

**USE OF CONFOCAL PROFILOMETRY TO QUANTIFY
EROSION OF WOOD AND SCREEN CHEMICALS FOR
THEIR ABILITY TO PHOTOSTABILIZE WOOD**

by

Chunling Liu

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE

in

The Faculty of Graduate Studies

(Forestry)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

June 2011

© Chunling Liu, 2011

ABSTRACT

Optical confocal profilometry is a new technology for characterizing the surfaces of materials. In this thesis, I hypothesize that confocal profilometry will be able to more accurately measure the erosion of wood during weathering than optical microscopy. Confocal profilometry may be able to screen photoprotective chemicals, and in this thesis I use confocal profilometry to test the hypothesis that PF resin can photostabilize wood. Confocal profilometry was used to measure the erosion of untreated western red cedar wood exposed to natural and artificial weathering. The erosion of western red cedar specimens increased with time. Specimens exposed in a xenon-arc weatherometer eroded significantly faster than specimens exposed in a QUV weatherometer. The profilometer was able to measure the erosion of specimens exposed for only 100 h in a xenon-arc weatherometer. There was a positive correlation between the size of the area of wood exposed to weathering and the erosion of wood during artificial and natural weathering. The erosion rate was about 2-20 times faster during artificial weathering compared to natural weathering. Profilometry was able to discern differences in the erosion of untreated specimens and specimens treated with PF resin. However, profilometry was not able to detect differences in erosion of specimens treated with different PF resin formulations. In contrast, the thin strip technique, which measured weight and tensile strength losses of treated wood veneers exposed to weathering, was able to discern differences between formulations. I conclude from measurements on western red cedar that confocal profilometry is a more accurate and less labor-intensive way of measuring the erosion of wood during weathering than optical microscopy. The exposure time required to produce erosion that can be measured using the profilometer is much less than that needed when using an optical microscope. But specimens need to be flat, free of checks and have eroded areas that are distinct from unweathered areas. Low molecular weight PF resin shows great promise as a treatment for photostabilizing wood.

TABLE OF CONTENTS

ABSTRACT	ii
TABLE OF CONTENTS.....	iii
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS.....	xiv
ACKNOWLEDGEMENTS	xv
CHAPTER 1: GENERAL INTRODUCTION.....	1
1.1 Introduction.....	1
1.2 General Hypothesis and Outline of Study.....	4
CHAPTER 2: LITERATURE REVIEW	6
2.1 Introduction.....	6
2.2 Effects of Weathering on Wood.....	6
2.2.1 Macroscopic Changes	6
2.2.1.1 Discoloration	6
2.2.1.2 Surface Erosion	8
2.2.2 Microscopic Changes	10
2.2.3 Chemical Changes	10
2.2.4 Changes in Wood Properties	11
2.3 Methods Used to Assess the Weathering of Wood.....	12
2.3.1 Weight Losses.....	12
2.3.2 Tensile Strength Losses	13
2.3.3 Measurement of the Erosion of Wood.....	14
2.3.3.1 Optical Microscopy	14
2.3.3.2 Laser Scanning System.....	15
2.3.3.3 Optical Confocal Profilometry	16
2.3.4 Measuring Color Changes.....	18
2.3.5 Measuring Chemical Changes at Wood Surfaces during Weathering Using Fourier Transform Infrared (FTIR) Spectroscopy.....	20
2.4 Chemical Systems Used to Protect Wood from Weathering.....	22
2.4.1 Inorganic Chemicals	22
2.4.2 Chemical Modification	23
2.4.3 UV Stabilizers.....	25
2.4.3.1 UV Absorbers (UVAs)	25
2.4.3.2 Hindered Amine Light Stabilizers (HALS)	29

2.4.4 Polymerizable Monomers	31
2.4.5 Additives.....	33
2.4.5.1 Wax.....	33
2.4.5.2 Lignin	34
2.5 Phenol Formaldehyde Resins	34
2.5.1 Synthesis of Phenol Formaldehyde Resins.....	35
2.5.2 Penetration of Phenol Formaldehyde Resins in Wood Cells	36
2.5.2.1 Penetration Pathway.....	36
2.5.2.2 Factors Influencing the Penetration of PF Resin	38
2.5.2.2.1 Properties of Resin	38
2.5.2.2.2 Wood Factors	40
2.5.3 Effects of PF Resin on Wood Properties	41
2.5.3.1 Effects of PF Resin on Weathering of Wood.....	41
2.5.3.2 Effects of PF Resin on other Properties of Wood.....	42
2.5.3.2.1 Dimensional Stability	42
2.5.3.2.2 Biological Resistance	44
2.5.3.2.3 Mechanical Properties	45
2.5.3.2.4 Heat Resistance	47
2.5.3.2.5 Electrical Resistance.....	47
2.5.3.2.6 Chemical Resistance.....	47
2.5.4 Commercial Treatment of Wood with Phenol Formaldehyde Resins	48
2.5.4.1 Impreg	48
2.5.4.2 Compreg	51
2.5.4.3 Kyushu Mokuzai Process	54
2.5.5 Improving Properties of PF Resin Using Additives.....	57
2.6 Conclusions.....	58
CHAPTER 3: USE OF CONFOCAL PROFILOMETRY TO QUANTIFY THE EROSION OF UNTREATED WOOD DURING ARTIFICIAL ACCELERATED WEATHERING AND NATURAL WEATHERING.....	60
3.1 Introduction.....	60
3.2 Materials and Methods	62
3.2.1 Experimental Design and Statistical Analyses.....	62
3.2.2 Preparation of Wood Samples and Metal Masks.....	63
3.2.3 Weathering	65
3.2.3.1 Artificial Weathering.....	65
3.2.3.2 Natural Weathering	66
3.2.4 Quantifying Erosion of Wood Using Optical Confocal Profilometry	68

3.2.5 SEM	69
3.3 Results.....	69
3.3.1 Weathering of Wood during Artificial Accelerated Weathering	69
3.3.1.1 Changes in the Appearance of Specimens.....	69
3.3.1.2 Erosion of Wood	71
3.3.1.2.1 Effect of Time and Weatherometer Type on Erosion	71
3.3.1.2.2 Effect of Mask Size on the Erosion of Wood during Artificial Accelerated Weathering	77
3.3.1.3 Micro-structural Changes.....	78
3.3.2 Erosion of Wood during Natural Weathering	86
3.3.2.1 Changes in the Appearance of Specimens.....	86
3.3.2.2 Erosion of Wood	86
3.3.2.2.1 Effect of Time on Erosion	87
3.3.2.2.2 Effect of Mask Size on the Erosion of Wood during Natural Weathering	90
3.3.2.3 Micro-structural Changes.....	92
3.3.3 Comparison of the Erosion of Specimens Exposed to Artificial Accelerated Weathering and Natural Weathering	95
3.4 Discussion.....	96
3.5 Conclusions.....	99
CHAPTER 4: ASSESSING THE ABILITY OF PHENOL FORMALDHYDE RESIN TO PHOTOSTABILIZE WOOD.....	101
4.1 Introduction.....	101
4.2 Materials and Methods	103
4.2.1 Experimental Designs and Statistical Analyses	103
4.2.2 Preparation of Specimens	104
4.2.2.1 Preparation of Wood Veneers.....	104
4.2.2.2 Preparation of Wood Composites from Sawn Veneers.....	106
4.2.3 Chemical Treatments	110
4.2.3.1 Treatment of Yellow Cedar Wood Veneers with PF Resin or PF Resin and Wax	110
4.2.3.2 Wood Veneers Treated with Aqueous Solutions Containing Different Additives.....	111
4.2.3.3 Wood Veneers Treated with PF Resin and Different Additives.....	112
4.2.3.4 Wood Composites Treated with PF Resin or PF Resin and Different Additives.....	113
4.2.4 Weathering	114
4.2.4.1 Weathering of Wood Veneers.....	114
4.2.4.2 Weathering of Wood Composites.....	115
4.2.5 Measurement of Physical Changes in Wood Veneers and Composites as a Result of Treatment and Exposure to Natural Weathering	116

4.2.5.1 Dry Weight Gains and Losses of Veneers.....	116
4.2.5.2 Tensile Strength of Veneers.....	117
4.2.5.3 Color Changes during Weathering.....	118
4.2.5.4 Erosion of Composite Specimens during Weathering	118
4.3 Results.....	119
4.3.1 Effects of PF resin and Wax on Weight Losses, Tensile Strength and Color Stability of Wood Veneers Exposed to Natural Weathering	119
4.3.1.1 Percentage Weight Losses.....	119
4.3.1.2 Tensile Strength.....	121
4.3.1.3 Color Changes.....	123
4.3.2 Effects of Additives on Weight Losses, Tensile Strength and Color Stability of Wood Veneers Exposed to Natural Weathering	125
4.3.2.1 Percentage Weight Losses.....	125
4.3.2.2 Tensile Strength.....	126
4.3.2.3 Color Changes.....	128
4.3.3 Effects of PF Resin and Additives on Weight Losses, Tensile Strength and Color Stability of Wood Veneers Exposed to Natural Weathering.....	129
4.3.3.1 Percentage Weight Losses.....	129
4.3.3.2 Tensile Strength.....	130
4.3.3.3 Color Changes.....	132
4.3.4 Effects of PF Resin and Additives on Color Stability and Erosion of Radiata Pine Veneer-Based Composites Exposed to Natural Weathering.....	133
4.3.4.1 Color Changes.....	133
4.3.4.2 Erosion.....	135
4.4 Discussion.....	137
4.5 Conclusions.....	141
CHAPTER 5: GENERAL DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH	143
5.1 General Discussion.....	143
5.2 General Conclusions.....	147
5.3 Suggestions for Future Research.....	148
REFERENCES	150
APPENDIX I: WESTERN RED CEDAR SPECIMENS EXPOSED TO ARTIFICIAL WEATHERING OR NATURAL WEATHERING	165
APPENDIX II: WOOD VENEERS TREATED WITH PF RESIN OR PF RESIN CONTAINING DIFFERENT ADDITIVES BEFORE AND AFTER EXPOSED TO NATURAL WEATHERING	177
APPENDIX III: WOOD COMPOSITE SPECIMENS TREATED WITH PF RESIN OR PF RESIN CONTAINING DIFFERENT ADDITIVES EXPOSED TO 2000 HOURS NATURAL WEATHERING.....	181

APPENDIX IV: CHARACTERISTICS OF PF RESIN USED TO TREATED WOOD VENEERS AND WOOD COMPOSITES.....	185
APPENDIX V: STATISTICAL ANALYSIS: CHAPTER 3.....	188
APPENDIX VI: STATISTICAL ANALYSIS: CHAPTER 4	215

LIST OF TABLES

Table 2.1 Microscopic changes of wood exposed to weathering (Borgin 1971; Chang <i>et al.</i> 1982; Hon and Feist 1986; Evans 1989; Williams 2005)	10
Table 2.2 Companies manufacturing Compreg for different end-uses.....	53
Table 3.1 Density and growth rate of parent western red cedar boards used to prepare specimens that were exposed to artificial accelerated weathering or natural weathering	63
Table 3.2 Weathering cycles employed by the QUV and xenon-arc weatherometers	66
Table 3.3 Meteorological conditions at the site in Vancouver where masked western red cedar specimens were exposed to natural weathering (April 2009 to June 2010)	67
Table 3.4 Statistical significance (p-values) of experimental factors on erosion of western red cedar specimens exposed to artificial accelerated weathering.....	71
Table 3.5 Statistical significance (p-values) of experimental factors on erosion of western red cedar specimens exposed to natural weathering	87
Table 3.6 Comparison of average erosion of western red cedar specimens exposed to artificial weathering (QUV or xenon-arc) or natural weathering for 1000 hours (XA: Xenon-arc; NW: Natural weathering)	95
Table 3.7 Comparison of times to reach similar average erosion depths (μm) of western red cedar specimens exposed to artificial weathering or natural weathering (XA: Xenon-arc; NW: Natural weathering)	96
Table 3.8 Comparison of times to reach similar average mass losses ($\mu\text{g}/\text{mm}^2$) of western red cedar specimens exposed to artificial or natural weathering (XA: Xenon-arc; NW: Natural weathering) ..	966
Table 4.1 Density and growth ring width of radiata pine boards used to make wood composites.....	108
Table 4.2 Solvent and concentrations of PF resin and wax (W) used to treat wood veneers.....	111
Table 4.3 Solvent and concentrations of additives in aqueous solutions used to treat wood veneers	112
Table 4.4 Solvent and concentrations of PF resin and additives used to treat wood veneers	113
Table 4.5 Solvent and concentrations of PF resin and additives used to treat sawn radiata pine veneers ..	113
Table 4.6 Meteorological conditions in Vancouver from September 2008 to November 2008.....	115
Table 4.7 Meteorological conditions in Vancouver from July 2009 to October 2009	115
Table 4.8 Percentage weight gains of veneers after treatment and percentage weight losses of veneers after weathering.....	121
Table 4.9 Tensile strength and tensile strength losses of veneers after weathering	123
Table 4.10 Color changes of veneers after 50 days natural weathering	125
Table 4.11 Tensile strength of veneers before and after weathering and tensile strength losses after weathering.....	127
Table 4.12 Color changes of veneers exposed to 35 days natural weathering.....	129
Table 4.13 Tensile strength of veneers and tensile strength losses after weathering	131
Table 4.14 Color changes of veneers exposed to 50 days natural weathering.....	133
Table 4.15 Color changes of radiata pine veneer-based composite specimens exposed to 2000 hours of natural weathering	134

LIST OF FIGURES

Figure 2.1 Optical confocal profilometer showing from left to right: AltiSurf [®] 500 scanning device, a CCD-spectrocolorimeter and a computer system	16
Figure 2.2 Principle of optical confocal profilometry (AltiProbe technical manual. www.cotec.fr).	17
Figure 2.3 Erosion of a King Billy pine (<i>Athrotaxis selaginoides</i> D. Don) shingle after 2500 hours of artificial weathering in xenon-arc weatherometer (Gare 2000)	18
Figure 2.4 Scheme for the reaction of wood hydroxyl groups with acetic anhydride to form acetylated wood and the by-product acetic acid.....	23
Figure 2.5 Esterification of wood with a vinyl ester to form esterified wood and acetaldehyde	24
Figure 2.6 Benzoylation of wood with benzoyl chloride to form benzoylated wood and hydrochloric acid	25
Figure 2.7 Structure of different organic ultraviolet light absorbers	26
Figure 2.8 Mechanism of action of organic ultraviolet light absorbers.....	26
Figure 2.9 Structure of a typical 2, 2', 6, 6'-tetramethylpiperidine (TMP) and a hindered amine light stabilizer (HALS) (Wicks <i>et al.</i> 1999; Kampmann <i>et al.</i> 2005)	29
Figure 2.10 Mechanism of action of a HALS.....	30
Figure 2.11 Phenol formaldehyde resin deposited in rays of southern pine impregnated with a low molecular weight PF resin (Wan and Kim 2006)	37
Figure 2.12 PF resin in lumen, cell wall and pits of southern pine impregnated with a low molecular weight of PF resin (Wan and Kim 2008).....	37
Figure 2.13 Bio-resistance test of PF resin treated wood in Japan: a, Decay test. (1-3. PF resin treated samples, 4-5. Controls). Note that there is no decay of PF treated samples, whereas untreated samples were damaged by decay fungi. b, Termite resistance test (1. Original wood; 2. PF resin treated sample, 3. Untreated sample). Note that the PF treated sample resisted termite attack, whereas the untreated sample was heavily attacked by termites) (Mokuzai Gakkaishi http://www.kyumoku.co.jp)	45
Figure 2.14 Examples of wood products made from PF resin treated wood: a, Samples made from PF resin treated wood, from left to right: PF impregnated laminated composite; PF impregnated compressed composite (Compreg); PF impregnated wood (Impreg). b, Engineering and Research Corporation (ERCO) variable pitch propellers made from Compreg. c, Variable pitch propeller made in Australia from Compreg (Boas 1947)	52
Figure 2.15 Appearance of timber treated with PF resin: a, Small deck made from Japanese cedar treated with PF resin; b, Close-up of the same deck as in a, and two small unweathered samples of Japanese cedar treated with PF resin. Note that weathering has changed the color of the PF treated Japanese cedar from a reddish brown to a tan-brown; c, Post treated with PF resin (left) and an untreated post (right). Note that the untreated post has checked badly and has weathered to a grey color. The PF resin treated post has no checks and is a pleasant tan color; d, PF resin treated poles used as roadside barriers. The poles have retained their brown color in earlywood.....	55
Figure 2.16 End-uses of wood treated with PF resin in Japan (a, Arbour; b, Bench; c, Building; d, Pergola)(Mokuzai Gakkaishi http://www.kyumoku.co.jp)	56
Figure 2.17 Process used to manufacture phenol formaldehyde impregnated wood at Kyushu Mokuzai(Mokuzai Gakkaishi http://www.kyumoku.co.jp).....	57
Figure 3.1 Metal mask screwed to the surface of a western red cedar specimen (left) and a close-up view of the unmasked areas (right). The holes in the mask provide unmasked areas that are susceptible to erosion during artificial accelerated weathering or natural weathering.....	64

Figure 3.2 Xenon-arc weatherometer (left) and a close-up view of xenon-arc chamber (right) used to accelerate the weathering of masked western red cedar specimens	65
Figure 3.3 QUV fluorescent weatherometer (left) and a close-up view of fluorescent lamps (right) used to accelerate the weathering of masked western red cedar specimens.	66
Figure 3.4 Rack containing the masked western red cedar specimens that were exposed to natural weathering.....	67
Figure 3.5 Optical confocal profilometer (left) and close-up of the 3 mm probe and a weathered western red cedar specimen on the x-y table of the profilometer	68
Figure 3.6 Appearance of western red cedar specimens exposed to artificial accelerated weathering in QUV weatherometer for 100, 250, 500 and 1000 hours. Note the differences in colour of the unmasked (circular) areas compared to the masked areas	70
Figure 3.7 Appearance of western red cedar specimens exposed to artificial accelerated weathering in xenon-arc weatherometer for 100, 250, 500 and 1000 hours. Note the differences in colour of the unmasked (circular) areas compared to the masked areas.....	70
Figure 3.8 Average erosion depth of western red cedar specimens exposed in xenon-arc or QUV weatherometers for 100, 250, 500 and 1000 hours (results averaged across samples containing unmasked areas of different sizes).....	72
Figure 3.9 Average mass loss of western red cedar specimens exposed in xenon-arc or QUV weatherometers for 100, 250, 500 and 1000 hours (results averaged across samples containing unmasked areas of different sizes).....	72
Figure 3.10 Erosion depth profiles of unmasked areas (30 mm in diameter) of western red cedar specimens exposed in a QUV weatherometer for different periods of time.....	74
Figure 3.11 Erosion depth profiles of unmasked areas (30 mm in diameter) of western red cedar specimens exposed in a xenon-arc weatherometer for different periods of time.....	75
Figure 3.12 Topographical images of unmasked western red cedar specimens exposed to artificial weathering for different periods of time (Left: QUV; Right: Xenon-arc. The size of the unmasked area is 506 mm ²).....	76
Figure 3.13 Average erosion depth of unmasked areas in western red cedar specimens exposed to artificial accelerated weathering for 100, 250, 500 and 1000 hours (results averaged across samples exposed to weathering in xenon-arc and QUV weatherometers).....	77
Figure 3.14 Average mass loss of unmasked areas in western red cedar specimens exposed to artificial accelerated weathering for 100, 250, 500 and 1000 hours (results averaged across samples exposed to weathering in xenon-arc and QUV weatherometers).....	78
Figure 3.15 Micro-structural changes at the surface of a western red cedar specimen exposed in a QUV weatherometer for 100 hours (a = Microchecking and enlargement of the aperture of a bordered pit; b = Longitudinal check).....	79
Figure 3.16 Micro-structural changes at the surface of a western red cedar specimen exposed in a QUV weatherometer for 250 hours (a = Enlargement of the aperture of a bordered pit; b = Longitudinal check in earlywood resulting from the enlargement of microcheck in bordered pits)	80
Figure 3.17 Micro-structural changes at the surface of a western red cedar specimen exposed in a QUV weatherometer for 1000 hours. Note the horizontal checks in earlywood (right) and the numerous vertical checks in earlywood and latewood.....	81
Figure 3.18 Micro-structural changes in latewood at the surface of a western red cedar specimen exposed in a QUV weatherometer for 1000 hours. Note the formation of longitudinal checks as a result of separation of latewood tracheids and detachment of slivers of wall material (right).....	82

Figure 3.19 Micro-structural changes in earlywood at the surface of a western red cedar specimen exposed in a QUV weatherometer for 1000 hours. Note the detachment of small plates of cell wall material formed as a result of the intersection of vertical and horizontal checks.....	82
Figure 3.20 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 100 hours. Note the check in earlywood	83
Figure 3.21 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 250 hours (a = Horizontal check in earlywood; b = Vertical check in latewood) .	84
Figure 3.22 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 500 hours.....	85
Figure 3.23 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 1000 hours. Note that horizontal check extend into latewood (arrowed, right)	85
Figure 3.24 Appearance of western red cedar specimens exposed to natural weathering for different periods of time.....	86
Figure 3.25 Average erosion depths of western red cedar specimens exposed to natural weathering for different periods of time (results averaged across samples containing unmasked areas of different sizes).....	87
Figure 3.26 Average mass losses of western red cedar specimens exposed to natural weathering for different periods of time (results averaged across samples containing unmasked areas of different sizes).....	88
Figure 3.27 Erosion depth profiles of 30 mm diameter unmasked areas in western red cedar specimens exposed to natural weathering for different periods of time.....	89
Figure 3.28 Topographic images of unmasked western red cedar specimens exposed to natural weathering for different periods of time	90
Figure 3.29 Average depth of erosion of unmasked areas in western red cedar samples exposed to natural weathering for 1000, 2500, 5000 and 10000 hours.....	91
Figure 3.30 Average mass loss of unmasked areas in western red cedar samples exposed to natural weathering for 1000, 2500, 5000 and 10000 hours.....	92
Figure 3.31 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 1000 hours	93
Figure 3.32 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 1000 hours. Note check in earlywood and evidence of fungal colonisation (right).....	93
Figure 3.33 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 10000 hours. Note numerous vertical checks and colonisation of surface by fungi	94
Figure 3.34 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 10000 hours. Note detachment of a small sliver of cell wall material	94
Figure 4.1 Sledge microtome and steel microtome blade used to cut thin wood veneers from a parent wood block (Left: Sledge microtome; Right: A close-up view of steel microtome blade holder and disposable blade)	105
Figure 4.2 Dimensions of parent wood boards, blocks and wood veneers	105
Figure 4.3 Digital micrometer used to measure the thickness of individual wood veneers.....	106
Figure 4.4 Dimensions and process of preparing sawn radiata pine veneers used to make treated composites	107
Figure 4.5 Dimensions and construction of the wood composites exposed to natural weathering	109

