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	2.64880151	0.22073346	13.57	<.0001
Error	48	0.78095009	0.01626979		
Uncorrected Total	60	3.42975160			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.00003600	0.00003600	0.00	0.9627
slope of Control vs Eth-Tol+W	1	0.02726865	0.02726865	1.68	0.0201
slope of Control vs Eth	1	0.02607045	0.02607045	1.60	0.2117
slope of Control vs Eth-W	1	0.02607045	0.02607045	1.60	0.0217
slope of Control vs water	1	0.03286963	0.03286963	2.02	0.0167

Appendix 7: Results of SAS Statistical GLM analysis of the change in Chromaticity Coordinate a (Δa)

Red pine

Dependent Variable: y

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	519.7577623	43.3131469	14.52	<.0001
Error	48	143.2022155	2.9833795		
Uncorrected Total	60	662.9599778			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.00111075	0.00111075	0.00	0.9847
slope of Control vs Eth-Tol+W	1	1.36353632	1.36353632	0.46	0.5023
slope of Control vs Eth	1	0.04781313	0.04781313	0.02	0.8998
slope of Control vs Eth-W	1	0.04781313	0.04781313	0.02	0.8998
slope of Control vs water	1	2.03163514	2.03163514	0.68	0.4133

Red Oak

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	1913.940105	159.495009	18.10	<.0001
Error	48	423.022787	8.812975		
Uncorrected Total	60	2336.962892			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.81851925	0.81851925	0.09	0.7619
slope of Control vs Eth-Tol+W	1	0.95674572	0.95674572	0.11	0.7432
slope of Control vs Eth	1	0.22863637	0.22863637	0.03	0.8727
slope of Control vs Eth-W	1	0.22863637	0.22863637	0.03	0.8727
slope of Control vs water	1	0.30915247	0.30915247	0.04	0.8522

Black Cherry

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	5085.368137	423.780678	25.82	<.0001
Error	48	787.708988	16.410604		
Uncorrected Total	60	5873.077125			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.89008210	0.89008210	0.05	0.8168
slope of Control vs Eth-Tol+W	1	0.53142585	0.53142585	1.03	0.8579
slope of Control vs Eth	1	0.26397577	0.26397577	0.02	0.8996
slope of Control vs Eth-W	1	0.26397577	0.26397577	1.02	0.8996
slope of Control vs water	1	0.29487884	0.29487884	1.02	0.8939

Appendix 8: Results of SAS Statistical GLM analysis of the Change in Chromaticity Coordinate b (Δb*)

The GLM Procedure

Red pine

Dependent Variable: y

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	4949.193842	412.432820	12.66	<.0001
Error	48	1563.557687	32.574118		
Uncorrected Total	60	6512.751529			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	1.06395061	1.06395061	0.03	0.8573
slope of Control vs Eth-Tol+W	1	3.43175696	3.43175696	0.11	0.7469
slope of Control vs Eth	1	3.06641410	3.06641410	0.09	0.7603
slope of Control vs Eth-W	1	3.06641410	3.06641410	0.09	0.7603
slope of Control vs water	1	1.25122533	1.25122533	0.04	0.8454

Red Oak

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	6360.880755	530.073396	11.26	<.0001
Error	48	2260.211656	47.087743		
Uncorrected Total	60	8621.092411			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.74104811	0.74104811	0.02	0.9007
slope of Control vs Eth-Tol+W	1	1.64684247	1.64684247	0.03	0.8524
slope of Control vs Eth	1	0.10877803	0.10877803	0.00	0.9619
slope of Control vs Eth-W	1	0.10877803	0.10877803	0.00	0.9619
slope of Control vs water	1	0.95133962	0.95133962	0.02	0.8876

Black Cherry

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	7245.018438	603.751537	15.89	<.0001
Error	48	1823.600448	37.991676		
Uncorrected Total	60	9068.618887			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	1.02227032	1.02227032	0.03	0.8704
slope of Control vs Eth-Tol+W	1	2.80859845	2.80859845	0.07	0.7869
slope of Control vs Eth	1	10.13132736	10.13132736	0.27	0.6079
slope of Control vs Eth-W	1	10.13132736	10.13132736	0.27	0.6079
slope of Control vs water	1	6.07743459	6.07743459	0.16	0.6910

Appendix 9: Results of SAS Statistical GLM analysis of the Change overall color change (ΔE)

The GLM Procedure

Red pine

Dependent Variable: y

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	11165.90822	930.49235	30.59	<.0001
Error	48	1460.18597	30.42054		
Uncorrected Total	60	12626.09418			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.73083593	0.73083593	0.02	0.8775
slope of Control vs Eth-Tol+W	1	22.09719696	22.09719696	0.73	0.0398
slope of Control vs Eth	1	17.59290517	17.59290517	0.58	0.4507
slope of Control vs Eth-W	1	17.59290517	17.59290517	0.58	0.0450
slope of Control vs water	1	63.49871865	63.49871865	2.09	0.0155

Red Oak

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	14490.51969	1207.54331	34.58	<.0001
Error	48	1676.09156	34.91857		
Uncorrected Total	60	16166.61125			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.03462916	0.03462916	0.00	0.9750
slope of Control vs Eth-Tol+W	1	7.22108860	7.22108860	0.21	0.6513
slope of Control vs Eth	1	24.57766428	24.57766428	0.70	0.4056
slope of Control vs Eth-W	1	24.57766428	24.57766428	0.70	0.0465
slope of Control vs water	1	40.36024841	40.36024841	1.16	0.0287

Black Cherry

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	25084.68622	2090.39052	45.77	<.0001
Error	48	2192.24783	45.67183		
Uncorrected Total	60	27276.93405			

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
slope of Control vs Eth-Tol	1	0.76783701	0.76783701	0.02	0.8974
slope of Control vs Eth-Tol+W	1	67.81642312	67.81642312	1.48	0.0290
slope of Control vs Eth	1	50.37613456	50.37613456	1.10	0.2989
slope of Control vs Eth-W	1	50.37613456	50.37613456	1.10	0.0298
slope of Control vs water	1	91.81589769	91.81589769	2.01	0.0162