Figure 4.6 Wood composite overlaid with a stainless steel metal mask (left) and a close-up of the wood composite with the stainless steel metal mask (right)	110
Figure 4.7 Glass plates containing treated wood veneers during a natural weathering trial	114
Figure 4.8 Weathering rack containing treated wood composite specimens	116
Figure 4.9 Pulmac TS 100 paper testing machine used to measure the zero-span tensile strength of thin wood veneers (left) and a close-up of the jaws of the testing device (right)	117
Figure 4.10 Percentage weight losses of treated veneers after 50 days natural weathering (Con = Control; W = 2.5% Wax; 12 P = 12% PF resin; 12 PW = 12% PF resin containing 2.5% wax; 24 P = 24% PF resin; 24 PW = 24% PF resin containing 2.5% wax; 36 P = 36% PF resin; 36 PW = 36% PF resin containing 2.5% wax; 48 P = 48% PF resin; 48 PW = 48% PF resin containing 2.5% wax). Error bars represent 95% confidence intervals.	120
Figure 4.11 Zero-span tensile strength of treated veneers after 50 days natural weathering (Con = Control; W = 2.5% wax; 12 P = 12% PF resin; 12 PW = 12% PF resin containing 2.5% wax; 24 P = 24% PF resin; 24 PW = 24% PF resin containing 2.5% wax; 36 P = 36% PF resin; 36 PW = 36% PF resin containing 2.5% wax; 48 P = 48% PF resin; 48 PW = 48% PF resin containing 2.5 % wax)	122
Figure 4.12 Appearance of treated wood veneers before and after weathering (a = Veneers without weathering; b = Veneers weathered. Con = Control; 12 P = 12% PF resin; 24 P = 24% PF resin; 36 P = 36% PF resin; 48 P = 48% PF resin; W = 2.5% Wax; 12 PW = 12% PF resin containing 2.5% wax; 24 PW = 24% PF resin containing 2.5% wax; 36 PW = 36% PF resin containing 2.5% wax; 48 PW = 48% PF resin containing 2.5% wax)	124
Figure 4.13 Percentage weight losses of veneers treated with different additives after 35 days natural weathering (Con = Control; IO = 1% Iron oxide; Lstab = 2% Lignostab 1198; Lig = 10% Lignosulphonate; PEG = 10% Polyethylene glycol). Error bars represent 95% confidence intervals	126
Figure 4.14 Zero-span tensile strength of treated veneers after 35 days natural weathering (Con = Control; IO = 1% Iron oxide; Lstab = 2% Lignostab; Lig = 10% Lignosulphonate; PEG = 10% Polyethylene glycol). Error bars represent 95% confidence intervals	127
Figure 4.15 Appearance of treated wood veneers before and after weathering (a = Veneers without weathering; b = Veneers after weathering. Con = Control; Lig = 10% Lignosulphonate; IO = 1% Iron oxide; Lstab = 2% Lignostab 1198; PEG = 10% Polyethylene glycol)	128
Figure 4.16 Percentage weight losses of treated wood veneers after 50 days natural weathering (Con = Control; PF = 12% PF resin; PFIO = 12% PF resin + 1% Iron oxide; PFLstab = 12% PF resin + 2% Lignostab; PFLig = 12% PF resin + 10% Lignosulphonate; PFFEG = 12% PF resin + 10% Polyethylene glycol). Error bars represent 95% confidence intervals	130
Figure 4.17 Zero-span tensile strength of treated veneers after 50 days natural weathering (Con = Control; PF = 12% PF; PFIO = 12% PF resin + 1% Iron oxide; PFLstab = 12% PF resin + 2% Lignostab; PFLig = 12% PF resin + 10% Lignosulphonate; PFPEG = 12% PF resin + 10% Polyethylene glycol). Error bars represent 95% confidence intervals	131
Figure 4.18 Appearance of treated veneers before and after natural weathering (a = Treated veneers without weathering; b = Treated veneers after weathering. Con = Control; P = 12% PF resin; PFPEG = 12% PF resin + 10% Polyethylene glycol; PFLig = 12% PF resin + 10% Lignosulphonate; PFLstab = 12% PF resin + 2% Lignostab; PFIO = 12% PF resin + 1% Iron oxide)	132
Figure 4.19 Appearance of treated radiata pine specimens after 2000 hours of natural weathering (The circular areas inside the specimens were exposed to natural weathering, whereas the areas outside the circles were covered by metal masks. Con = Control; 10PF = 10% PF resin; 20PF = 20% PF resin; 30PF = 30% PF resin; PFPEG = 10% PF resin + 10% Polyethylene glycol; PFIO = 10% PF resin + 1% Iron oxide; PFLstab = 10% PF resin + 2% Lignostab)	134

Figure 4.20 Mass losses of treated radiata pine specimens exposed to 2000 hours of natural weathering (Con = Control; 10PF = 10% PF resin; 20PF = 20% PF resin; 30PF = 30% PF resin).....	135
Figure 4.21 Erosion depth of treated radiata pine specimens exposed to 2000 hours of natural weathering (Con = Control; 10PF = 10% PF resin; 20PF = 20% PF resin; 30PF = 30% PF resin).....	136
Figure 4.22 Mean erosion depths of treated radiata pine specimens exposed to 2000 hours of natural weathering (Con = Control; 10PF = 10% PF resin; PFIO = 10% PF resin + 1% Iron oxide; PFLstab = 10% PF resin + 2% Lignostab 1198; PFPEG = 10% PF resin + 10% Polyethylene glycol)	137

LIST OF ABBREVIATIONS

PF: Phenol Formaldehyde

UV: Ultraviolet

SEM: Scanning Electron Microscopy

PEG: Polyethylene Glycol

LMW: Low Molecular Weight

WPL: Weight Percentage Loss

TS: Tensile Strength

WPG: Weight Percentage Gain

WRC: Western Red Cedar

CCA: Copper Chromium Arsenate

ACQ: Alkaline Copper Quaternary

HPLC: High Performance Liquid Chromatography

MOE: Modulus of Elasticity

MOR: Modulus of Rupture

IB: Internal Bond Strength

OSB: Oriented Strand Board

WR: Water Repellent

ACKNOWLEDGEMENTS

First and foremost to my supervisor Dr. Philip Evans. I am indebted for his tireless endeavours and endless patience during the journey of my study. I am inspired by his creative approach and passion for wood research. I am also grateful for his support for my participation in international conferences.

I would like to thank Dr. Taraneh Sowlati and Dr. Frank Lam for acting as my committee members. I would like to thank Ms. Sara Gibson for synthesizing the PF resin used in my research. I thank Mr. Dave Minchin and FP Innovations for their in-kind support. I thank International Research Group on Wood Protection (IRG) (Ron Cockcroft Award) for a travel grant which enabled me to participate in the 40th IRG meeting in Beijing in 2009. I also thank Arch Timber Protection Ltd. for the award of a Gareth Williams Scholarship (for the best paper presented by a student at the IRG meeting in Beijing). Finally, I thank Arclin and NSERC for their financial support.

I thank my fellow research group members: Arash Jamali, Ian Cullis, Jahangir Chowdhury, Siti Hazneza Abdul Hamid, Vicente Hernandez Jonathan Haase, Stephan Vollmer and Kenny Cheng for their assistance and friendship. I had the pleasure of working with you and sharing your ideals and discoveries, and learning and growing together.

Furthermore, I thank those friends: Narinder Ahlawat, Felix Xue, Xinmei Shi, Isabella, Sarah Delaney, Ye Wang and Lian Zhou for your friendship and encouragement. I thank all the people who have enriched my life and made the journey memorable.

Finally, I would like to express my deep gratitude to my family members for your unconditional love and unyielding support. I have strived for excellence to make my mother, sisters and daughter proud of me. You are my inspiration and strength. My special thanks go to my grandparents who wholeheartedly love me and believe in me. You are in my heart forever.

CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Wood is susceptible to environmental degradation or weathering when it is used outdoors. Sunlight especially ultra-violet (UV) light is the most damaging factor responsible for the weathering of wood (Browne and Simonson 1957; Kalnins 1966; Derbyshire and Miller 1981). Other environmental factors involved in the weathering of wood include: moisture, oxygen, heat/cold, chemicals and abrasion by wind-blown particles (Raczkowski 1980; Hon and Feist 1981; Hon *et al* 1982; Williams 1987). The natural beauty of wood appeals to end-users of building products, but weathering disfigures wood. Hence, weathering is of great concern to people (Feist and Hon 1984; Evans *et al.* 2005). In addition, weathering of wood accelerates other forms of degradation such as mildew and decay. These forms of degradation act in concert to degrade wood, alter its surface properties and reduce the service life of wood products (Williams 2005). Therefore, protecting wood from weathering is of great importance.

The chemical and coatings' industries have been active in developing chemicals to protect wood from weathering and photodegradation (Chang *et al.* 1982; Feist and Hon 1984; Williams and Feist 1988; Schmalzl and Evans 2003; Hayoz *et al.* 2003; de la Caba *et al.* 2007). The methods that have been used to develop and screen chemicals for their ability to photostabilize wood include: (1) Assessing the losses in weight and tensile strength of treated wood strips or veneers exposed to natural or artificial accelerated weathering (Raczkowski 1980, Derbyshire and Miller 1981, Evans 1988, Evans and Schmalzl 1989); (2) Using optical microscopy to measure the depth of erosion of treated wood exposed to natural or artificial weathering (Rowell *et al.* 1981; Feist and Rowell 1982); (3) Assessing changes in the colour and chemical

composition of wood using spectrophotometry and FTIR spectroscopy, respectively (Wengert 1966; Chang and Cheng 2001; Pastore *et al.* 2004; Kishino and Nakano 2004; Hon and Chang 1984; Evans *et al.* 1992, 1996).

Chemical treatments applied to wood can alter wood's color and mask infra-red peaks that provide information on wood's chemical composition. The thin strip technique is widely used to assess the ability of chemicals to photostabilize wood because measurements of weight or tensile strength losses of thin wood veneers exposed to weathering provide information on the effectiveness of the chemicals at protecting lignin and cellulose, respectively (Evans and Schmalzl 1989). The validity of the thin strip technique rests on the assumption that degradation of wood at the surface of the strips is similar to that at the surface of solid wood. To-date this assumption has not been tested although research on the photodegradation of polymers has shown that photodegradation of thin films differs from that of bulk materials (Davis and Sim 1983; Nepotchatykh and Power 2000). This limitation of the thin strip technique is not shared by the assessment technique that measures the depth of erosion of treated wood exposed to artificial accelerated weathering (Rowell *et al.* 1981; Feist and Rowell 1982). However, long exposure times are needed to produce reproducible differences in the erosion of wood that can be measured using optical microscopy (Sell and Feist 1986, Arnold *et al.* 1991, Williams *et al.* 2001d). In addition, the use of optical microscopy to measure erosion requires three to six measurements per sample (Sell and Feist 1986, Arnold *et al.* 1991, Williams *et al.* 2001a, b, c, d). The error of such erosion measurements is also quite high, approximately $\pm 20 \mu\text{m}$. The limitations of optical microscopy for measuring the erosion of wood during weathering led Arnold *et al.* (1992) to employ laser scanning profilometry to measure erosion of wood. Laser scanning profilometry obtained erosion data more rapidly than optical microscopy, but there was

also large variation in the data. Furthermore, the laser profilometer had to be individually calibrated for individual wood species (Arnold *et al.* 1992). Optical confocal profilometry is a newer technology that has been developed to study the surface characteristics of materials (Wilken *et al.* 2003; Thecharopoulos *et al.* 2010). Optical confocal profilometry can measure surface topography, generate depth profiles and calculate volumes taken from surfaces with high accuracy (www.altimet.fr). This technology has been used to precisely measure the erosion of metals and ceramics with a resolution of 20 nm and an accuracy of ± 300 nm (Wilken *et al.* 2003). Recently, Thecharopoulos *et al.* (2010) used confocal profilometry to quantify erosion of human tooth enamel. However, confocal profilometry has not been used to assess the erosion of wood. Confocal profilometry potentially offers some advantages compared to optical microscopy for measuring the erosion of wood. Firstly, erosion measurements are based on intensive measurements of eroded areas. Secondly, the profilometer can be programmed to measure erosion on multiple samples, potentially allowing rapid assessment of the ability of large numbers of chemicals to restrict the weathering of wood. Finally, the profilometer has the potential to quantify erosion with high levels of accuracy and resolution, as mentioned above.

A large research effort has been devoted to finding chemicals that can photostabilize wood, as mentioned above. Chemical treatments that introduce aromatic groups (benzoyl groups or vinyl esters) into wood are remarkably effective at photostabilizing wood (Evans *et al.* 2002; Jebrane *et al.* 2009). Previous research has shown that benzoyl groups modify the UV absorption properties of wood and reduce the concentration of free radicals formed when wood is exposed to UV light (Evans *et al.* 2002). The chemical treatments that have been used to introduce aromatic groups into wood (benzoylation or esterification with vinyl benzoate), however, require solvents, catalysts and high temperatures to modify wood. Furthermore, both treatments generate

toxic by-products, hydrochloric acid for benzylation and acetaldehyde for esterification with vinyl benzoate (Evans *et al.* 2002; Jebrane *et al.*, 2009). An alternative, more practical method of introducing “aromatic groups” into wood cell walls is to treat wood with low molecular weight phenol formaldehyde (PF) resin (Stamm and Seborg 1941; Furuno *et al.* 2004). PF resin treatments dimensionally stabilize wood and increase its resistance to bio-deterioration (Stamm and Seborg 1936, 1939; Stamm and Baechler 1960; Ryu *et al.* 1991). Low molecular weight PF resin can restrict discoloration and surface checking of wood exposed outdoors (Stamm and Baechler 1960; Sudiyani *et al.* 1999; Imamura 2007), but the photostability of wood treated with PF resin has not been examined.

1.2 General Hypothesis and Outline of Study

I hypothesize that optical confocal profilometry will be able to rapidly and accurately quantify the erosion of wood during weathering and hence it will be a good method for screening new chemical treatments such as low molecular weight PF resins for their ability to photostabilize wood.

Following this introduction, Chapter 2 reviews relevant literature on methods for assessing the weathering of wood and screening chemicals for their ability to photostabilize wood. Background information on weathering and photoprotection of wood is also included in this chapter. Chapter 3 examines the ability of optical confocal profilometry to rapidly and accurately quantify the erosion of untreated wood exposed to both artificial accelerated weathering and natural weathering. Chapter 4 uses both the thin strip technique and optical confocal profilometry to assess the ability of low molecular weight PF resin to photostabilize wood. Chapter 5 discusses the results of both experimental chapters to reach a conclusion as to whether confocal

profilometry is a good method of screening chemicals for their ability to photostabilize wood. Chapter 5 also offers suggestions for further research.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter reviews the following: research on the effects of weathering on the properties of wood; methods used to measure the erosion of wood and to screen chemicals for their ability to photostabilize wood; different chemical systems used to photostabilize wood; and the protection of wood using phenol formaldehyde (PF) resins.

2.2 Effects of Weathering on Wood

2.2.1 Macroscopic Changes

2.2.1.1 Discoloration

Color changes are the earliest and most obvious signal of the degradation of wood exposed outdoors. Light colored woods darken at first, while dark colored woods fade initially before they turn to yellow or brown, and eventually become gray as weathering continues (Kalnins 1966; Feist and Hon 1984; Feist 1990; Evans *et al.* 2005). The color of weathered wood does not vary greatly with species and exposure environment (Sandermann and Schlumbom 1962; Sullivan 1967; Feist and Hon 1984).

Color changes of wood exposed outdoors occur because of photodegradation of extractives and lignin (Kishino and Nakano 2004, Evans *et al.* 2005). Degradation of lignin results in the formation of low molecular weight, unsaturated, aromatic compounds that cause wood to become yellow. For example, Leary (1967, 1968) and Müller *et al.* (2003) found that quinones and cyclohexadienones formed from the photodegradation of lignin caused the yellowing of wood.

The greying of wood exposed outdoors has been attributed to the following factors: (1) Colonization of the weathered surface layer of wood by blue-stain fungi (Sell and Wälchli 1969). Evidence in support of the involvement of blue-stain fungi in the greying of weathered wood is the observation that weathered wood is yellow or greyish-white instead of grey if the wood is free of fungal attack (Sell and Wälchli 1969); (2) Leaching out of colored matter. Some colored extractives in wood are water-soluble and other coloring materials may be decomposed by UV light and become water-soluble. Leaching of these compounds from wood during weathering may alter the color of wood (Sell and Wälchli 1969); (3) Leaching of water soluble products of decomposed lignin increases the concentration of cellulose at the weathered wood surface making the wood lighter (the color of cellulose) (Feist and Hon 1984).

The primary factor causing the discoloration of wood is UV light (Browne and Simonson 1957). Browne and Simonson (1957) observed that when wood was exposed only to visible light, the discoloration process was many times slower, and in the absence of all light, color changes could not be measured. Sullivan (1967) reported the maximum yellowing of wood happened when wood was exposed to UV light with wavelengths of 305-335 nm. Leary (1967) found that yellowing of wood still occurred at wavelengths of 355-400 nm, which is nearer the visible region of the solar spectrum. Chang and Cheng (2001) found that visible light could also discolor wood. For example, the color of sugi (*Cryptomeria Japonica* D.Don) heartwood changed from a yellow-brown color to red when it was exposed to light with wavelengths above 600 nm. The discoloration of wood by UV radiation is influenced by the presence of oxygen (Leary 1967). Chang and Cheng (2001) found that the color of sugi heartwood changed from yellow-brown to reddish blue when it was exposed to both light and oxygen. Accordingly, Wengert (1966) found that gases and impurities in the atmosphere influenced the darkness of wood exposed to UV light.

He exposed wood samples to UV radiation in air, oxygen, nitrogen, or argon atmospheres. All the samples darkened at first (~7h). Then samples exposed to oxygen or air became lighter. However, samples continued to darken throughout the exposure period if they were irradiated in a nitrogen or argon atmosphere. The darkening of wood varied with wood species and was also related to temperature, roughness, surface moisture content and extractive content (Sandermann and Schlumbom 1962; Sullivan 1967).

2.2.1.2 Surface Erosion

Degradation of wood occurs rapidly when it is exposed to sunlight. Evans *et al.* (1996) used FTIR spectroscopy to examine chemical changes at the surface of radiata pine (*Pinus radiata* D.Don) veneers exposed outdoors for short periods of time. Their results showed perceptible lignin loss after only four hours exposure and complete loss of lignin after only six days exposure. Nevertheless, the erosion of wood during natural weathering is reported to be slow. For example, most softwood erodes at a rate of 6 mm/century and hardwoods at 3 mm/century (Williams *et al.* 2001a).

Feist and Mraz (1978) compared the erosion rates of five softwood species exposed to natural or accelerated weathering. Erosion rate was inversely related to the density of the species. However, Douglas fir (*Pseudotsuga menziesii* (Mirbel) Franco), which had the highest density of all species (0.57 g/cm³), eroded at the same rate as redwood (*Sequoia* sp.), which had a much lower density (0.37g/cm³). They attributed this discrepancy to differences in the lignin and extractives contents of the two species. Anderson *et al.* (1991b) exposed four hardwood species to artificial weathering and found that higher density species were more resistant to weathering. However, Williams *et al.* (2001d) found that there was little correlation between wood density

and erosion rate when they examined the erosion of ten different Bolivian hardwoods exposed to accelerated weathering.

Miniutti (1964, 1967) found that there was greater erosion of low density earlywood compared to higher density latewood in several wood species exposed outdoors for more than ten years. Williams *et al.* (2001b) found that erosion was more rapid in species with distinct earlywood and latewood. Erosion appeared to be more rapid in the central portion of the earlywood in species with growth rings that showed a gradual change from earlywood to latewood. Wood species with wide latewood bands weathered less than species with thin latewood bands (Williams *et al.* 2001b). Williams *et al.* (2001a) also found that erosion rates of earlywood and latewood in Douglas fir and southern pine (*Pinus* sp.) differed greatly during the first 7 years of weathering. Significant differences in the erosion of latewood and earlywood in these species persisted after 7 years. However, for western red cedar (*Thuja plicata* Donn ex D.Don) and redwood, there was no difference in the erosion rates of earlywood and latewood after 7 years exposure.

Williams *et al.* (2001c) examined the erosion of western red cedar exposed at various angles to the horizontal. They found that most species showed little difference in erosion rate when exposed between 0° and 45°, but erosion was lower when samples were exposed at 90° (vertical). They explained these findings as follows: (1) Degradation products and dirt that accumulates at surfaces shields wood surfaces from light. However, these materials are rapidly leached from exposed surfaces inclined at 45°; (2) Specimens exposed at 0° and 45° are more likely to stay wet for longer than specimens exposed at 90°. Thus they are more prone to decay; (3) Horizontal exposure (0°) maximizes levels of received UV radiation (Evans 1989).

Williams *et al.* (2001c) found little difference in erosion rate of radial and tangential surfaces in most wood species except earlywood in western red cedar and southern pine.

2.2.2 Microscopic Changes

Microscopic changes take place at wood surfaces during weathering before any macroscopic damage is perceptible (Evans *et al.* 2005). The most obvious micro-scale changes are summarized in **Table 2.1**.

Table 2.1 Microscopic changes in wood exposed to weathering (Borgin 1971; Chang *et al.* 1982; Hon and Feist 1986; Evans 1989; Williams 2005)

Wood surface	Microscopic changes
Transverse section	Cell walls were thinner, delaminated and collapsed. Middle lamella was degraded. Resin canals were enlarged. Epithelial cells were destroyed.
Radial section	Micro-checks developed in pits. The checks passed through the bordered pits. Apertures of bordered pits were enlarged. Half bordered pits, pit domes, margo and torus were degraded and lost. Numerous large checks appeared within vessels, between adjacent vessels and fibre walls, and between parenchyma cells in hardwoods or between tracheids, fibre walls or between ray parenchyma cells in softwoods.
Tangential section	Checks appeared between rays, vessels or within rays or between adjacent fibre walls in hardwoods. Checks in softwoods were in rays, adjacent tracheid walls and vertical resin ducts, especially in latewood.

2.2.3 Chemical Changes

It has been found that lignin is very susceptible to UV light. Lignin in wood is depolymerised extremely rapidly when wood is exposed to weathering (Hon and Minemura 1991). The absorption of UV photons by lignin results in the formation of free radicals. These aromatic free radicals react with oxygen and water to form hydroperoxides. Both free radicals and hydroperoxides initiate dissociation of chemical bonds in wood, which results in further depolymerization of lignin and wood's other chemical components, hemicelluloses and cellulose

(Kalnins 1966; Hon and Feist 1981; Evans *et al.* 1992). However, extractives within rays appeared to be resistant to photodegradation (Miniutti 1967).

Weathering decreased the methoxyl and lignin content of wood and increased acidity, carbonyl and carboxylic functional groups (Leary 1967; Leary 1968; Hon and Chang 1984). The degradation products resulting from the irradiation of wood included CO, CO₂, hydrogen, water, methanol, formaldehyde and organic acids (Kalnins 1966). The depth of weathering varies from 200 µm - 2540 µm due to differences in weathering methods, exposure time of wood and techniques used to analyze depth of weathering (Browne and Simonson 1957; Hon and Ifju 1978; Evans *et al.* 2005).

2.2.4 Changes in Wood Properties

Wood absorbs moisture, and swells and shrinks when exposed outdoors. These dimensional changes can result in warping, cupping and face checking (Stamm 1936). As wood weathers, the surface becomes less water-repellent. For example, the contact angles of water droplets on western red cedar and southern pine wood surfaces decreased after outdoor weathering (Kalnins and Knaebe 1992; Kalnins and Feist 1993). The wettability of Sitka spruce (*Picea sitchensis* (Bong.) Carr) also increased when it was exposed to xenon-arc radiation and water spray (Williams 2005). Kishino and Nakano (2004) investigated changes in the wettability of eight tropical wood species during artificial weathering. They showed that wettability varied with species. They attributed this to differences in the structural degradation of the different species. Increases in the wettability of wood during weathering have been explained by an increase in hydroxyl groups originating from both exposed cellulose and adsorbed water, and loss of more hydrophobic extractives and lignin (Kishino and Nakano 2004; Williams 2005). Weathering has

little influence on mechanical properties of wood because UV light does not penetrate deeply into wood (Evans 2005).

2.3 Methods Used to Assess the Weathering of Wood

2.3.1 Weight Losses

Measurement of weight losses has been used to assess the weathering of polymers (Davis 1981; Qayum and Davis 1984). Weight losses of wood during weathering reflect lignin degradation and leaching of water-soluble lignin fragments from wood surfaces (Evans 1988). Jemison (1937) used weight loss to quantify the weathering of wooden dowels exposed to natural weathering for 7 to 10 years. But he found that weight losses were small (Jemison 1937). Rowell *et al.* (1981) used weight losses to assess the resistance of chemical modified southern pine sapwood (2.4 cm x 2.4 cm x 0.6 cm) to artificial weathering. However, the differences in percentage weight losses of treated samples and controls after weathering were very small. Weight losses of thin wood strips exposed to natural weathering are much larger and hence have been used to quantify the weathering of wood (Evans 1988, 1989, 1996; Evans and Schmalzl 1989). Weight losses of treated thin wood strips during weathering have also been used to screen chemical modification agents and inorganic chemicals for their ability to photostabilize wood (Evans and Schmalzl 1989; Kiguchi and Evans 1998; Evans *et al.* 2002; Schmalzl and Evans 2003; Jebrane *et al.* 2009).

Weight loss is easy to measure with low variation between veneer samples, and the test species can be varied (Evans 1988). However, weight losses during weathering are only a small portion of large wood samples because UV light only affects the wood surface (Evans *et al.*

2005). Therefore, this method is not suitable for large-sized wood samples, as Jemison (1937) demonstrated.

2.3.2 Tensile Strength Losses

Tensile strength losses occur during weathering because UV light depolymerizes cellulose (Derbyshire and Miller 1981). Turkulin and Sell (2002) found that tensile strength changes were consistent with micro-structural changes in wood during weathering, and the mechanism of failure of wood was due to degradation of cellulose in latewood.

Raczkowski (1980) investigated seasonal variation in the weathering of Norway spruce (*Picea abies* (L.) Karst) by measuring tensile strength parallel to grain of thin wood veneers exposed to natural weathering. He found that the tensile strength of weathered wood strips decreased the most in summer due to the higher intensity of solar radiation during this season. Tensile strength losses during winter were influenced by the presence of sulphur dioxide in the air (from the burning of coal). Derbyshire and Miller (1981) found that tensile strength losses of veneers were an accurate method of assessing weathering because reductions in tensile strength were “an exponentially decreasing function of radiation dose”.

Evans (1988) and Derbyshire *et al.* (1995) used a Pulmac short span paper tester to test zero-span and finite-span tensile strength of thin wood veneers exposed to the weather. A finite-span test measures mechanical properties of both cellulose micro-fibrils and the matrix (lignin and hemicelluloses). In contrast, a zero-span tensile strength test measures mechanical properties of micro-fibrils. Such testing increased the information on the effects of weathering on the polymers in wood, and reduced testing times. Measurement of micro-tensile strength losses of thin wood strips after weathering provides a rapid, consistent and reliable method of assessing

photodegradation of wood (Derbyshire *et al.* 1995). The level of variation can be reduced by optimizing clamping pressure and properly selecting and preparing veneer samples (Derbyshire *et al.* 1996).

Measurement of tensile strength losses of thin wood veneers during weathering has been widely used together with measurement of weight losses to screen chemicals for their ability to photostabilize wood, as mentioned above (Evans 1989; Kiguchi and Evans 1998; Evans *et al.* 2002; Schmalzl and Evans 2003; Jebrane *et al.* 2009).

2.3.3 Measurement of the Erosion of Wood

2.3.3.1 Optical Microscopy

Feist and Mraz (1978) used an optical reflecting-light microscope equipped with a numerically calibrated focusing drum to measure the depth of erosion of wood exposed to weathering (Feist and Mraz 1978). They placed erosion resistant stainless steel masks over part of the specimens and then exposed them outdoors or to artificial accelerated weathering. The mask was removed after weathering and the difference in height of the exposed wood surface and the wood under the mask was measured using the optical microscope. The difference in height was calculated by focusing on weathered and adjacent unweathered areas and noting the difference in the numbers on the focusing drum (Feist and Mraz 1978; Sell and Feist 1986; Arnold *et al.* 1991; Williams *et al.* 2001d). Erosion measurements obtained using optical microscopy were influenced by the texture and anatomy of the wood samples (Arnold *et al.* 1991). It was easier to apply the technique to softwoods than to hardwoods because softwoods have distinct differences in the erosion of earlywood and latewood, and it is easy to focus on both tissue types. In contrast, in hardwoods the large earlywood vessels in ring porous species

made focussing on this tissue type difficult. Hence, erosion measurements for hardwoods were restricted to latewood (Arnold *et al.* 1991). Another disadvantage of optical microscopy is that long exposure times are required to produce measurable differences between the unmasked and masked areas. The minimum time required to produce measurable levels of erosion of untreated wood exposed to artificial weathering was 600 hours (Sell and Feist 1986; Arnold *et al.* 1991; Williams *et al.* 2001d). In addition, every measurement made using optical microscopy was done manually, and it took a relatively long time to perform several measurements (Sell and Feist 1986; Arnold *et al.* 1991; Williams *et al.* 2001d). Generally, erosion measurements employing optical microscopy have used 3 to 6 measurements per sample and erosion values for different species were the average of 40 measurements in total (Feist and Mraz 1978; Sell and Feist 1986, Arnold *et al.* 1991; Williams *et al.* 2001a, b, c, d). Finally, the measurement error when using optical microscopy to measure the erosion of wood is very high, approximately $\pm 20 \mu\text{m}$ (Sell and Feist 1986; Arnold *et al.* 1991; Williams *et al.* 2001d).

2.3.3.2 Laser Scanning System

Arnold *et al.* (1992) investigated the use of laser scanning technology to measure the erosion of wood during weathering. Specimens were masked (as above for optical microscopy) and exposed to weathering. A laser scanning system measured the intensity of light reflected from the masked and unmasked areas. The difference in intensity of light reflected from the unmasked and masked areas was used to calculate the erosion of the weathered wood. This laser scanning system offered the advantage of greater accuracy and the possibility of collecting more erosion data (Arnold *et al.* 1992). However, many factors, such as the color of the wood, grain direction, cracks and sharp edges on the surface of samples affected the reflectance of laser light

and the accuracy of results. In addition the device had to be individually calibrated for different wood species, which made the use of the technique time-consuming (Arnold *et al.* 1992).

2.3.3.3 Optical Confocal Profilometry

Optical confocal profilometry is a new technique for profiling the roughness of surfaces. An optical confocal profilometer consists of a CCD-spectrocolorimeter, a light source and a computer system (**Figure 2.1**).

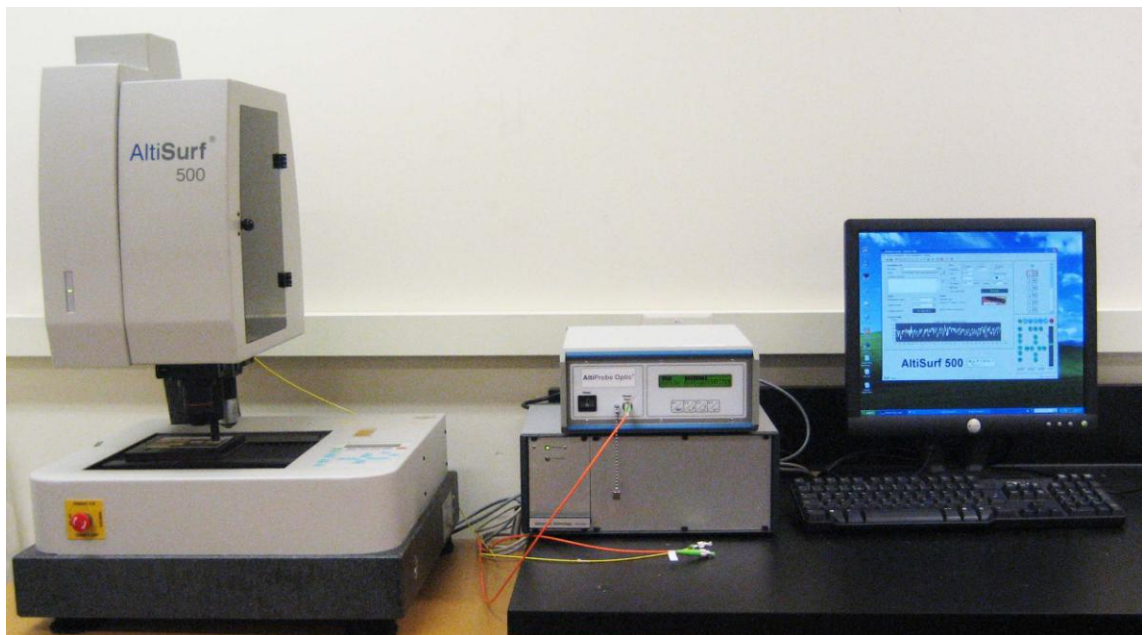


Figure 2.1 Optical confocal profilometer showing from left to right: AltiSurf[®] 500 scanning device, a CCD-spectrocolorimeter and a computer system

Figure 2.2 schematically illustrates the basic principle of optical confocal profilometry. The confocal profilometer measures the roughness and surface topography of a material based on chromatic white light aberration. A halogen (white) light spot is focussed on the surface through a 2-way optical fibre and then a final lens that has spherical aberration. The lens acts like a prism and separates the wavelengths of the visible white light into different frequencies. Frequencies (wavelengths) that are perfectly focussed give a maximum peak on a CCD-spectrocolorimeter,

which is converted to an altitude (www.cotec.fr).

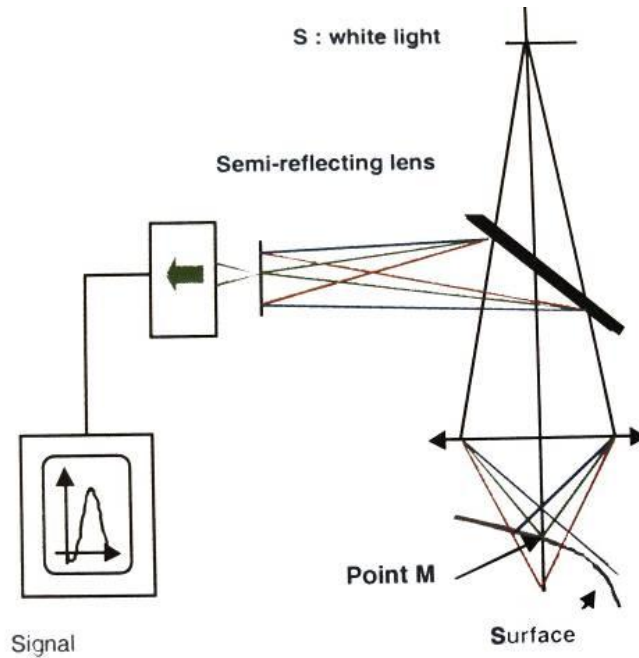


Figure 2.2 Principle of optical confocal profilometry (AltiProbe technical manual. www.cotec.fr)

Confocal profilometry is capable of making rapid, accurate and repeated measurements on surfaces. It can analyze 2-D roughness, waviness, shape, step height, depth distribution and distance etc. It is also capable of providing topographic information in 3-D (**Figure 2.3**). Furthermore, the associated software can calculate mean erosion depth and volume taken from a surface (www.altimet.fr).

Confocal profilometry can be used to study ageing, wear, and porosity of materials (www.altimet.fr). It has been used to precisely measure the erosion of metals, ceramics, human tooth enamel and dental glass-ceramics, as mentioned above (Wilken *et al.* 2003; Theocharopoulos *et al.* 2010).

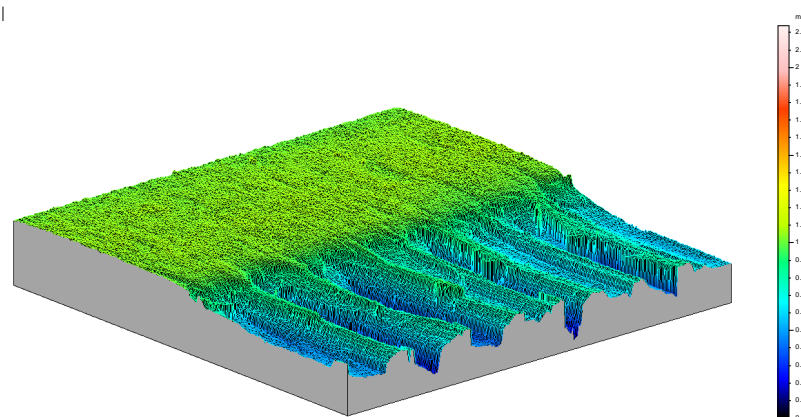


Figure 2.3 Erosion of a King Billy pine (*Athrotaxis selaginoides* D.Don) shingle after 2500 hours of artificial weathering in xenon-arc weatherometer (Gare 2000)

2.3.4 Measuring Color Changes

The colour of wood changes very quickly when it is exposed to UV radiation or natural weathering, as mentioned above. Researchers have noted the changes in colour of different wood species and wood treated with photoprotective chemicals. However, the magnitude of changes in the colour of wood has not been widely used to rank chemical treatments for their ability to photostabilize wood.

The color of wood can be quantified using a spectrophotometer. These instruments express color using internationally approved parameters developed by Commission Internationale de l'Eclairage (C.I.E). The color parameters that were used in the past were: three tristimulus values (X, Y and Z), three trichromatic coefficients (x, y and z), dominant wavelength and saturation (Loos 1964; Sullivan 1967; Wengert 1966). Now the CIE Lab system is used to express colour: L^* , a^* , b^* values (L^* = brightness; a^* = green to red; b^* = blue to yellow) (Chang *et al.* 1998; Chang and Cheng 2001; Pastore *et al.* 2004; Kishino and Nakano 2004). These parameters show consistent colour spacing values and simplify the description of color.

Wengert (1966) measured color changes in redwood and birch (unknown species) exposed to UV radiation in different atmospheric gases. His results indicated that atmospheric gases play an important role in the color changes of wood exposed to UV radiation. Chang and Cheng (2001) found that color changes of sugi heartwood were greater when the wood was exposed to both light and oxygen rather than to light on its own. The color of sugi heartwood changed from yellowish to red when it was exposed to light at wavelengths above 600 nm during 32 hours of artificial weathering. Kishino and Nakano (2001) investigated the correlation between color changes, especially yellowing, and chemical changes of eight tropical woods exposed to 600 hours of artificial weathering. They found that changes in all three CIE Lab parameters were correlated with exposure time and varied with species. There was a good correlation between the appearance of a non-conjugated carbonyl band at 1740 cm^{-1} in FTIR spectra of exposed woods and yellowing. Pastore *et al.* (2004) measured color changes of four tropical hardwoods exposed to artificial weathering. Their results also showed that color changes varied with wood species.

Leary (1968) found that yellowing of wood was restricted if it was acetylated or methylated before the wood was exposed to UV light. Plackett *et al.* (1992) and Chang and Chang (2001) found that acetylation restricted discoloration of China fir (*Cunninghamia lanceolata* var. *lanceolata* (Lamb.) Hook.) exposed to artificial weathering. Prakash *et al.* (2006) found that esterification reduced discoloration of rubberwood (*Hevea brasiliensis* Müll.Arg.) exposed to artificial weathering. Other chemical modification techniques such as methylation, alkylation and butyrylation also restricted discoloration of wood exposed to weathering (Kalnins 1984; Chang and Chang 2001). Chang *et al.* (1998) found that pre-treatment of Taiwania (*Taiwania cryptomeriodes* Hay.) heartwood with UV stabilizers or polyethylene glycol (PEG) or semicarbazide, followed by application of a polyurethane clear coating containing a

photostabilizer restricted discoloration of wood exposed to natural weathering. Recently, Liu *et al.* (2010) found that iron oxide and UV stabilizers were more effective than cerium dioxide nanoparticles at restricting discoloration of yellow cedar (*Chamaecyparis nootkatensis* (D.Don) Spach) veneers exposed to natural weathering.

2.3.5 Measuring Chemical Changes at Wood Surfaces during Weathering Using Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy has been widely used to study chemical changes at the wood surfaces exposed to weathering. It has also been used in some studies to rank treatments for their ability to photostabilize lignin. In addition, FTIR spectroscopy provides evidence for the mechanisms of photodegradation of wood and the ability of chemical treatments to photostabilize wood.

Hon and Chang (1984) observed that carbonyl and carboxylic peaks at wavenumbers of 1720 and 1735 cm^{-1} increased, and aromatic peaks at 1265-1510 cm^{-1} decreased when southern pine was exposed to artificial weathering. These changes in FTIR spectra indicated degradation and loss of lignin. Evans *et al.* (1996) confirmed these findings for radiata pine exposed to natural weathering, as mentioned above. Anderson *et al.* (1991a, b) used a xenon light source with borosilicate filters to weather several different hardwoods and softwoods. FTIR spectroscopy revealed that the absorption peaks at 1650 cm^{-1} and 1730-1740 cm^{-1} increased at first and then decreased, and the peak at 1514 cm^{-1} decreased. These changes indicate degradation of lignin and formation of quinones and quinone methides. Košíková and Tolvaj (1998) found that OH bands, and non-conjugated carbonyl increased, and ring-conjugated carbonyl, aromatic ring and aromatic and methoxy groups decreased in big tooth aspen (*Populus grandidentata* Michaux.) exposed to 50 hours of artificial weathering.

FTIR spectroscopy has been widely used to assess chemical changes at the surface of wood treated with photoprotective chemicals and /or coatings and then exposed to either artificial or natural weathering. Hon and Chang (1985) found that a clear coating containing a UV absorber restricted the photodegradation of southern yellow pine exposed to different periods of weathering. FTIR spectra indicated that there was no change in the peaks assigned to wood's chemical components beneath the coating. FTIR spectroscopy revealed that aqueous chromium trioxide was more effective than ferric salts at photostabilizing lignin at the surface of treated radiata pine veneers exposed to natural weathering (Evans *et al.* 1992). Ohkoshi (2002) used FTIR spectroscopy to show that acetylation and polyethylene glycol (PEG) treatment reduced the generation of carbonyl compounds and degradation of lignin in several softwood species exposed to artificial weathering. Schmalzl and Evans (2003) assessed the ability of some titanium, zirconium and manganese compounds to photostabilize wood. FTIR spectroscopy showed that manganese oxidants protected lignin, some titanates protected cellulose, but most of titanates and zirconates were not able to protect lignin (Schmalzl and Evans 2003). Evidence from FTIR spectroscopy supported their findings for weight and tensile strength losses of treated radiata pine veneers exposed to natural weathering. Schaller (2007) used FTIR spectroscopy to examine the chemical changes at the surface of radiata pine specimens that were treated with different photostabilizers and exposed to artificial weathering. FTIR analysis showed that both UV light and visible light up to 500 nm was capable of degrading lignin and generating chromophores. The photoprotective effect of UV stabilizers and a coating depended on quantity and type of UV stabilizer and degree of pigmentation of the coating (Schaller 2007). FTIR spectroscopy has also shown that grafting of a UV absorber, or linseed and tall oil treatments can photostabilize lignin

in wood exposed to natural or artificial weathering, respectively (Kiguchi and Evans 1998; Temiz *et al.* 2007).

FTIR spectroscopy has been used to examine the ability of chemical modification to photostabilize wood. FTIR spectroscopy of Scots pine (*Pinus sylvestris* L.) veneers acetylated to different weight gains and exposed to natural weathering revealed that acetylation to 20% weight gain restricted degradation of lignin, whereas acetylation to low weight gains accelerated photodegradation of lignin (Evans *et al.* 2000). FTIR spectroscopy also revealed that esterification of wood with benzoyl chloride or vinyl benzoate were able to restrict the degradation of lignin in wood veneers exposed to natural weathering (Evans *et al.* 2002; Jebrane *et al.* 2009).

2.4 Chemical Systems Used to Protect Wood from Weathering

2.4.1 Inorganic Chemicals

Inorganic chemicals such as chromic acid, copper and cobalt chromates, ferric chloride, ferric nitrate, manganese, titanium and zirconium compounds can photostabilize lignin and cellulose to various degrees. Hence, they can protect wood from weathering (Black and Mraz 1974; Chang *et al.* 1982; Schmalzl and Evans 2003). Hexavalent chromium compounds are the most effective chemicals at photostabilizing wood. They restrict micro-checking (Chang *et al.* 1982), surface erosion (Black and Mraz 1974; Feist 1979), and weight losses (Evans and Schmalzl 1989) of wood exposed to artificial or natural weathering. They also improved the performance of clear finishes on wood exposed outdoors (Williams and Feist 1988). However, chromium VI compounds are carcinogenic and they change the color of wood to green.

Therefore the commercial use of these compounds as surface treatments for wood has been limited (Hon *et al.* 1985; Evans and Schmalzl 1989).

2.4.2 Chemical Modification

Acetylation is a process that chemically modifies wood to make it more dimensionally stable and resistant to decay. Acetylated wood (**Figure 2.4**) also has increased short term color stability and it is less susceptible to checking than unmodified wood (Kalnins 1984; Plackett *et al.* 1992; Chang and Chang 2001). Feist *et al.* (1991) found that acetylation reduced the erosion of aspen (*Populus* sp.) during artificial weathering by about 50%. Brelid and Westin (2007) found that acetylation greatly increased the service life of an opaque acrylic finish on Scots pine exposed to 13 years natural weathering. Acetylation hindered the formation of chromophoric derivatives such as quinones at wood surfaces exposed to UV radiation. Therefore it restricted discoloration of wood (Plackett *et al.* 1992; Chang and Chang 2001). The photoprotective effects of acetylation are achieved only when the wood reacts with acetic anhydride to achieve weight gains of 15% or more (**Figure 2.5**) (Kalnins, 1984; Feist *et al.*, 1991; Evans *et al.* 2000).

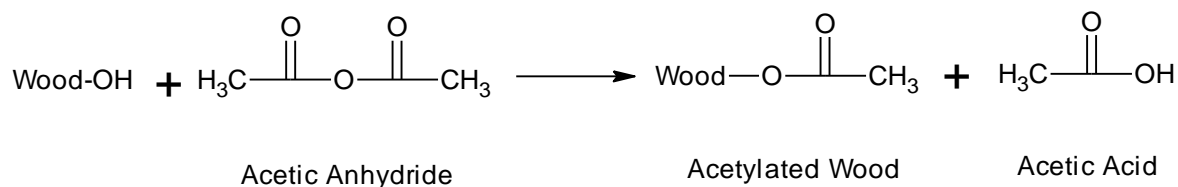


Figure 2.4 Scheme for the reaction of wood hydroxyl groups with acetic anhydride to form acetylated wood and the by-product acetic acid

Acetylation is an esterification reaction. Alternative esterification reactions can also increase the resistance of wood to weathering. For example, esterification of wood (**Figure 2.5**) with phthalic anhydride and the epoxide epichlorohydrin reduced microstructural damage to hinoki cypress wood (*Chamaecyparis obtusa* (Siebold & Zucc.) Endl.) exposed to artificial

weathering (Murakami and Matsuda 1990). Prakash *et al.* (2006) found that esterification of rubberwood with octanoyl chloride reduced discoloration of wood exposed to artificial weathering. Esterification with the aromatic vinyl ester, vinyl benzoate was effective at restricting photodegradation of yellow cedar because it photostabilized lignin (**Figure 2.5**). The degree of protection achieved with vinyl benzoate was positively correlated with modification level (Jebrane *et al.* 2009).

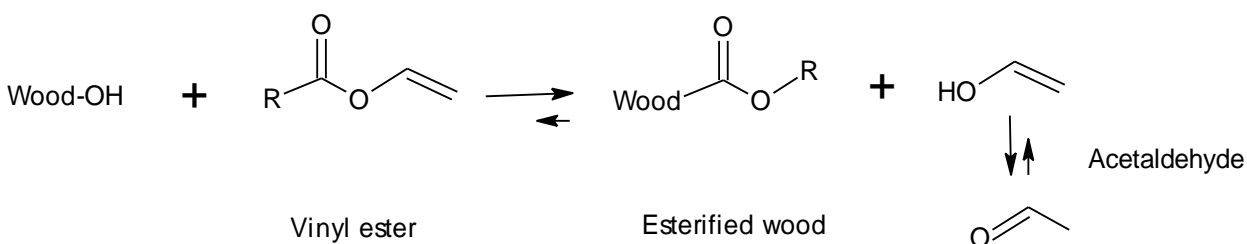


Figure 2.5 Esterification of wood with a vinyl ester to form esterified wood and acetaldehyde

Esterification of wood with benzoyl chloride (**Figure 2.6**) reduced weight and tensile strength losses of Scots pine veneers exposed to natural weathering (Evans *et al.* 2002). It also restricted color changes of wood exposed to UV light (Pandey and Chandrashekar 2006). Scanning electron microscopy of benzoylated surfaces exposed to natural weathering revealed that benzoylation photostabilized lignin and restricted the degradation of the lignin rich middle lamella. It also reduced the concentration of free radicals that formed when wood was exposed to UV light (Evans *et al.* 2002). Chemical treatments that introduce aromatic groups into wood (benzoylation or esterification with vinyl benzoate) appear to be very effective at photostabilizing wood, but they require the use of solvents, catalysts and high temperature to modify wood (Evans *et al.* 2002; Williams 2005). They also generate toxic by-products, hydrochloric acid for benzoylation and acetaldehyde for esterification with vinyl benzoate (Evans *et al.* 2002; Jebrane *et al.* 2009).

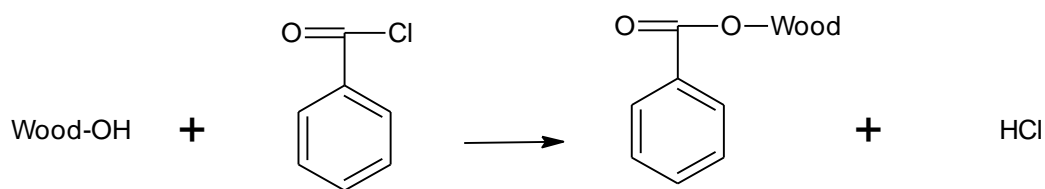


Figure 2.6 Benzoylation of wood with benzoyl chloride to form benzoylated wood and hydrochloric acid

Other chemical modification systems, for example methylation, alkylation and butyrylation can also prevent discoloration of wood during weathering, but they cannot photostabilize lignin (Kalnins 1984; Chang and Chang 2001). The combination of acetylation or butylene oxide, methy-isocyanate or butyl-isocyanate modification and methyl methacrylate monomer impregnation increased the photostability of wood exposed to natural or artificial weathering (Feist *et al.* 1991). The subject of the photostability of chemically modified wood was recently reviewed by Evans (2009).

2.4.3 UV Stabilizers

2.4.3.1 UV Absorbers (UVAs)

UV absorbers include inorganic and organic UV absorbers. Inorganic UV absorbers photostabilize materials through reflecting, absorbing and scattering UV light, whereas organic UVAs photostabilize materials by transferring chemical energy to thermal energy and harmlessly dissipating the energy (Hawkins 1984; Blackburn *et al.* 1991; Aloui *et al.* 2007) (**Figures 2.7 and 2.8**).

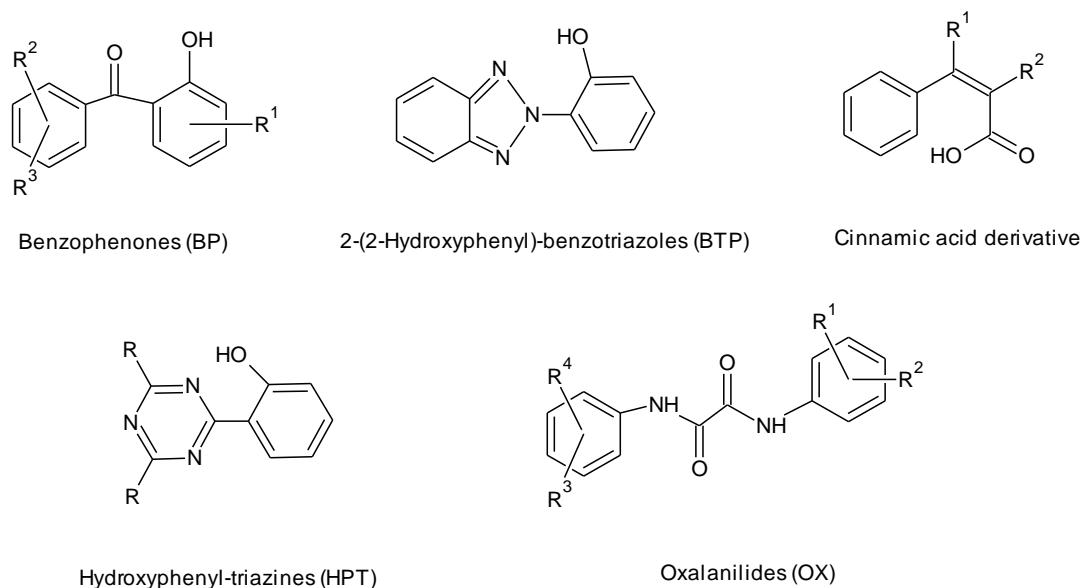


Figure 2.7 Structure of different organic ultraviolet light absorbers

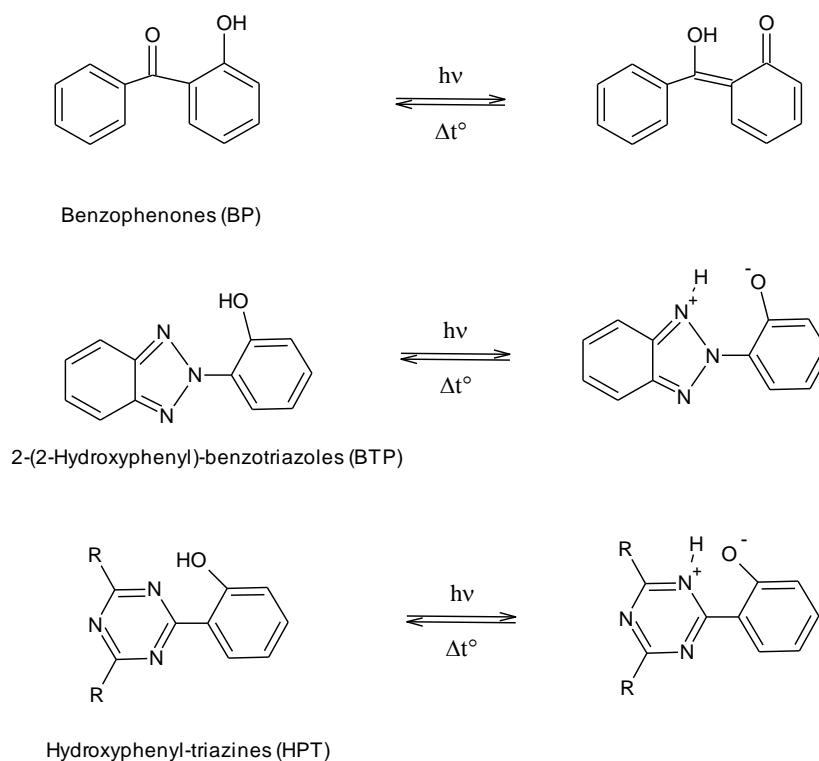


Figure 2.8 Mechanism of action of organic ultraviolet light absorbers

Inorganic UV absorbers such as iron oxides, TiO_2 , CeO_2 , ZnO and carbon black have been widely used to protect polymers from UV radiation (Allen *et al.* 2002; George *et al.* 2005;

Clayton and Sawitowski 2006). Iron oxide has been used for a long time in Scandinavian countries to prevent wood from photodiscoloration (Sharrock 1990). Blackburn *et al.* (1991) found that the combination of 1-2% of fine particulate titanium dioxide and an oil based alkyd coating containing 2% iron oxide provided better protection to western white pine (*Pinus monticola* Dougl. ex Lamb.) panels exposed to artificial weathering than a conventional coating containing UVA/HALS. George *et al.* (2005) found that micronized iron oxides, TiO₂, ZnO and silica powder photostabilized clear coated wood. Allen *et al.* (2002) found that nano-particulate anatase and rutile TiO₂ incorporated into clear acrylic coatings were effective at restricting discoloration, mass loss and gloss loss of wood panels exposed to artificial weathering. Both rutile and anatase TiO₂ were superior to UVA/HALS additives. Cerium dioxide nanoparticles have been used in exterior coatings, plastics, automobiles and textiles (Clayton and Sawitowski 2006), However, Liu *et al.* (2010) found that cerium dioxide nanoparticles were less effective than conventional photostabilizers (UVA/HALS, or micronized iron oxide) at restricting weight and strength losses and color changes of wood veneers exposed to natural weathering. Aloui *et al.* (2007) found that iron oxides were more effective at restricting discoloration of wood and coatings than organic UVAs because they had broader light absorption. However, iron oxides and inorganic UVAs decrease the flexibility of clear coatings. As a result, cracks and roughness at the surface of weathered coatings containing inorganic UVAs can be quite pronounced (Aloui *et al.* 2007).

Organic UVAs incorporated into clear coatings restricted the darkening of certain furniture woods and increased the service lives of the finishes (Gantz and Sumner 1957; Kiefer and Chairman 1967). Williams (1983) found that grafting of an organic UVA retarded the erosion rate of western red cedar and improved the performance of a clear coating on grafted wood

exposed to artificial weathering. Hon *et al.* (1985) found that a clear polymeric coating containing a UVA restricted the photodegradation of southern pine. Organic UVAs also prevented the discoloration of clear topcoats and the underlying wood surfaces of specimens exposed to weathering (Schaller and Rogez 2007; de la Caba *et al.* 2007). The photoprotective effects of UV absorbers depend on the types of UVA used. Forsthuber and Gröll (2010) claimed that organic UVAs are more effective than inorganic UVAs at restricting color changes. Organic UVAs can prevent coated wood substrates from cracking, and they also restrict the blistering, flaking, peeling, and cracking of the coating (George *et al.* 2005; Allen *et al.* 2002; Aloui *et al.* 2007).

Organic UVAs have limited light-fastness and photo-permanence because they tend to migrate or decompose during exposure. Hence, high concentrations are required to provide good protection (Aloui *et al.* 2007). The photoprotective effects of organic UVAs depend on the thickness of the polymer substrates, wood species and structure of the UVAs (Zweifel 1997; Ávár and Bechtold 1999). Conventional UVAs are designed to absorb UV light from 300-350 nm. However, UV light at 350-400 nm and visible light can also cause discoloration of wood (Derbyshire and Miller 1981). Hayoz *et al.* (2003) reported on a new photostabilizer that has absorption closer to the visible spectrum (red-shifted). This new photostabilizer was better than a conventional photostabilizer at restricting discoloration, cracking and loss of gloss of clear-coated balsam fir (*Abies balsamea* (L.) Mill.) and Douglas fir exposed to artificial weathering. Furthermore, lower concentrations of this new UVA were required to provide good protection (Hayoz *et al.* 2003). The photostability and effectiveness of organic UVA in coatings can also be improved by combining them with an inorganic UVA or a hindered amine light stabilizer (Mahltig *et al.* 2005).

2.4.3.2 Hindered Amine Light Stabilizers (HALS)

Hindered amine light stabilizers (HALS) are mainly derivatives of 2,2',6,6'-tetramethylpiperidine (TMP) (**Figure 2.9**). HALS are very effective at photostabilizing most polymers (Bauer *et al.* 1990). HALS prevent surface erosion, gloss reduction, discoloration, micro-cracking and chalking in clear coats, and improve their adhesion to wood and other substrates (Gijsman 2002).

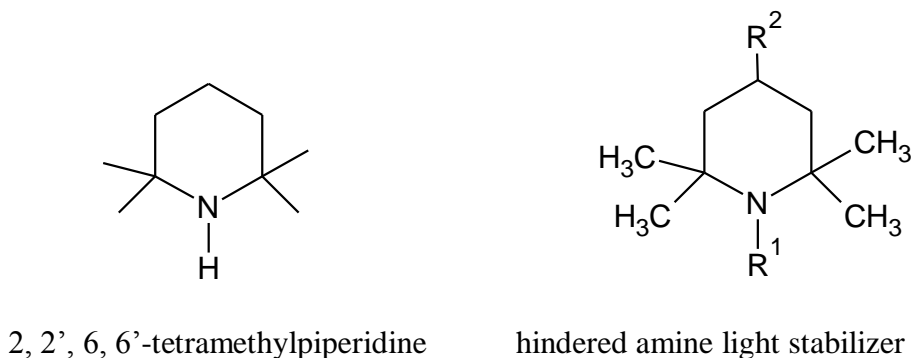


Figure 2.9 Structure of a typical 2, 2', 6, 6'-tetramethylpiperidine (TMP) and a hindered amine light stabilizer (HALS) (Wicks *et al.* 1999; Kampmann *et al.* 2005)

HALS do not absorb UV light. Instead they interact with radicals generated by UV light and form nitroxide derivatives, which scavenge free radicals (Patel and Usilton 1978). The high efficiency and longevity of HALS results from a cyclic reaction where the HALS are regenerated rather than being consumed (Patel and Usilton 1978; Carlsson *et al.* 1984; Step *et al.* 1994) (**Figure 2.10**). The mechanism of action of HALS has not been fully elucidated and other mechanisms to the one described above have been proposed including: (1) HALS act as antioxidants (Patel and Usilton 1978); (2) HALS quench the excited singlet state of chemicals to their ground-state (Fairgrieve and MacCallum 1984; Bortolus *et al.* 1992; Zweifel 1997).

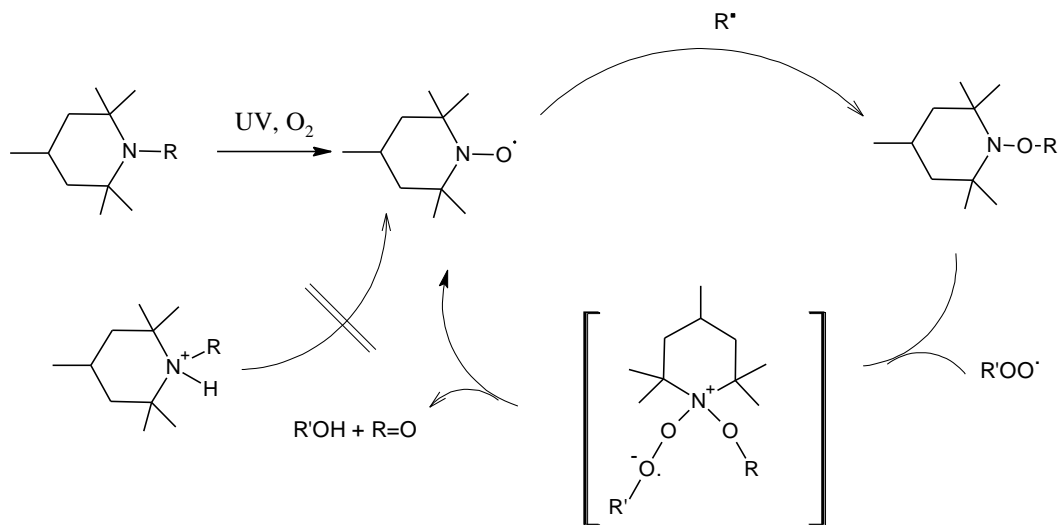


Figure 2.10 Mechanism of action of a HALS

It has become common practice to combine UVAs with HALS, as mentioned above, because the combination provides synergistic effects for photoprotection of polymers and also wood (Kurumada *et al.* 1987; Schaller 2007). The synergistic effects of UVA/HALS may be due to their different modes of action. UVAs protect the deeper layers of a coating and the interface between wood and coating, whereas HALS protect the surface (Kurumada *et al.* 1987; George *et al.* 2005). The protective effects of UVA/HALS are influenced by the ratio of UVA to HALS, the type of polymer to which they are added and the types of UVAs and HALS (Kurumada *et al.* 1987; Ávár and Bechtold 1999; George *et al.* 2005; Muasher and Sain 2006). The combination of a UVA/HALS in a coating and pre-treatment of wood restricted discoloration of coated wood samples exposed to artificial weathering (Hayoz *et al.* 2003). The effects of the treatments on pale wood species such as ash and maple (unknown species) were better than on darker wood species such as cherry and nut (unknown species) (Hayoz *et al.* 2003). De la Caba *et al.* (2007) applied UV stabilizers (UVA/HALS) and PMMA (poly methyl methacrylate) film on the surface of phenol formaldehyde resin treated wood panels and exposed the wood panels to

3000 hours of artificial weathering. Their results revealed that the photostabilizers reduced the cracking and loss of gloss of the coated panels. Donath *et al.* (2007) combined HALS and a UV absorber with different type of monomeric silanes and used the solution to treat the sapwood of Scot pine. The treated samples were exposed to artificial weathering. Their results showed that the combinations of UV light stabilizers and silanes were effective at restricting photodegradation of wood, whereas silanes on their own were ineffective.

2.4.4 Polymerizable Monomers

Wood can be stabilized by impregnating it with polymerizable monomers and then curing the monomer with heat or radiation. The polymerized monomers form a polymer that penetrates the wood microstructure and sometimes covers the exposed surface of wood (Hawkins 1984; de la Caba *et al.* 2007). Polymerizable monomers that can improve the resistance of wood to weathering include: melamine formaldehyde, water soluble amino resins, 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), silicon compounds, and water soluble low molecular weight phenol formaldehyde resin (Rowell *et al.* 1981; Hawkins 1984; Xie *et al.* 2005; Hansmann *et al.* 2006; Temiz *et al.* 2006; Evans 2009).

Rowell *et al.* (1981) found that impregnation with methyl methacrylate monomers reduced the erosion of southern pine exposed to artificial weathering. Wood treated with melamine formaldehyde resin and a coating of varnish also showed decreased erosion when exposed to 2 years of natural weathering (Rapp and Peek 1999). Hansmann *et al.* (2006) treated heartwood of Norway spruce and black poplar (*Populus nigra* L.) with low molecular weight melamine formaldehyde resins, with low degrees of methylolation. Treated samples were exposed to artificial weathering. Their results showed that the treated samples were less susceptible to

discoloration and surface cracking than the untreated control. Nano-sized polymeric silica SiO_2 [$\text{mSiO}_2 \cdot n\text{H}_2\text{O}$ or $[\text{Si}(\text{OH})_4]$] can restrict the discoloration of Scots pine sapwood exposed to artificial weathering (Xie *et al.* 2005; Temiz *et al.* 2006).

Sudiyani *et al.* (1999) treated sapwood of albizzia (*Paraserianthes falcata* Becker.) and sugi with acetic anhydride, propylene oxide, DMDHEU or a low molecular weight PF resin and exposed the samples to 1 year of natural weathering or 1080 hours of artificial weathering. The low molecular weight PF resin and acetylation were superior to DMDHEU at restricting the discoloration, surface checking, weight loss and decay of treated samples. Xie *et al.* (2005) treated Scots pine veneer with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) and exposed samples to artificial weathering for 144 hours. Their results showed that samples treated to high weight gains (48%) lost less weight and tensile strength than untreated controls. The most significant finding was that DMDHEU restricted cell wall degradation (Xie *et al.* 2005). However, high weight gains were required to get reasonable protective effects (Xie *et al.* 2005).

Chang *et al.* (1998) found that a finishing system consisting of a PEG pre-treatment and a polyurethane coating containing a UV absorber reduced the discoloration of Taiwan heartwood exposed to artificial weathering. Clear finishes on the top of Douglas fir plywood pre-treated with 10% PEG lasted for 2 years without failure, whereas the coated controls failed after 6 months (Kiguchi *et al.*, 1996). Ohkoshi (2002) impregnated the heartwood of four softwood species: sugi, hinoki cypress, karamatsu (*Larix leptolepis* Gordon.), and akamatsu (*Pinus densiflora* Sieb. et Zucc.) with PEG, and exposed samples to UV light for 100 and 1000 hours. They found that PEG impregnation decreased the generation of unsaturated aromatic compounds arising from the degradation of lignin. As a result, color changes of PEG treated specimens during weathering were less than those of the untreated controls. However, longer periods of

irradiation with UV light caused degradation of PEG, and hence reduced the effectiveness of the treatment (Ohkoshi 2002). In addition, PEG was easily leached from treated wood (Stamm 1974; Ohkoshi 2002).

2.4.5 Additives

2.4.5.1 Wax

Wax is an effective water repellent because it is hydrophobic (Borgin and Corbett 1970). Treatment of wood with wax reduces the water uptake and swelling of wood, and hence reduces cracking and warping of wood exposed to weathering (Borgin and Corbett 1970). A wax additive in water-repellent preservatives helped to reduce the erosion of treated wood during weathering (Feist 1992). Jackson *et al.* (1992) treated radiata pine with CCA, CCA/oil and CCA/wax and exposed the samples to artificial weathering. Their results showed that the additives greatly reduced warping and end-grain checking of wood. Cui and Zahora (2000) found that acid copper chromate (ACC) or ACQ containing a water repellent reduced moisture fluctuations and surface checking of treated wood exposed to natural weathering. The water repellent had a better effect on the performance of ACC than on ACQ. Zahora (2000) compared the effects of “wax” type additives on the performance of CCA-treated decking boards exposed to natural weathering for 9 years. He showed that the “wax” additives greatly improved the performance of the CCA-treated wood. Boards treated with CCA-wax developed few large checks. Corrosion of fasteners was also reduced and boards were more dimensionally stable. Evans *et al.* (2009) compared the effects of wax and oil emulsion additives on the performance of CCA-treated radiata pine boards exposed to natural weathering. Their results showed both type of additives were able to reduce

the checking, water absorption and swelling of treated wood. However, oil emulsions were better than wax emulsions at dimensionally stabilizing wood exposed to weathering.

2.4.5.2 Lignin

Lignin strongly absorbs UV radiation, especially in the range of UVB (280-320 nm). Therefore, lignin is potentially a natural UV protectant (El-Salamouny *et al.* 2009). UV stabilizers like HALS are very expensive, whereas lignin is an abundant renewable natural material that is non-toxic and cheap (Feldman 2002). Lignin is cost-effective as an additive for UV stabilization (Gosselink *et al.* 2004).

Lignin has good compatibility with many chemicals and has been blended with a variety of different polymers (Feldman 2002). Lignin has been used as a filler in polyethylene and polypropylene to improve their photostability (Alexy *et al.* 2000; Gosselink *et al.* 2004). De Paoli and Furlan (1985) found that sugar cane bagasse-lignin was an effective photo-stabilizer for butadiene rubber.

Lignosulphonates have also been evaluated for use as photostabilizers in pesticide formulations containing baculovirus (Tamez-Guerra *et al.* 2000; Farrar and Ridgway 2000; El-Salamouny *et al.* 2002). Both magnesium and sodium lignosulphonates preserved virus activity better than a calcium lignosulphonate (El-Salamouny *et al.* 2002).

2.5 Phenol Formaldehyde Resins

Phenol formaldehyde resin (PF resin) was invented in 1907 by Baekeland and it was the first synthetic polymer to be developed (Knop and Scheib 1979). PF resins have been widely used as molding powders, adhesives and in surface coatings (Knop and Scheib 1979; Saunders 1988). PF resins can also be used to treat wood. The PF resin imparts many beneficial properties

to the wood including hardness, compressive strength, thermal stability, and chemical and biological resistance. Hence, PF resins have been used commercially to improve the performance of wood (Stamm and Seborg 1939; Weatherwax and Stamm 1956; Lloyd and Stamm 1958; Stamm and Baechler 1960; Stamm 1975; Ryu *et al.* 1991; Yusuf *et al.* 1999; Deka and Saikia 2000; Furuno *et al.* 2004).

2.5.1 Synthesis of Phenol Formaldehyde Resins

PF resins are synthesized by reacting phenol with formaldehyde. The reaction of phenol and formaldehyde can be divided into three stages: (1) A stage, a phenol links with formaldehyde via a methylene bridge at any one of its three possible sites. The resulting reaction product is hydroxymethyl phenol. The reaction products at this stage consist of a mixture of monomers and dimers ($\text{HOC}_6\text{H}_5 + \text{CH}_2\text{O} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_2\text{OH}$); (2) B stage, the hydroxymethyl group reacts with either free ortho or para sites on phenol rings ($\text{HOC}_6\text{H}_4\text{CH}_2\text{OH} + \text{HOC}_6\text{H}_5 \rightarrow (\text{HOC}_6\text{H}_4)_2\text{CH}_2 + \text{H}_2\text{O}$) or with another hydroxymethyl group to form an ether bridge ($2\text{HOC}_6\text{H}_4\text{CH}_2\text{OH} \rightarrow (\text{HOC}_6\text{H}_4\text{CH}_2)_2\text{O} + \text{H}_2\text{O}$). At this stage, polymerization starts and monomers and dimers generate trimers, tetramers and higher oligomers; (3) C stage, the products mentioned in B start to cross-link and form a highly extended 3-dimensional network (Knop and Scheib 1979; Marra 1992).

The chemical kinetics of the reaction of phenol and formaldehyde is very complex. PF resin products depend on the molar ratio of phenol to formaldehyde, catalyst, pH, reaction time, temperature, solvents and presence of other compounds (Knop and Scheib 1979; Marra 1992). Low molecular weight PF resins consisting of dimers, trimers and oligomers are used to treat wood, whereas highly cross-linked resins are used as adhesives. The Division of Forest Products

(Concnil for Scientific and Industrial Research) in Australia systematically investigated the effects of many types of PF resins on the properties of wood (Boas 1947). They found that a water-soluble PF resin with a molecular ratio of 1 (phenol): 0.88 (formaldehyde) was the best at improving the properties of wood (Boas 1947). Burr and Stamm (1956) summarized the most desirable properties of PF resins for wood modification as “high solids content; miscibility with water in all proportions; long storage life; low viscosity; light color; and ability to function as a bonding as well as a stabilizing agent”.

2.5.2 Penetration of Phenol Formaldehyde Resins in Wood Cells

The effectiveness of PF resin at improving the properties of wood depends on the penetration and even distribution of PF resin within wood cells, and also the ability of the resin to bond with cell wall components. Uneven or partial penetration of wood by resin results in checking or honeycombing because of differential stresses that develop in treated and untreated wood (Seborg *et al.* 1962; Burr and Stamm 1956). Optimizing the treatment process and using resin efficiently are commercially important.

2.5.2.1 Penetration Pathway

There are two scales of penetration of PF resin into wood according to Kamke and Lee (2007): (1) micro-penetration and (2) nano-penetration. Penetration of resin into the porous microstructure of wood including vessels, longitudinal and ray tracheids, cell lumens and pits is called micro-penetration. Penetration of resin through the cell wall is called nano-penetration (Kamke and Lee 2007). Wan and Kim (2006) reported that PF resin mostly flowed through ray tracheids in softwoods and less so in longitudinal tracheids and parenchyma. Modzel *et al.* (2011) measured the depth of penetration of PF resin into different wood species. PF resin

penetrated red oak (*Quercus rubra* L.) and hybrid Poplar (*Populus deltoids* x *Populus trichocarpa*) to depths of 400 μm , and Douglas fir to depths of 100 μm . They confirmed that PF resin penetrated the longitudinal fibers and parenchyma of oak and the longitudinal tracheids of Douglas fir. Wan and Kim (2008) found that the penetration pathway within cell walls was through the middle lamella and primary walls because cellulose micro-fibrils in the primary wall were loosely packed, whereas they were more densely packed in the secondary cell wall, which restricted resin from penetrating via cell lumens. However, they found that the largest amount of resin was deposited in the S₂ layer of the secondary wall (**Figures 2.11 and 2.12**).

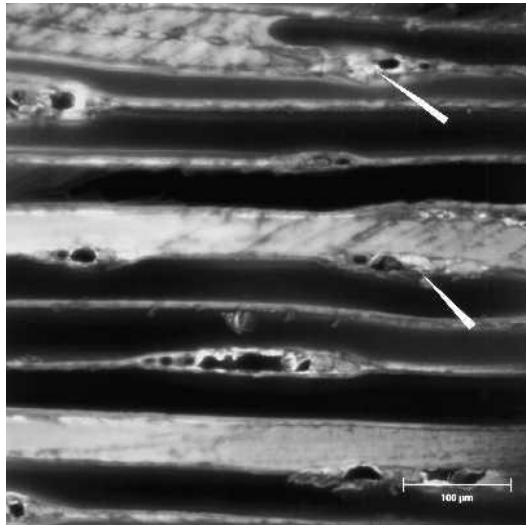


Figure 2.11 Phenol formaldehyde resin deposited in rays of southern pine impregnated with a low molecular weight PF resin (Wan and Kim 2006)

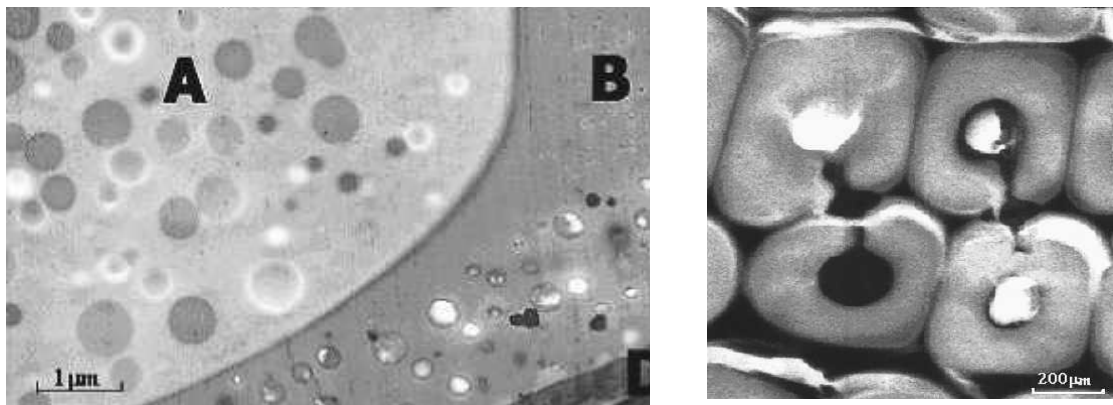


Figure 2.12 PF resin in lumen, cell wall and pits of southern pine impregnated with a low molecular weight of PF resin (Wan and Kim 2008)

2.5.2.2 Factors Influencing the Penetration of PF Resin

2.5.2.2.1 Properties of Resin

Stamm and Seborg (1939) summarized three essential elements for the penetration of PF resin into wood: firstly, the resin solution must be unpolymerized or only slightly polymerized so that PF resin molecules are small enough to penetrate into wood cell walls. Secondly, the resin must be soluble in polar solvents because such solvents have a better swelling effect than non polar solvents, and hence efficiently open up the wood structure and enable the resin to diffuse faster and more completely into the wood. Finally, the resin itself must be polar, so it can orient and bond to compatible polar groups in wood.

The permeability of softwood to PF resin depends on the fine capillary structure of the wood, and in particular the number of bordered pits, their degree of aspiration and the size of openings in the pit membrane or margo. High molecular weight PF resins cannot access cell walls and may also have difficulties penetrating wood's coarser microstructure because they can be blocked by aspirated bordered pits (Kajita and Imamura 1991; Ryu *et al.* 1993; Kamke and Lee 2007; Wan *et al.* 2008). Gollob *et al.* (1985) treated Douglas fir plywood with PF resin and found that there was less penetration of higher molecular weight PF resin into drier regions of the plywood. Stephen and Kutscha (1987) treated aspen (*Populus tremuloides* Michx.) with PF resin composed of different molecular weight fractions. Their results showed that the lowest molecular weight fraction penetrated 1-2 cells deep, whereas there was little penetration of the higher molecular weight fraction. Furuno *et al.* (2004) treated wood with labelled PF resins with molecular weights of 290, 470 and 820. They found that the lowest molecular weight PF resin could easily penetrate wood cell walls. Some of the medium molecular weight PF resin deposited in cell walls, whereas the high molecular weight PF resin only filled cell lumens. Laborie *et al.*

(2006) studied the adhesive interphase of wood/phenol-formaldehyde system using dynamic mechanical analysis and C^{13} charge polarized magic angle spinning nuclear magnetic resonance spectroscopy (CP/MAS NMR). They found that a low molecular weight PF resin greatly increased the relaxation time of the treated wood and enhanced intermolecular interactions. In contrast, a high molecular weight PF resin did not affect the wood's behaviour. Their results imply that nano-penetration of wood cell walls only occurs with low molecular weight resin. High molecular weight PF resin and wood are separated systems.

Low molecular weight water-soluble PF resins are superior to any other resin for the modification of wood (Millett and Stamm 1947; Stamm and Baechler 1960; Seborg *et al.* 1962; Erickson *et al.* 1966; Deka and Saikia 2000). Phenol is a very good swelling agent for wood and the affinity of phenol for wood is superior to that of water because phenol is better than water at opening up the fine capillary structure of wood and facilitating diffusion of PF resin into cell walls (Stamm and Seborg 1936). Hydrodynamic flow and capillary action are the two main forces driving the penetration of PF resin into wood (Kamke and Lee 2007). A solution containing low concentrations of PF resin easily flows into wood because of its low viscosity. However, a solution containing a low concentration of PF resin is incapable of creating a highly cross-linked resin network in treated wood. On the other hand, lack of water in concentrated, highly viscous, PF resin solutions results in reduced penetration of the PF resin into wood (Marra 1992). Sodium hydroxide can increase the penetration of PF resin into wood because it swells cell walls and reduces the viscosity of the resin (Kamke and Lee 2007).

Stamm and Baechler (1960) suggested that solutions containing 30% or more of PF resin should be used to treat wood. Stamm and Seborg (1962) suggested that wood cell walls were saturated with resin when wood was impregnated with solutions containing 30-40% PF resin.

Solutions containing higher concentrations of PF resin deposited excess resin in the coarse capillary structure and this had little effect on the dimensional stability of the treated wood. Hence, they concluded that it was not cost-effective to treat wood with PF resin solutions that had a resin content of greater than 30%. Wan and Kim (2006) quantified the amount of resin in PF resin solutions that led to good improvements in the properties of treated wood. They suggested that the amount of resin should be about 2% of the wood's volume. At this level the resin was able to fill ray tracheids and pits and form an interlocking network between pit pairs and hence stabilize the wood.

2.5.2.2.2 Wood Factors

Penetration of PF resin was much greater in earlywood than in the latewood of Douglas fir, southern pine, western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) and noble fir (*Abies procera* Rehd.) due to the larger lumen diameters and larger pits in earlywood (Kamke and Lee 2007, Wan and Kim 2006). There was no difference in the penetration of PF resin into the earlywood and latewood of aspen. The similarity of penetration of PF resin in earlywood and latewood of aspen was explained as being due to the lack of large differences in the structure of these tissue types in aspen and other diffuse-porous species (Kamke and Lee 2007). Aspirated pits in ray tracheids of southern pine reduced the penetration of PF resin into rays according to Kamke and Lee (2007).

Penetration of PF resin was greater in some hardwoods than in softwood because vessels are very permeable when they lack tyloses. Accordingly, penetration of a PF resin in red oak and hybrid poplar was greater than that in Douglas-fir (Modzel *et al.* 2011). Penetration was also better in yellow poplar (*Liriodendron tulipifera* L.) than that in southern pine (Kamke and Lee

2007). Penetration of PF resin in heartwood was small, even in small dimension specimens (Stamm and Seborg 1936). Penetration of PF resin in green wood was greater than that in dry wood because dry wood absorbed water from the resin, which increased the viscosity of the resin and reduced the flow of the resin into the wood's microstructure (Kamke and Lee 2007). Research on the effect of wood moisture content on penetration of PF resin into aspen showed that more rapid penetration of PF resin occurred at a wood moisture content of 25%. However, penetration of PF resin was greater when the moisture content of the wood was 15% (Kamke and Lee 2007). Penetration of PF resin in the longitudinal direction was much greater than in the transverse directions, as expected (Kamke and Lee 2007). Penetration was greater in cross-grained veneer than in straight grained veneer (Stamm 1975).

2.5.3 Effects of PF Resin on Wood Properties

2.5.3.1 Effects of PF Resin on Weathering of Wood

Face checking is pronounced in plywood when the plywood is exposed outdoors (Stamm and Seborg 1939). In order to solve this problem, Stamm and Seborg (1939) applied water-soluble low molecular weight PF resin to plywood and exposed the treated samples to weathering for 3 months. Their results showed that the PF resin significantly reduced checking and also the roughening of the plywood surface. Douglas fir plywood is very susceptible to checking, but the face checking of Douglas fir plywood was greatly reduced by treating the face ply with a water-soluble PF resin (Stamm and Seborg 1962). Lloyd and Stamm (1958) also found that PF resin treatment greatly reduced face checking, grain raising and erosion of both hardwood and softwood species. They compared the effects of a PF resin treatment that involved impregnation of wood with PF resin (Impreg) versus a treatment that involved impregnation and

densification of the PF resin treated wood (Compreg) on the checking of different wood species. Their results showed that the Impreg treatment was more effective with hardwoods than softwoods, whereas Compreg was equally effective with both hardwoods and softwoods. Yusuf *et al.* (1999) treated particleboards with low molecular weight PF resin and adhesive resin, and exposed the samples to 12 months natural weathering. Particleboards treated with 7.5% or 10% resin had enhanced resistance to both decay and termite attack. Treated boards retained a relatively high proportion of their bending strength, modulus of elasticity and internal bond strength after 12 months natural weathering. Imamura (2007) also reported that PF resin treatment improved the color stability and reduced the cracking of wood exposed to weathering.

Kyushu Mokuzai in Japan (2001) treated wood with 10% PF resin or the wood preservative copper azole and exposed samples outdoors for 3 years. Their results showed that samples treated with PF resin had less cracking and color changes, and maintained their mechanical strength and dimensional stability. In contrast, copper azole was less effective than the PF resin at protecting the wood from weathering (<http://www.kyumoku.co.jp>).

2.5.3.2 Effects of PF Resin on other Properties of Wood

2.5.3.2.1 Dimensional Stability

PF resin treatments can increase the dimensional stability of wood because resin solids bulk wood cell walls and reduce the absorption of water (Stamm and Seborg 1939). Stamm and Seborg (1936) found that the swelling and shrinkage of redwood samples were reduced by up to 70% when the wood was treated with a 30% PF resin solution. Stamm and Seborg (1962) found that the antishrink efficiency of water-soluble PF resin treated plywood was positively correlated with resin uptake. The maximum effect was obtained with a 30-40% solution. When plywood

was treated with 20 and 40% water soluble PF resin the permeability of the plies to water was reduced to 10 and 5%, respectively, of that of untreated plies. Gotô and Kadita (1956) found that the anti-shrink efficiency of PF resin-treated wood was greatest when the wood was treated at moisture contents of 6-10%. Gotô and Kadita (1956) also examined the effects of treating wood with PF resin in different solvents (water, methyl alcohol, ethyl alcohol, isopropyl alcohol, n-butyl alcohol, acetone and aniline) on the dimensional stability of the treated wood. Their results showed that wood treated with PF resin diluted with acetone or aniline had the highest anti-shrink efficiency. The use of monohydric alcohol as a solvent decreased anti-shrink efficiency. Water, methyl and ethyl-alcohol had similar effects although the velocity of penetration of PF resin solutions containing these solvent was different. Ryu *et al.* (1993) and Furuno *et al.* (2004) examined the effect of resin molecular weight on the dimensional stability of PF resin treated wood. Their results showed that lower molecular weight resins were more effective than higher molecular weight resins at dimensionally stabilizing wood. Furuno *et al.* (2004) found that there was no difference in the effect of a neutralized PF resin and an alkaline resin on the dimensional stability of treated wood. However, the neutralized resin did not change the original color of the wood, whereas the alkaline type resin changed the color of the wood to red-brown.

Dimensional instability is more serious problem with wood composites such as particleboard and OSB than for solid wood. Hence, there has been a lot of interest in treatments that can dimensionally stabilize wood composites. Kajita and Imamura (1991) used a low molecular weight PF resin to treat particleboard to weight gains of 5, 10, 15, 20 and 30%. Their results showed that the resin treatments reduced the thickness swelling of boards. Boards treated to a high resin loading of 20% were the most dimensionally stable. The concentration of PF resin used to treat particleboard was lower than that used to treat solid wood. Paridah *et al.* (2006)

impregnated OSB with low molecular weight PF resin. A treatment solution containing 7% PF resin significantly reduced the thickness swelling and water absorption of the OSB. The dimensional stability of a three-layer board was greater than that of a five-layer board.

2.5.3.2.2 Biological Resistance

PF resin treatments reduce the hygroscopicity and moisture content of wood, which inhibits fungal growth and termite attack and therefore increases the biological resistance of the treated wood (Stamm and Baechler 1960). Untreated Douglas fir heartwood specimens exposed to the fungus (*Trametes serialis* (Fr.) Fr.) for 8 months, lost 40% of their weight, whereas the weight losses of samples treated with 32-49% PF resin were only 3-5% (Stamm and Seborg 1939). The weight losses for untreated sugar pine (*Pinus lambertiana* Dougl.) specimens incubated with the fungus (*Lenzites trabea* (Pers.) Fr.) were 42%, whereas the weight losses of samples treated with 15 and 30% PF resin were only 5.3 and 1.2%, respectively (Stamm and Seborg 1939). Furthermore, the treated samples were mechanically sound, whereas the untreated controls were heavily damaged. PF resin treated wood was also resistant to termite and marine borer attack (Edmondson 1953, Stamm and Seborg 1962). Kajita and Imamura (1991) found that particleboard was resistant to attack by a brown-rot fungus when it was treated with PF resin to a weight gain of 15%. Attack by a white-rot fungus was completely suppressed even at low resin loading, and all treated samples resisted termite attack.

The effect of PF resin on the decay and termite resistance of treated wood is influenced by wood species, resin properties and biological factors. Ryu *et al.* (1991) reported that impregnation of sugi and western hemlock with a 10% water-soluble PF resin (molecular weight of 170) prevented brown and white rot decay. But a solution containing 20% resin was required

to produce the same decay resistance in Japanese beech (*Fagus crenata* Blume.). Impregnation of the three species with solutions containing 5% to 15% PF resin was able to prevent termite attack. Furuno *et al.* (2004) found that treatment of Japanese cedar with a 15% neutralized PF resin or a 10% alkaline PF could prevent both brown rot and white-rot decay.

Kyushu Mokuzai in Japan (2001) also investigated the ability of PF resin treatments to prevent the decay and termite attack of wood. They treated wood with 10% water-soluble PF resin and measured mass losses of the treated wood after 6 and 7 years outdoor exposure in different areas of Japan. Their results showed that the PF resin treatment greatly reduced decay and termite attack of wood (**Figure 2.13**) ([http:// www.kyumoku.co.jp](http://www.kyumoku.co.jp)).

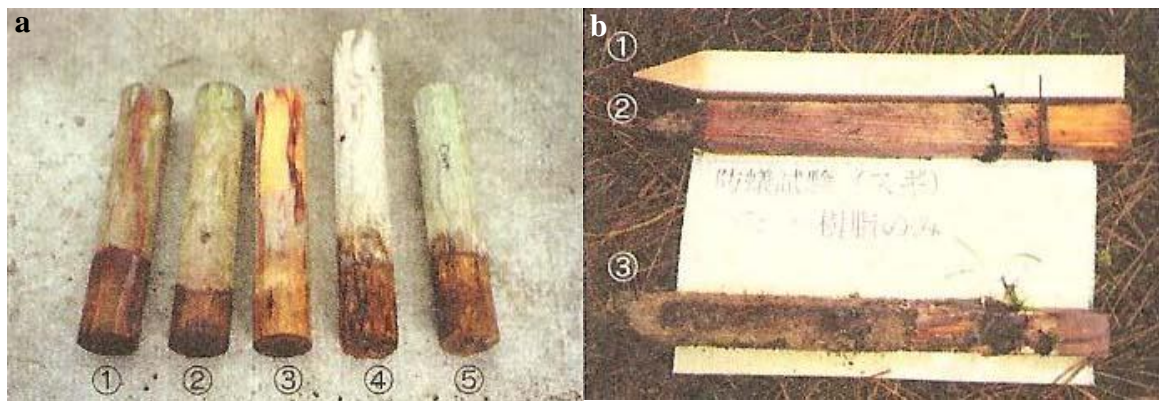


Figure 2.13 Bio-resistance test of PF resin treated wood in Japan: a, Decay test. (1-3. PF resin treated samples, 4-5. Controls). Note that there is no decay of PF treated samples, whereas untreated samples were damaged by fungi. b, Termite resistance test (1. Original wood; 2. PF resin treated sample, 3. Untreated sample). Note that the PF treated sample resisted termite attack, whereas the untreated sample was heavily attacked by termites. Mokuzai Gakkaishi. [http:// www.kyumoku.co.jp](http://www.kyumoku.co.jp))

2.5.3.2.3 Mechanical Properties

PF resin treatment significantly increased the compressive and bending strength, shear, hardness and stiffness of redwood and yellow birch (*Betula alleghaniensis* Britt.) (Erickson and Faulkes 1966). Stamm and Seborg (1962) reported that PF resin treatment increased compression strength perpendicular to grain more than in the direction parallel to the grain. However, Panshin

(1962) found that PF resin treatment embrittled the wood, if the wood was treated to high weight gains. Accordingly, Stamm and Baechler (1960) found that the brittleness of PF resin treated wood increased with increased resin loadings. Gotô and Kadita (1957) reported that the tensile strength of PF resin impregnated wood after curing decreased parallel to grain, but increased perpendicular to the grain. Erickson and Faulkes (1966) found that PF resin treatment slightly reduced the tensile strength, toughness and izod impact strength of yellow birch. Deka and Saikia (2000) reported 12-20% increases for MOR and 5-12% increases for MOE when Kadamba wood (*Anthocephalus cadamba* Miq.) was treated with a PF resin to weight gains of 33-35%.

Kajita and Imamura (1991) examined the effect of a PF resin treatment on the mechanical properties of particleboard. They found that increases in dry MOR were proportional to resin uptake when a conventional PF resin adhesive was used to treat the particleboard. The same effect was observed when particleboard was treated with low molecular weight PF resin. PF resin treated particleboard samples also retained a greater percentage of their MOR and MOE when they were exposed to water and tested in the wet condition. The bending strength of the treated particleboard increased with an increase in resin loading and reached a maximum at 20% resin loading. Paridah *et al.* (2006) impregnated OSB with different concentrations of low molecular weight PF resin. They found that treatment with a 7% PF resin greatly improved MOE, MOR and IB of boards. The PF resin treatment was better at improving the mechanical properties of a three-layer strand board than at improving the mechanical properties of a five-layer board.

2.5.3.2.4 Heat Resistance

Stamm and Seborg (1939) found that PF resin treatment did not change the fire resistance of wood, but it prevented the spread of fire because the resin itself did not combust. Seborg *et al.* (1962) stated that Compreg was more resistant to flaming than Impreg because of its greater density. Kim *et al.* (2001) impregnated southern pine with PF resin and tested the fire resistance of the treated wood. Their results showed that the PF resin treatment enhanced the fire resistance of the wood without decreasing strength properties.

2.5.3.2.5 Electrical Resistance

PF resin treatment increased the electrical resistance of wood because it reduced the wood's hygroscopicity (Stamm and Seborg 1962). Weatherwax and Stamm (1956) treated ten different species of wood with PF resin and tested the electrical resistivity of the treated wood. They found that the resistivity of treated wood samples was ten times that of normal wood at 30% relative humidity, and almost 1,000 times that of normal wood at 90% relative humidity. Impreg and Compreg had similar electrical resistivity. Their results indicated that wood treated with PF resins is very suitable for various dielectric uses even under relatively high humidity conditions.

2.5.3.2.6 Chemical Resistance

Stamm and Seborg (1939) found that PF resin treatment increased the resistance of southern pine to hydrochloric and sulfuric acid, but it did not increase the wood's resistance to alkali. Panshin *et al.* (1950) found that Compreg resisted mild acids, alcohols and other solvents. The chemical resistance of Compreg was superior to that of Impreg because Compreg was less permeable than Impreg (Seborg *et al.* 1962).

2.5.4 Commercial Treatment of Wood with Phenol Formaldehyde Resins

There have been a number of commercial processes developed to modify wood with PF resin. Two of the processes (Impreg and Compreg) were developed in the USA. A third process has been commercialized in Japan by Kyushu Mokuzai in 2003 (<http://www.kyumoku.co.jp>). This section examines all three of these processes.

2.5.4.1 Impreg

‘Impreg’ involves treating wood with phenol resin and curing the resin without compressing the wood (Stamm and Seborg 1939). The manufacture of Impreg includes three stages: impregnating, drying and curing. Stamm (1975) indicated that ‘Impreg’ only uses an ‘A’ stage PF resin because an “A” stage resin is only slightly polymerized, and the low molecular weight fractions can easily penetrate wood cell walls.

There are three methods of treating wood with PF resin: soaking, spraying and pressure impregnation (Seborg *et al.* 1962). Soaking is the simplest method, but it is very slow, and can only be applied to freshly cut green or dry veneer (Stamm and Seborg 1962). Increased soaking times are needed to obtain desired resin loadings with thicker veneer and denser specimens. On the other hand, soaking times can be reduced by treating wood with higher moisture contents or using warm solutions (Stamm and Seborg 1941, 1962). Pressure impregnation of wood reduces treatment times and is the only method that can treat solid wood and thicker veneer to desired resin loadings (Stamm and Seborg 1962). Vacuum treatment (<100 kPa), however, does not greatly improve resin uptake (Stamm and Seborg 1939).

The processes involved in the pressure treatment of veneer with PF resin are as follows: (1) Impregnation: Veneers are placed inside a treatment cylinder and immersed in the PF resin; (2)

Pressure stage: Pressure is applied until the amount of solution taken up by the veneer is the same as the dry weight of the veneer. The pressures and pressing times used were 138 to 517 kPa and ¼ to 5 hours, respectively. A final resin content in dry wood of 30-35% is desirable (Stamm and Seborg 1962); (3) Diffusion: Treated veneers are stacked and covered with canvas under non-drying condition for 1-2 days so that the resin can diffuse into wood cell walls. This step is necessary because the PF resin solution only enters wood's coarse capillary structure during pressure treatment (Stamm and Seborg 1941). After resins diffuse uniformly into wood veneers, the treated veneers are dried at a temperature less than 93 °C because higher temperature (>100 °C) cause water inside the wood to boil, which forces resin onto the surface of treated wood. A continuous veneer dryer and a kiln dryer were used for drying and curing. Drying of treated wood in a continuous dryer was faster and only took about 30 minutes. Longer drying times were required when treated veneer was dried in a kiln. However, slower drying at a higher humidity of 65-70% can help resin to diffuse into cell walls. After drying the PF resin is cured. The curing temperature for PF resin is around 154 °C. Treated veneer can be dried in about 30 minutes in a continuous veneer dryer. The curing time in a kiln was longer because lower temperatures were used (Stamm and Seborg 1941; Stamm and Seborg 1962; Seborg *et al.* 1962).

Spraying is not as effective as soaking or pressure impregnation because it is unable to force the resin into the wood structure. However, spraying is the most economical treatment method (Wan and Kim 2006). Spraying can be suitable for wood that requires lower resin content, wood flakes, particleboard, and oriented strandboard (Talbot 1959; Seborg *et al.* 1962; Haygreen and Gertjeansen 1971; Kajita and Imamura 1991).

The Impreg process was mostly used to treat wood veneer that was less than 8.47 mm thick, because penetration of PF resin was much slower if thicker veneer was treated. Furthermore,

thicker sections tended to develop internal checks (honeycombing) during subsequent drying (Stamm 1975, Rowell and Konkol 1987). Millett and Stamm (1947) found that uniform and deep penetration of PF resin could be most easily obtained by treating the sapwood of permeable species such as cottonwood (*Populus deltoides* Bartr. ex Marsh.) and yellow birch. Stamm and Baechler (1960) reported that the rate of impregnation of green wood was faster than that of dry wood. It was much more difficult, as expected, to treat refractory (less permeable) wood species. Stamm and Seborg (1962) found that the treatment time for solid wood was much longer than that required for the treatment of veneers. Furthermore, the hardness and moisture resistance of treated solid wood was less than that of treated veneer panels. It was also difficult to treat large-sized wood specimens with PF resin even for the most readily treated species. Hence, they concluded that PF resin treatment was more suitable for sheets of veneer than for solid wood.

Many efforts were made to improve the Impreg treatment process. Compression rolling was invented to force PF resin into wood and improve the penetration of PF resin into veneers (Stamm 1975). Johnson and Gjovik (1970) found that pre-treating wood with a fungus (bio-incising) improved the penetration of PF resin into loblolly pine (*Pinus taeda* L.) and Douglas fir. Imamura (2007) developed a pre-compression method, which increased penetration of PF resin into wood by controlling moisture, heat and press conditions. Fukuta *et al.* (2008) found that creating incisions and drill holes in wood was the most effective method of improving the penetration of PF resin and preventing subsequent deformation of the treated wood. Gabrielli *et al.* (2010) combined PF resin impregnation and viscoelastic thermal compression (VTC), a process involving the use of dynamic heat, steam and mechanical compression, to treat hybrid poplar. Their results showed that treatment with both high and low molecular weight PF resin improved dimensional stability of the wood, but reduced Young's modulus.

Impreg has many desirable properties. Moisture absorption is greatly reduced because resin fills the space inside and between cells (Stamm and Seborg 1939). Impreg shows reduced swelling, shrinkage, grain raising and surface checking and increased resistance to decay, termites and marine borers. Impreg has improved hardness, compression strength, acid and electrical resistance and reduced spring-back (Stamm and Seborg 1936, 1939). Impreg is less prone to splitting and it is easily machined (Rowell and Konkol 1987). The good electrical properties of Impreg led to its use for packaging critical military components during World War II. Another military application of Impreg was for aircraft carrier decking. Impreg has also been used for pattern and die models in the automobile industry (Seborg *et al.* 1962; Stamm 1975).

2.5.4.2 Compreg

Compreg evolved from Impreg and is defined as PF resin treated wood that has been compressed to a high density during curing (Stamm and Seborg 1941). Compreg absorbs less moisture because its capillary voids are smaller than those of Impreg. Therefore, it is also more dimensionally stable than Impreg (Stamm and Seborg 1962, Stamm 1975). Compreg is very resistant to decay, termites, and marine borers (Stamm and Seborg 1941, Rowell and Konkol 1987). The strength properties, abrasion resistance, electrical, acid and fire resistance of Compreg are also superior to those of Impreg (Seborg *et al.* 1962, Rowell and Konkol 1987). Seborg *et al.* (1962) mentioned that Compreg could be polished to produce a very smooth surface. The properties of inferior species such as cottonwood can be greatly improved by the Compreg process (Seborg *et al.* 1962). Compreg has the potential to replace other materials (Shams *et al.* 2004). For example, during World War II, Compreg was used for aeroplane propellers and ship's screw bearings (**Figure 2.14**). It has also been used for 'dies and jigs,

weaving shuttles, knife handles, glass door pulls, and railroad track connectors' (Stamm 1975).

Compreg is still manufactured today in India, Japan, Poland and the USA (Table 2.2).

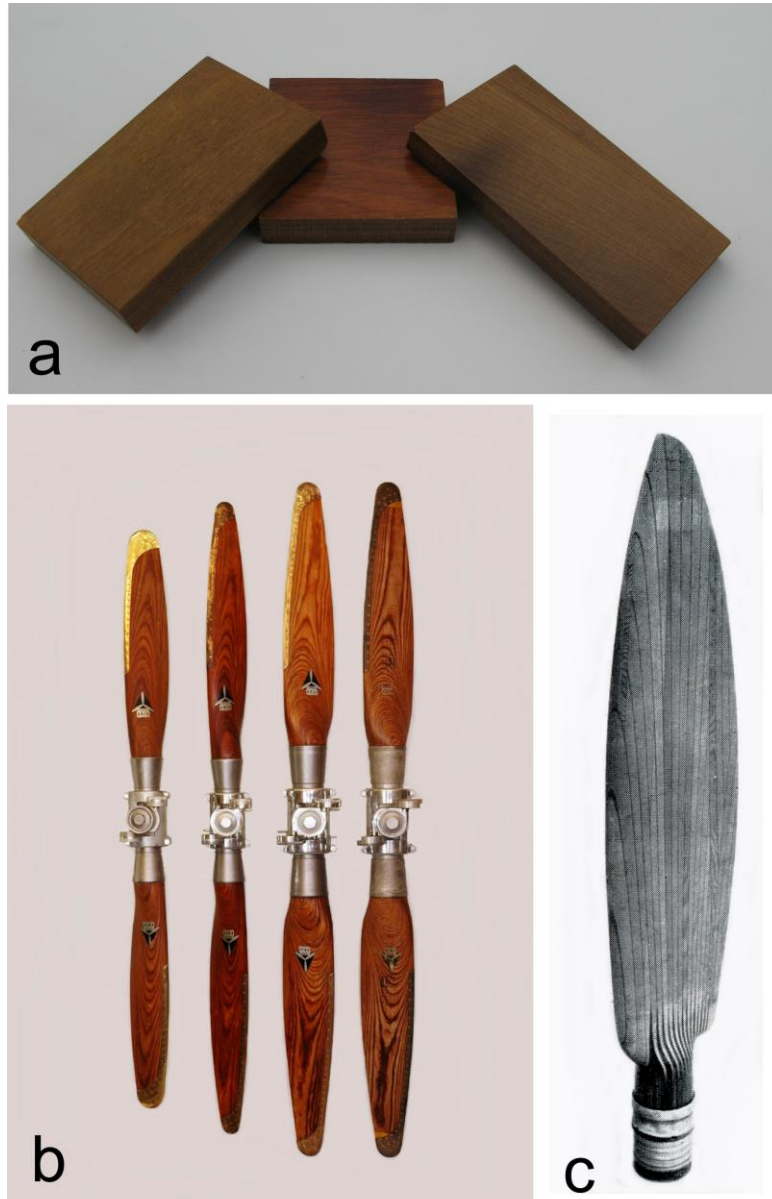


Figure 2.14 Examples of wood products made from PF resin treated wood: a, Samples made from PF resin treated wood, from left to right: PF impregnated laminated composite; PF impregnated compressed composite (Compreg); PF impregnated wood (Impreg). b, Engineering and Research Corporation (ERCO) variable pitch propellers made from Compreg. c, Variable pitch propeller made in Australia from Compreg (Boas 1947)

Table 2.2 Companies manufacturing Compreg for different end-uses

Company's name	Wood species and products	Location
Rutland Plywood Corporation	Hardwood species. Dymondwood® for archery stock, pistol grips, crafts, knitting needles, ornaments, pens, brushes, awards, frames, billiard tables, pool cues and musical instruments	Rutland Vermont, U.S.A
Nittax Corporation	COMPLITE. Knife handles, door handles, decorative usage, LNG/LPG tank load bearing supports and many industrial parts	Tokyo, Japan
Fabryka Sklejka-Pisz. S.A.	Hardwood (beech, birch). Machined Compreg. Self-lubricating Compreg. Aircraft Compreg "Delta"	Pisz, Poland/EU
Tawakkal Wood Products Private Limited	Compreg board. Compreg board for floor, film faced densified shuttering plates, high density resin treated laminate board, match plates for foundry applications and wood for electrical insulation applications	Mumbai, Maharashtra, India

The manufacture of Compreg involves: (1) impregnation. Wood is impregnated with PF resin using any of the processes used to make Impreg. The amount of resin used depends on strength requirement of the final products. Solutions containing 25-30% PF resin based on the oven dry weight of the untreated wood, and uniform distribution of the resin are required to maximize dimensional stability (Seborg et al. 1962); (2) Drying. Treated wood is dried at around 60 °C, until the moisture content of the treated wood is reduced to 6-8%. The drying temperature and moisture content depended on wood species. For less compressible species such as birch, the drying temperature was 77 °C and the final moisture content was 2%. Milder drying conditions were needed to obtain a product with good mechanical strength properties (Burr and Stamm 1956); (3) Curing and compressing. High temperature and pressure were applied to wood veneers to cure and compress the wood. The curing temperature used was around 150 °C. The pressure used depended on the resin, volatile contents and distribution of resin in wood veneers. If wood was compressed to a specific gravity of 1.3 to 1.4, the pressure used was around 6.89 x

10^3 to 8.27×10^3 kPa. The pressing time was around 30 to 40 minutes (Seborg *et al.* 1962; Rowell and Konkol 1987).

The properties of Compreg are affected by the wood's moisture content before and at the time of testing, the drying condition, curing temperature and time, resin type and content, and the specific gravity of the final product (Millett *et al.* 1943). The pressures used to compress the resin-treated wood depended on the properties and distribution of resin and wood species (Rowell and Konkol 1987). If the resin content of the wood exceeded 30%, resin exuded from the glued laminated veneers (Stamm and Seborg 1962). However, for less compressible species, additional resin improved the bonding of laminates (Burr and Stamm 1956).

Compreg required high pressures during the pressing of resin impregnated veneers, which made it difficult to make. Stamm and Seborg (1962) found that Impreg could be compressed using lower pressures than dry, untreated wood because PF resin plasticized wood cell walls. Shams *et al.* (2004) investigated the deformation behaviour of PF resin treated wood during compression and found that the collapse of cell walls was strain dependent. Pressing pressure can be reduced by using an appropriate combination of pressure and steaming. Shams *et al.* (2006) reduced the pressures required to compress Japanese cedar treated with PF resin by using a steam pre-treatment step during the manufacture of Compreg. They suggested that the steam pre-treatment caused partial hydrolysis of hemicelluloses, which increased the compressibility of the wood.

2.5.4.3 Kyushu Mokuzai Process

Kyushu Mokuzai in Japan worked on a method for treating wood with PF resin (<http://www.kyumoku.co.jp>). Their research showed that treatment of wood with a low

molecular weight water-soluble PF resin improved wood's decay, termite and weathering resistance and increased its dimensional stability and mechanical strength. In addition, treated wood was easy to paint/coat, and maintain. The wood could be recycled and hence it was environmentally friendly. Subsequently, PF resin treated wood was commercialized in Japan by the Kyushu Mokuzai Company in 2003. The treated wood has been used in buildings and in outdoor landscape applications such as benches, decks and arbours (**Figures 2.15 and 2.16**).

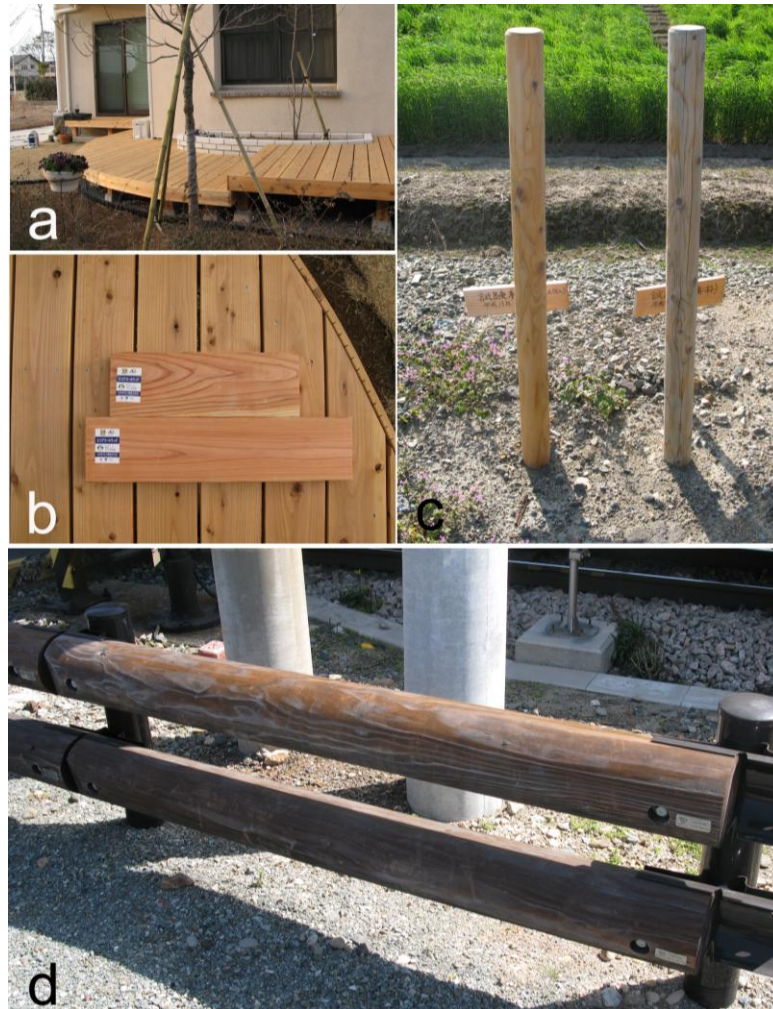


Figure 2.15 Appearance of timber treated with PF resin: a, Small deck made from Japanese cedar treated with PF resin; b, Close-up of the same deck as in a, and two small unweathered samples of Japanese cedar treated with PF resin. Note that weathering has changed the color of the PF treated Japanese cedar from a reddish brown to a tan-brown; c, Post treated with PF resin (left) and an untreated post (right). Note that the untreated post has checked badly and has weathered to a grey color. The PF resin treated post has no checks and is a pleasant tan color; d, PF resin treated poles used as roadside barriers. The poles have retained their brown color in earlywood

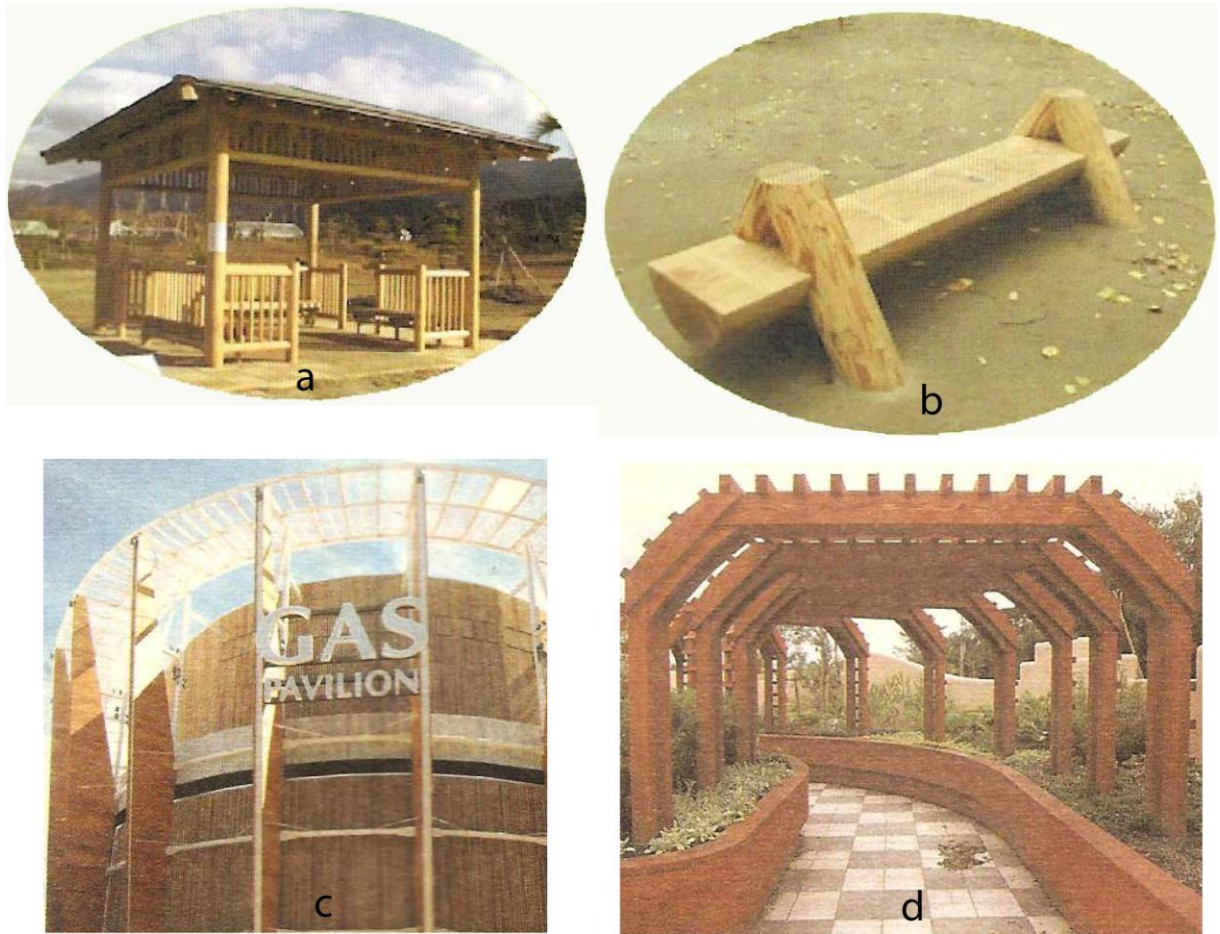


Figure 2.16 End-uses of wood treated with PF resin in Japan (a, Arbour; b, Bench; c, Building; d, Pergola) (Mokuzai Gakkaishi. [http: // www.kyumoku.co.jp](http://www.kyumoku.co.jp))

The process used to treat wood with PF resin in Japan is different from that used to make Impreg. Japanese cedar is impregnated with chilled PF resin at a temperature of 5 °C in a pressure cylinder. It is important for resin to evenly penetrate wood cell walls, but complete penetration of Japanese cedar is not obtained. The treated wood is air dried at room temperature, and cured at a maximum temperature of 130 °C. Finally the treated wood is conditioned for several days (**Figure 2.17**).



Figure 2.17 Process used to manufacture phenol formaldehyde impregnated wood at Kyushu Mokuzai
a, Pressure treatment cylinder and tank in back-ground (left) used to store chilled PF resin; b, Inside of pressure treatment cylinder; c, Charge of timber after treatment with PF resin. Note the excess PF resin solution on treated Japanese cedar; d, Penetration of PF resin into Japanese cedar timber; e, Kilns used to cure the timber treated with PF resin; f, PF-treated timber air drying after treatment (Mokuzai Gakkaishi. [http:// www.kyumoku.co.jp](http://www.kyumoku.co.jp))

2.5.5 Improving Properties of PF Resin Using Additives

Different chemicals are sometimes added to PF resin to impart some special characteristics, change penetration properties, increase durability and reduce cost (Marra 1992). The addition of

a drying oil imparts flexibility, air-drying and film-forming properties to coatings containing PF resin (Martin 1956). Hydrophobic agents like paraffin wax are added to PF resin to reduce absorption of liquid water by particleboard and OSB. Likewise, fungicides and insecticides are added to improve resistance to biodeterioration. Flame retardant materials are added to increase fire resistance (Knop and Scheib 1979). Additives like coconut shell flour have been used to reduce excessive penetration and brittleness of adhesive joints in exterior grades of plywood. They change wetting characteristics and help to produce more uniform joints. They also reduce cost (Knop and Scheib 1979). Wood flour, nutshell flour, asbestos, mineral flour and lubricants were used to reduce water absorption, shrinkage during cure, improve mechanical strength, fluidity, surface quality, chemical, thermal and electrical resistance, and to reduce costs of molding powders containing PF resin (Knop and Scheib 1979). Anikin *et al.* (1992) used C, Si, B, Cu, Zr, Ti, Ta, Hf and ZrB₂ additives to modify PF resins and increase their heat resistance. However, adequate bonding strength was not achieved below 600°C because PF resins are carbonized at 300–700°C. Jiang *et al.* (2007) modified PF resin using boron carbide (B₄C). Their results showed that B₄C effectively improved the high temperature performance of PF resin.

2.6 Conclusions

Optical confocal profilometry is an advanced technology capable of measuring the erosion of materials. Firstly, it is easier and faster to use than optical microscopy and it is less labour intensive. Secondly, it provides accurate and reliable measurements and powerful analytical capabilities for measurement of surface roughness, erosion depth and volume taken of materials (www.altimet.fr). Confocal profilometry has been used to quantify the surface erosion of metals, ceramics and human tooth enamel, but not wood.

Water-soluble low molecular weight phenol formaldehyde resins have potential to be developed as a practical treatment to photostabilize wood. Firstly, they can easily penetrate the wood where they can deposit aromatic groups in wood cell walls. Then they can form secondary chemical bonds with cell wall components and create a highly cross-linked structure when cured (Seborg *et al.* 1962; Sudiyani *et al.* 1999; Furuno *et al.* 2004; Kamke and Lee 2007; Wan and Kim 2008). Secondly, PF resin can improve the dimensional stability, biological resistance, and many other properties of wood (Stamm and Seborg 1939; Stamm and Seborg 1941; Seborg *et al.* 1962). PF resin can also restrict discoloration and cracking of wood during weathering (Stamm and Baechler 1960; Sudiyani *et al.* 1999; Imamura 2007). Finally, PF resin is easily applied to wood. It is cost-effective and non-toxic after curing (Stamm and Baechler 1960; Stamm 1975). A large amount of research has been done to examine the ability of low molecular weight PF resins to improve the dimensional stability, mechanical properties and biological resistance of wood. In comparison, relatively little work has been carried out on the weathering resistance and photostability of wood modified with PF resin.

CHAPTER 3: USE OF CONFOCAL PROFILOMETRY TO QUANTIFY THE EROSION OF UNTREATED WOOD DURING ARTIFICIAL ACCELERATED WEATHERING AND NATURAL WEATHERING

3.1 Introduction

The methods that have been used to screen chemicals for their ability to prevent the photodegradation of wood have evolved, in part, from those that are used to characterize photodegraded polymers. The latter involve: assessing losses in mechanical properties (tensile, impact, elasticity), or changes in physical properties (weight and colour) or surface chemistry of stabilized and unstabilized polymers exposed to artificial or natural weathering (Davis and Sims 1983). Hence, a common method of screening photoprotective treatments for wood is assessing the loss in weight and tensile strength of treated wood veneers exposed to natural or artificial accelerated weathering (Evans 1988; Evans and Schmalzl 1989; Kiguchi and Evans 1998; Evans *et al.* 2002; Schmalzl and Evans 2003; Jebrane *et al.* 2009). Weight and tensile strength losses of thin wood veneers during weathering provide a “rapid, consistent and reliable method of assessing weathering” (Derbyshire *et al.* 1995). However, thin wood veneers may not respond to photodegradation in the same way as solid wood substrates do, as has been found for polymer films versus bulk polymer substrates (Davis and Sims 1983; Nepotchatykh and Power 2000).

These limitations of the thin strip (veneers) technique can be overcome by measuring the erosion of solid wood substrates during exterior exposure using optical microscopy (Black and Mraz 1974; Feist and Mraz 1978; Williams 1983; Williams *et al.* 2001 a, b, c, d). However, there are some disadvantages of this method, as pointed out in Chapter 2. The limitations of optical microscopy for measuring the erosion of wood during weathering led to interest in using laser-scanning profilometry to measure the erosion of weathered wood (Arnold *et al.* 1992). This

method of measuring the erosion of wood also has its limitations. An alternative to laser scanning profilometry is optical confocal profilometry, as pointed out in Chapter 2. Optical confocal profilometry has not been used to quantify the erosion of weathered wood, even though it has been used to measure the erosion of metals, ceramics and human tooth enamel (Wilken *et al.* 2003; Theocharopoulos *et al.* 2010).

The erosion of untreated wood during natural weathering occurs slowly, approximately 2 to 5 mm per century for hardwoods, and 5 to 10 mm per century for softwoods (Sell and Feist 1986). The rate of erosion of wood can be increased five to twenty times by exposing wood specimens to artificial accelerated weathering (Arnold *et al.* 1991), and by selecting low density species, which erode faster than higher density species (Sell and Feist 1986). Previous studies of the erosion of untreated wood during accelerated weathering have exposed wood for a minimum of 600 hours of artificial accelerated weathering before using optical microscopy to measure the erosion of wood (Sell and Feist 1986, Arnold *et al.* 1991, Williams *et al.* 2001d). Untreated woods such as western red cedar are used outdoors for siding, fences and shingles. Hence, there is interest in the resistance of untreated wood species (western red cedar) to weathering. In this chapter, I hypothesize that exposure of a low density wood species to artificial weathering and the use of optical confocal profilometry will make it possible to rapidly and accurately measure the erosion of wood during weathering and shorten the exposure time required to produce reproducible differences in the erosion of masked and unmasked wood subjected to weathering. I test this hypothesis by exposing the low density wood species western red cedar to artificial weathering in xenon-arc and QUV weatherometers for 100, 250, 500 and 1000 hours, and quantifying erosion of wood using optical confocal profilometry. I also exposed specimens to natural weathering for 1000, 2500, 5000 and 10000 hours and examined the relationship between

the erosion of wood subjected to artificial weathering and natural weathering. Specimens exposed to both artificial and natural weathering contained metal masks with unmasked areas of different sizes. The effect of this parameter on the erosion of wood exposed to artificial and natural weathering was also quantified.

3.2 Materials and Methods

3.2.1 Experimental Design and Statistical Analyses

A factorial experiment was designed to examine the effect of three fixed factors on the erosion of wood during artificial weathering: (1) Weatherometer type (xenon-arc or QUV); (2) Exposure time (separate samples exposed to artificial accelerated weathering for 100, 250, 500 and 1000 hours); (3) Size of unmasked area (1, 31.7 mm²; 2, 126.6 mm²; 3, 284.9 mm²; 4, 506 mm²) in wood samples.

Specimens cut from eight different western red cedar boards provided replication at the higher level. Each board was subdivided into two samples and each sample was randomly allocated to weatherometer type. Each of these samples was cut into four specimens, which were randomly allocated to the four different exposure times. Finally, each specimen was overlaid with a rectangular metal mask containing four different sized holes, which were randomly allocated to the four quadrants of the mask (**Figure 3.1**). The resulting split-split plot design accounted for random variation at three levels: Variation between boards and samples and variation between and within specimens. Analysis of variance was used to examine the effect of fixed and random factors on the response variables: average depth of erosion and mass of wood removed from weathered wood. Statistical analysis was done using Genstat (version 12) (VSN International 2009). Before the final analysis, diagnostic checks were performed to determine whether data conformed to the underlying assumptions of analysis of variance, i.e., normality

with constant variance. Statistically significant results ($p < 0.05$) are presented graphically and least significant difference (lsd) bars ($p < 0.05$) or 95% confidence intervals can be used to compare differences between individual means.

Another experiment was performed to examine the erosion of wood exposed to natural weathering. This experiment examined the effects of exposure time (1000, 2500, 5000 and 10000 hours) and size of unmasked area (as above) on the response variables (as above). Allocation of materials to fixed factors was similar to that described above. Analysis of variance for a split-plot design was used to examine the effects of exposure time and mask area on the erosion of wood during natural weathering. Statistical analysis and presentation of results are similar to those described above.

3.2.2 Preparation of Wood Samples and Metal Masks

Western red cedar was chosen for its low density. Eight different wooden boards measuring 25.4 mm x 203 mm x 2438 mm were used for the experiment. Care was taken to ensure that sample material came from different trees by selecting boards with different densities and rates of growth (**Table 3.1**).

Table 3.1 Density and growth rate of parent western red cedar boards used to prepare specimens that were exposed to artificial accelerated weathering or natural weathering

Wood board	Growth rings/cm	Density (g/cm ³)
1	2.6	0.29
2	3.0	0.29
3	4.5	0.35
4	4.2	0.27
5	2.7	0.31
6	4.6	0.30
7	4.6	0.28
8	4.5	0.31
Average	3.8	0.30

Each board was planed using a Martin T44 planer and cut into three samples, which were allocated to the two different artificial weatherometers or natural weathering (as above). Each of these samples was cut into four specimens measuring 158.6 mm x 63.45 mm x 6.345 mm, which were exposed to weathering for four different time periods. The specimens were conditioned in a constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for 2 months before they were exposed to artificial weathering, and for 6 months before they were exposed to natural weathering.

Sixteen gauge (0.795 mm thick) stainless steel metal sheets were cut into rectangular shaped masks measuring 95.2 mm x 63.45 mm. Four circular holes measuring: 1, 31.7 mm²; 2, 126.6 mm²; 3, 284.9 mm²; 4, 506 mm² were drilled into each metal mask using a drill press.

The different sized holes were randomly allocated to the different quadrants of the metal mask. The metal masks were fixed to the wood specimen using stainless steel screws (**Figure 3.1**).

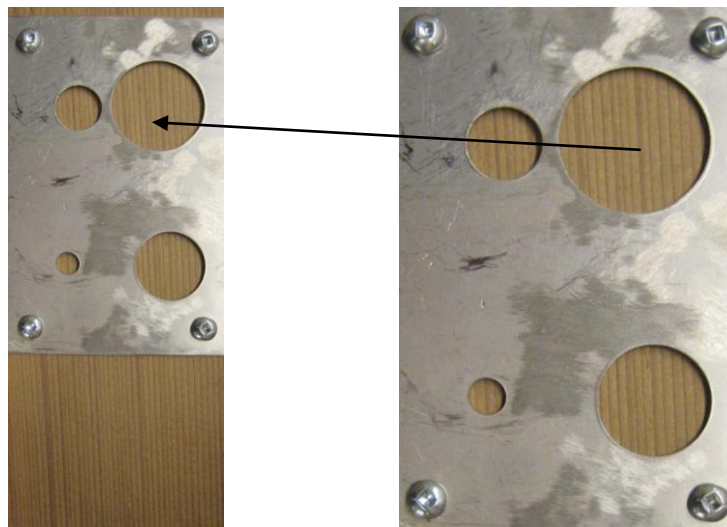


Figure 3.1 Metal mask screwed to the surface of a western red cedar specimen (left) and a close-up view of the unmasked areas (right). The holes in the mask provide unmasked areas that are susceptible to erosion during artificial accelerated weathering or natural weathering

3.2.3 Weathering

3.2.3.1 Artificial Weathering

Thirty-two masked samples were randomly placed in a Ci65 Atlas weatherometer and exposed to UV radiation produced by a water-cooled 6500-Watt xenon-arc lamp (irradiance 0.35w/m^2) (**Figure 3.2**). A similar number of masked samples were randomly placed in a QUV weatherometer (Q-Panel Lab Products, QUV spray model) and exposed to UV radiation (295 to 370 nm) generated by 40 Watt UV fluorescent tubes (irradiance 0.68w/m^2) (**Figure 3.3**). The weathering cycle employed by the Xenon-arc and QUV devices both exposed specimens to 102 minutes of light and 18 minutes of water spray (**Table 3.2**). These cycles were repeated for the duration of the weathering tests. The chamber temperature in both weathering devices was 60°C .

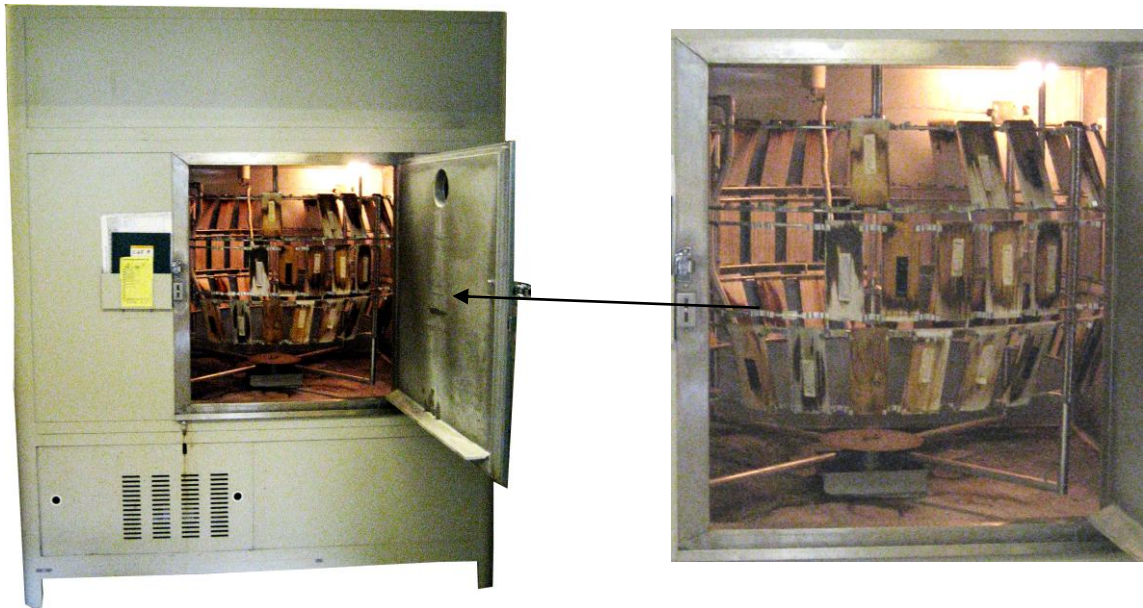


Figure 3.2 Xenon-arc weatherometer (left) and a close-up view of xenon-arc chamber (right) used to accelerate the weathering of masked western red cedar specimens

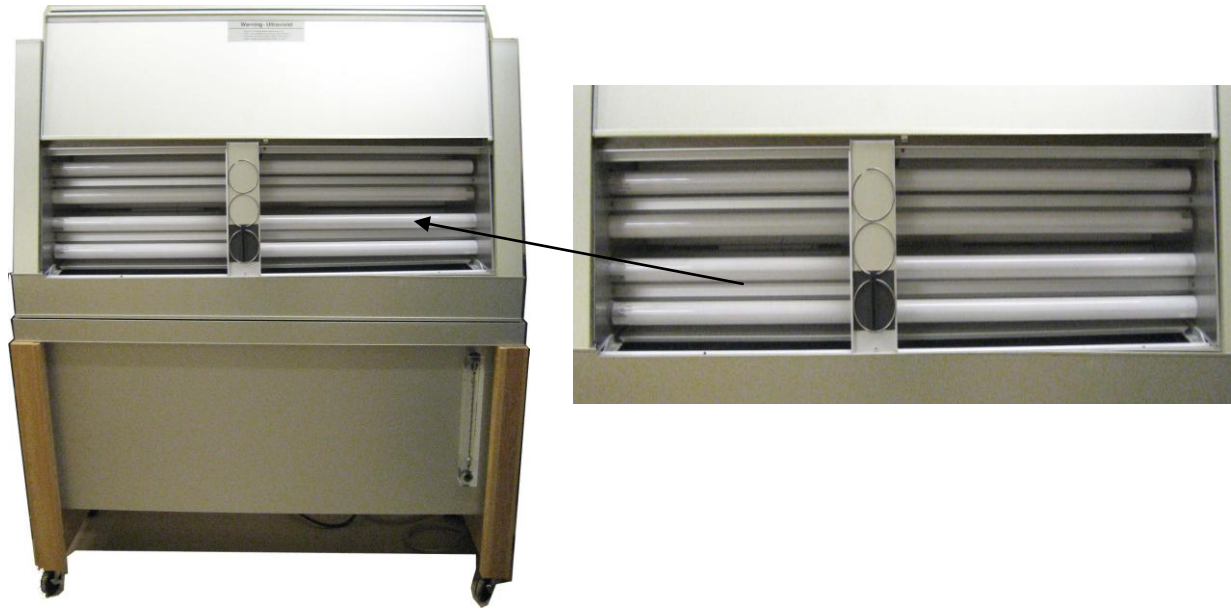


Figure 3.3 QUV fluorescent weatherometer (left) and a close-up view of fluorescent lamps (right) used to accelerate the weathering of masked western red cedar specimens

Table 3.2 Weathering cycles employed by the QUV and xenon-arc weatherometers

Light source	Temperature of chamber (°C)	Light exposure (min)	Water-spray (min)
QUV (fluorescent lamps)	60	102	18
Xenon-arc (xenon-arc lamp)	60	102	18

3.2.3.2 Natural Weathering

Thirty-two masked specimens (as above) were randomly placed on a weathering rack (**Figure 3.4**) at an inclination of 45° facing south. Samples were exposed to natural weathering from April 2nd 2009 to June 2nd 2010 at UBC's Vancouver campus (Latitude: 49°11'42.000" N; Longitude: 123°10'55.000"; Elevation: 04.30 m). The meteorological conditions during the natural weathering trial are shown in **Table 3.3**. Eight samples were removed from the weathering rack for erosion measurements after each exposure time (1000, 2500, 5000 and 10000 hours).



Figure 3.4 Rack containing the masked western red cedar specimens that were exposed to natural weathering

Table 3.3 Meteorological conditions at the site in Vancouver where masked western red cedar specimens were exposed to natural weathering (April 2009 to June 2010) (Source: Environment Canada. <http://www.weatheroffice.gc.ca>)

Month	Mean Max Temp (°C)	Mean Temp (°C)	Mean Min Temp (°C)	Highest Temp (°C)	Lowest Temp (°C)	Total Snow (cm)	Total Precip (mm)	Total Sunshine (h/m)	Mean Sunshine (h/d)
Apr (09)	13.0	9.1	5.1	19.4	0.6	0.0	77.6	227.9	7.6
May	16.9	12.7	8.4	26.1	4.3	0.0	71.8	267.5	8.6
Jun	21.7	17.4	13.0	25.9	9.3	0.0	10.8	302.1	10.1
Jul	24.1	19.6	15.0	34.4	10.6	0.0	20.0	330.2	10.7
Aug	22.0	18.0	14.0	26.7	10.4	0.0	26.6	265.7	8.6
Sep	19.8	15.7	11.6	27.8	5.0	0.0	65.6	220.1	7.3
Oct	13.4	10.0	6.7	17.6	0.4	0.0	168.0	115.6	3.7
Nov	9.8	7.1	4.4	13.8	-0.4	0.0	282.0	41.6	1.4
Dec	5.1	2.1	-0.8	10.3	-6.3	2.4	77.4	55.4	1.8
Jan (10)	9.9	7.2	4.5	14.1	-2.7	0.0	182.8	36.4	1.2
Feb	10.3	7.1	3.9	13.1	-0.4	0.0	102.2	101.9	3.6
Mar	11.1	7.7	4.2	16.4	0.2	0.0	108.2	128.3	4.1
Apr	13.1	9.6	6.0	20.4	1.0	0.0	88.0	156.6	5.2
May	15.8	12.0	8.2	21.1	2.6	0.0	54.2	221.8	7.2
Ave.	14.7	11.1	7.4	20.5	2.7	0.2	95.4	176.5	5.8

3.2.4 Quantifying Erosion of Wood Using Optical Confocal Profilometry

The erosion of specimens during artificial accelerated weathering and natural weathering was measured using a non-contact confocal white light profilometer (AltiSurf® 500). The unmasked areas that were exposed to accelerated or natural weathering and the areas immediately adjacent to the unmasked areas were scanned using a 3 mm (3000 nm to 92 nm) probe. The following measurement parameters were used: gauge resolution, 0.333 nm; spacing between measurement points, 12 µm x 12 µm; and scan speed, 3 mm/s. The times taken to scan the four different sized areas on each mask were: (1) 1 h, 15 m, 45 s; (2) 2 h, 55 m, 50 s; (3) 5 h, 43 m, 50 s; (4) 8 h, 49 m, 37 s. The software PaperMap was used to calculate the average depth of erosion (mm), and volume of material removed from specimens (mm³). The same software was used to generate topographical images of eroded areas. The erosion of wood during weathering was also expressed as the mass loss of wood from unmasked areas. Mass losses were calculated as follows: $\text{Mass loss (mg/mm}^2\text{)} = \text{density (mg/mm}^3\text{)} \times \text{volume taken (mm}^3\text{)}/\text{exposure area (mm}^2\text{)}$.

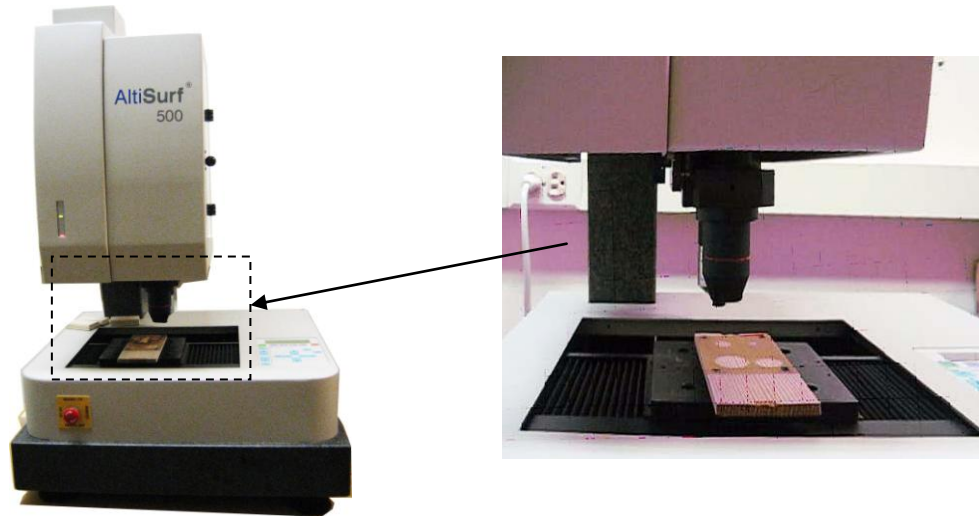


Figure 3.5 Optical confocal profilometer (left) and close-up of the 3 mm probe and a weathered western red cedar specimen on the x-y table of the profilometer (right)

3.2.5 SEM

A RYOBI® BS 902 band saw and single-edged razor blades (Blu-strike E2010) were used to cut specimens, measuring 4 mm x 3 mm x 2 mm, from an unweathered specimen and from specimens that were exposed to artificial weathering or natural weathering for different periods of time. All the specimens were cut from largest unmasked areas (506 mm²) on samples from board 7. The specimens were attached to 12.5 mm-diameter aluminum stubs using double sided tape and stored in a vacuum desiccator over silica gel for 7 days. They were then sputter coated with a 10 nm layer of gold and the radial surfaces of the specimens were examined using a Cambridge 360 scanning electron microscope (SEM) at an accelerating voltage of 5 kV, or a Zeiss UltraPlus analytical field emission SEM at an accelerating voltage of 15 kV. Secondary electron images were stored as TIFF files.

3.3 Results

3.3.1 Weathering of Wood during Artificial Accelerated Weathering

3.3.1.1 Changes in the Appearance of Specimens

The exposed areas of the western red cedar specimens eroded and changed color during artificial weathering. Specimens exposed to artificial weathering in the QUV device turned a darker brown after 100 and 250 hours exposure. Thereafter the exposed areas became grey. The texture of the exposed areas became rough and the depth of erosion increased with time. Earlywood valleys and latewood ridges created by differential erosion of these tissue types became more obvious with time (**Figure 3.6**). Specimens exposed to artificial weathering in the xenon-arc device became gray after only 100 hours of weathering. Unmasked areas in specimens exposed in the xenon-arc weatherometer became progressively lighter with increasing exposure.

Color changes were more pronounced in specimens exposed in the xenon-arc weatherometer than in those exposed in the QUV weatherometer (Figures 3.6 and 3.7).

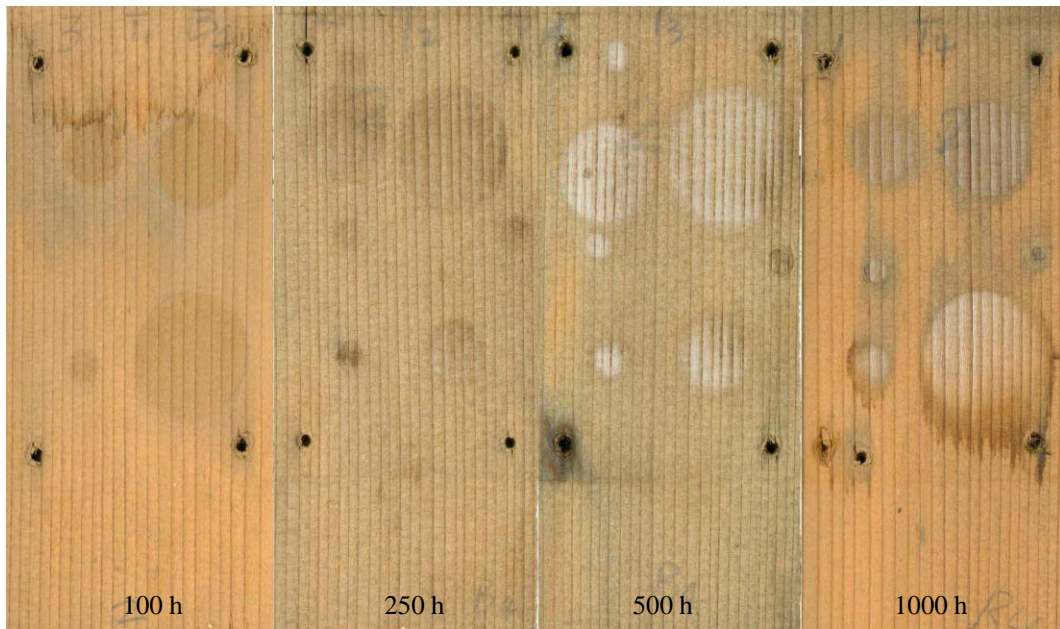


Figure 3.6 Appearance of western red cedar specimens exposed to artificial accelerated weathering in QUV weatherometer for 100, 250, 500 and 1000 hours. Note the differences in colour of the unmasked (circular) areas compared to the masked areas

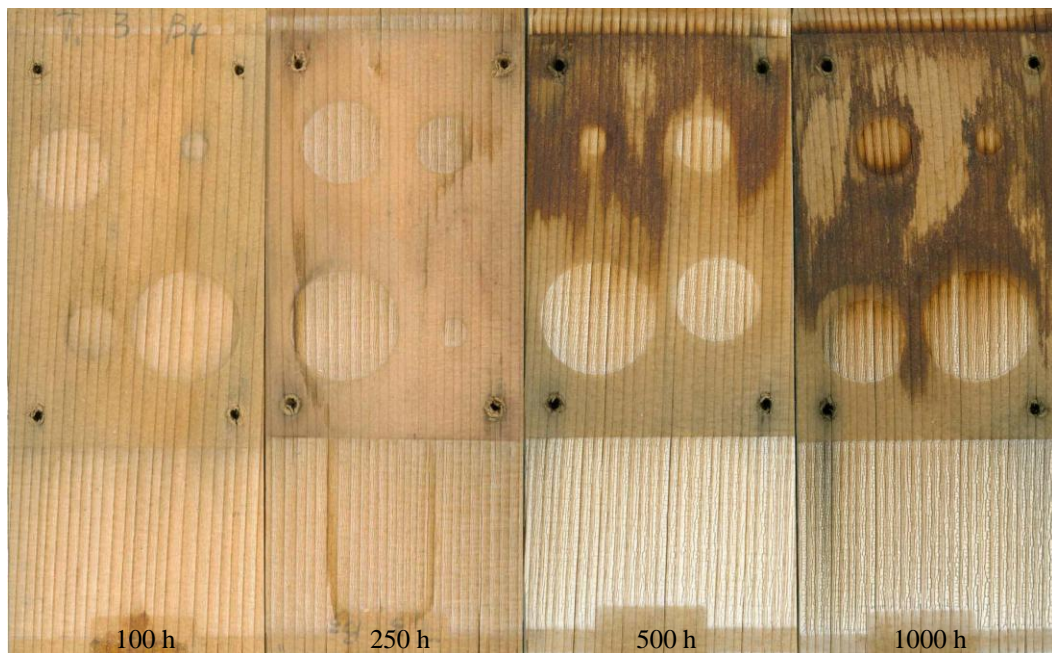


Figure 3.7 Appearance of western red cedar specimens exposed to artificial accelerated weathering in xenon-arc weatherometer for 100, 250, 500 and 1000 hours. Note the differences in colour of the unmasked (circular) areas compared to the masked areas

3.3.1.2 Erosion of Wood

There were highly significant ($p < 0.001$) effects of weatherometer type, exposure time and size of unmasked area on the erosion of western red cedar specimens during artificial accelerated weathering (**Table 3.4**). The interactions of weatherometer type with exposure time and size of unmasked area were also highly significant ($p < 0.001$). There was a highly significant ($p < 0.001$) interaction of exposure time and size of unmasked area on erosion (**Table 3.4**). There was also a highly significant ($p < 0.001$) 3-way interaction of weatherometer type, exposure time and size of unmasked area on mass of wood eroded from specimens during artificial weathering. The interaction of these parameters on the average depth of erosion was also statistically significant ($p = 0.041$) (**Table 3.4**).

Table 3.4 Statistical significance (p-values) of experimental factors on erosion of western red cedar specimens exposed to artificial accelerated weathering

Factor	Parameter	
	Average erosion depth	Average mass loss
Weatherometer type (W)	<0.001	<0.001
Exposure time (T)	<0.001	<0.001
Size of unmasked area (S)	<0.001	<0.001
W x T	<0.001	<0.001
W x S	<0.001	<0.001
T x S	<0.001	<0.001
W x T x S	0.041	<0.001

3.3.1.2.1 Effect of Time and Weatherometer Type on Erosion

The erosion of specimens during artificial accelerated weathering increased with time, as expected. Measurable erosion of specimens occurred after only 100 hours weathering. Specimens exposed in the xenon-arc weatherometer eroded significantly ($p < 0.05$) faster than specimens exposed in the QUV weatherometer. This difference in erosion of specimens exposed in the xenon-arc and QUV weatherometers became more pronounced with increasing exposure

time, which explains why there was a significant ($p < 0.001$) weatherometer x time interaction on average erosion depth and mass loss (Table 3.4; Figures 3.8 and 3.9).

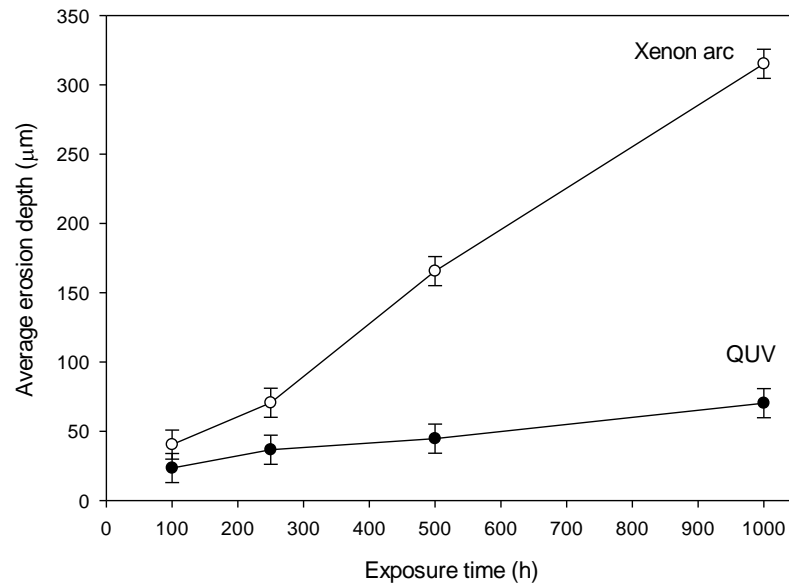


Figure 3.8 Average erosion depth of western red cedar specimens exposed in xenon-arc or QUV weatherometers for 100, 250, 500 and 1000 hours (results averaged across samples containing unmasked areas of different sizes)

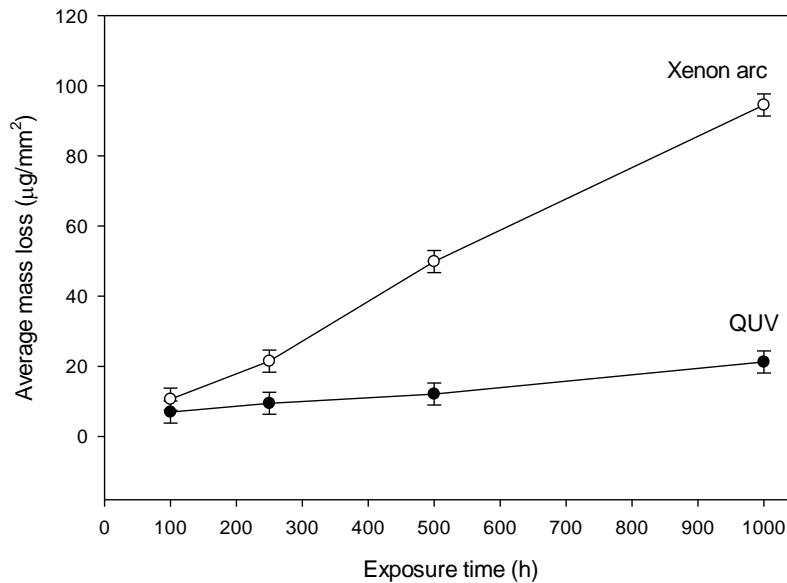


Figure 3.9 Average mass loss of western red cedar specimens exposed in xenon-arc or QUV weatherometers for 100, 250, 500 and 1000 hours (results averaged across samples containing unmasked areas of different sizes)

Two dimensional erosion depth profiles of weathered specimens confirmed that erosion increased with exposure time and they also show that the surface of unmasked area became rougher due to differences in the erosion of earlywood and latewood. In some of the profiles, it is possible to see that there is less erosion at the edges of the unmasked areas (**Figures 3.10 and 3.11**) than that at the center of the unmasked areas.

Three dimensional topographic images of weathered specimens provide graphic evidence of the main trends described above. It is very clear from these images that erosion of western red cedar specimens exposed to accelerated weathering in the xenon-arc weatherometer was more pronounced than that of specimens exposed in the QUV weatherometer (**Figure 3.12**). Erosion increased with time as mentioned above, and differences in the erosion of earlywood and latewood also appear to be more pronounced in specimens exposed in the xenon-arc weatherometer compared to those exposed in the QUV weatherometer.

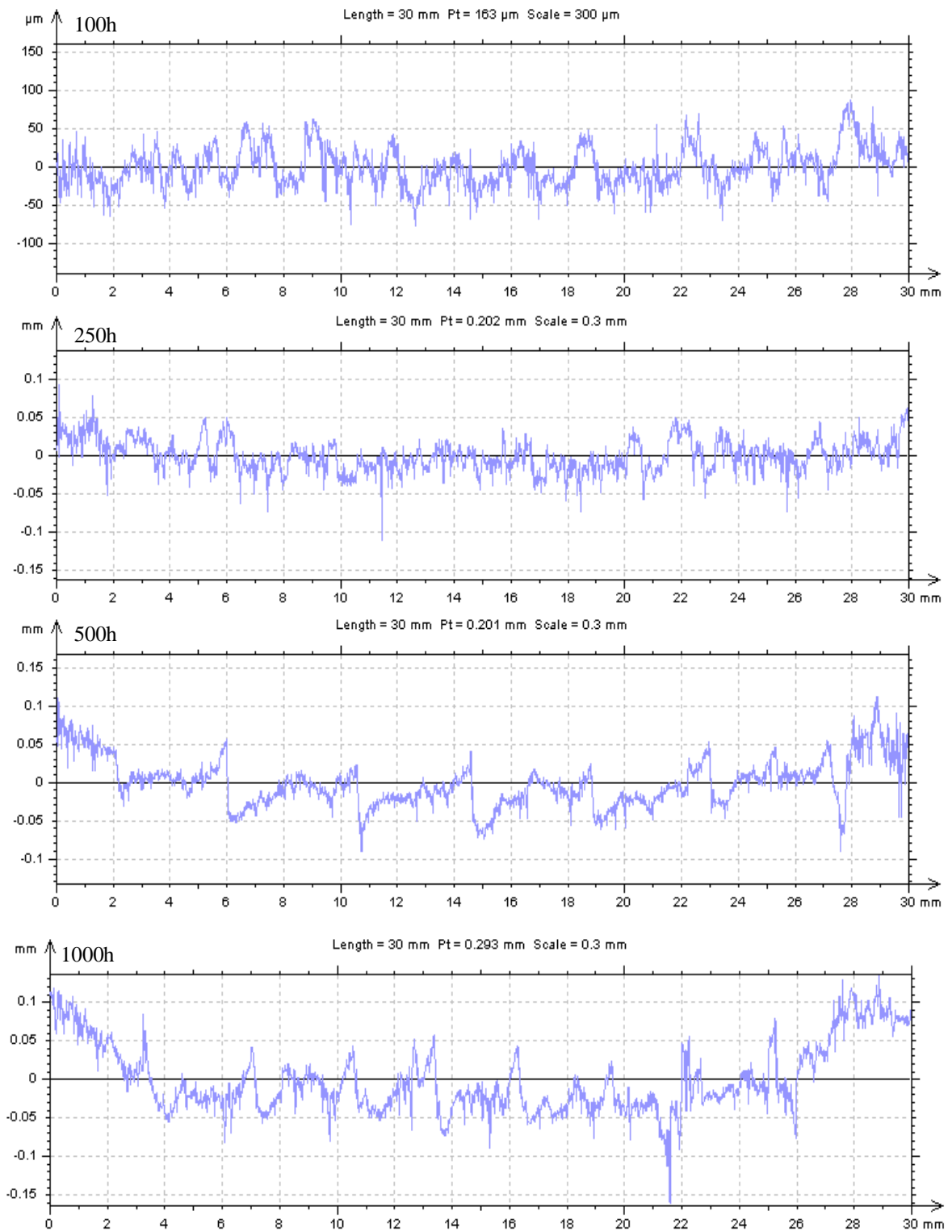


Figure 3.10 Erosion depth profiles of unmasked areas (30 mm in diameter) of western red cedar specimens exposed in a QUV weatherometer for different periods of time

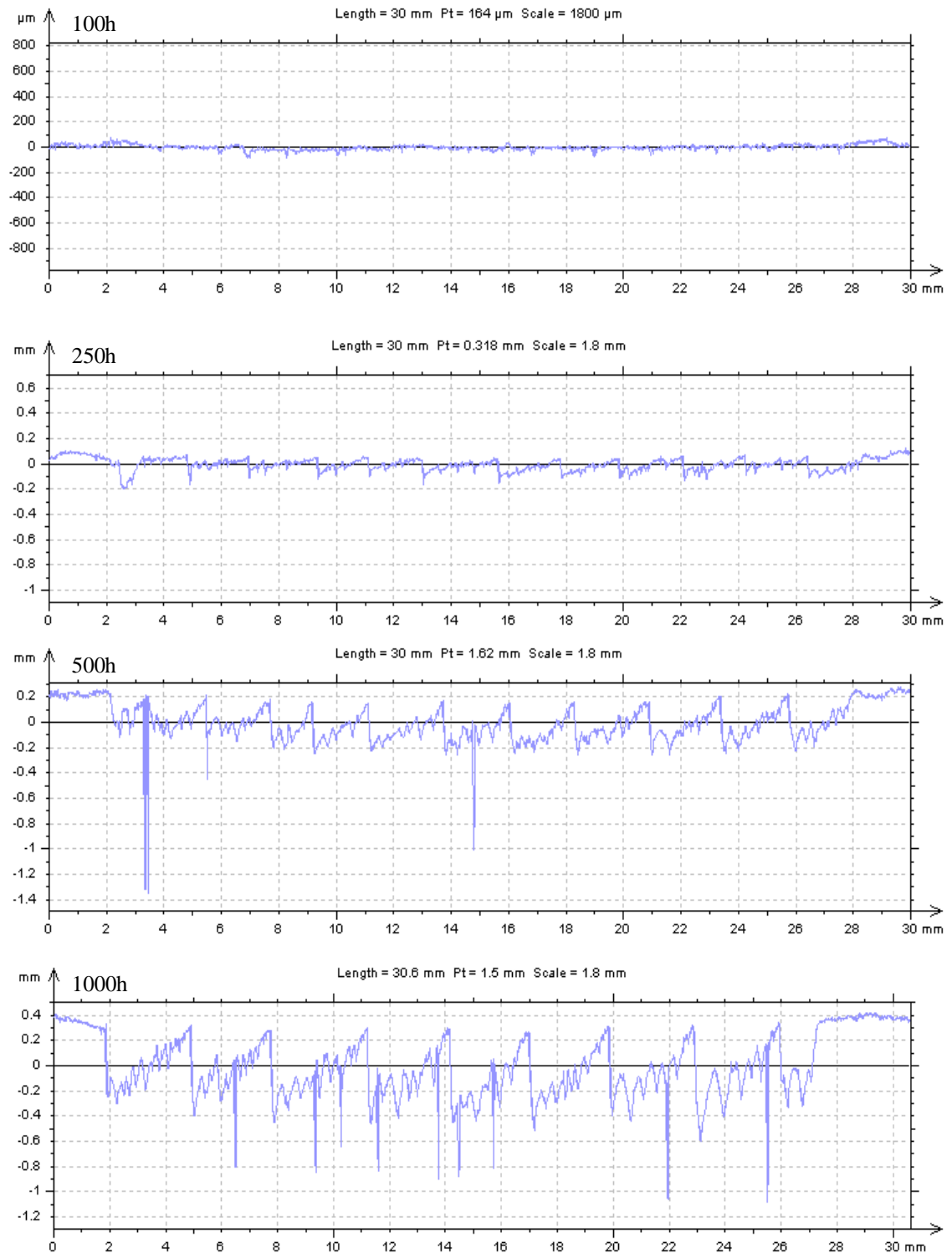


Figure 3.11 Erosion depth profiles of unmasked areas (30 mm in diameter) of western red cedar specimens exposed in a xenon-arc weatherometer for different periods of time

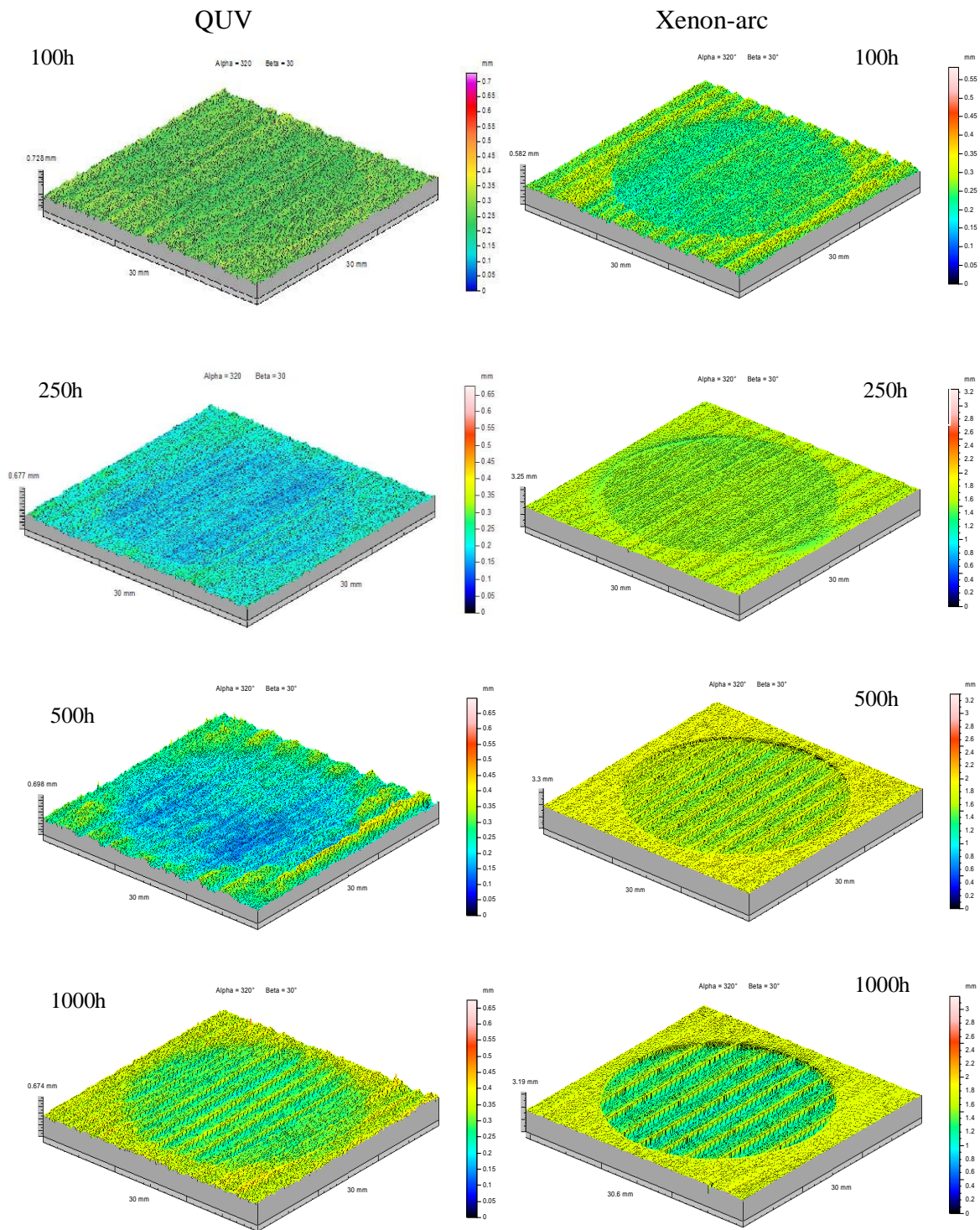


Figure 3.12 Topographical images of unmasked western red cedar specimens exposed to artificial weathering for different periods of time (Left: QUV; Right: Xenon-arc. The size of the unmasked area is 506 mm²)

3.3.1.2.2 Effect of Mask Size on the Erosion of Wood during Artificial Accelerated Weathering

The erosion of samples was also affected by the size of the unmasked area on the stainless steel plates that covered samples during artificial accelerated weathering. This is reflected in the significant effect ($p < 0.001$) of size of unmasked area on erosion of weathered samples, and the significant interactions between size of unmasked area and other experimental parameters (**Table 3.4**). **Figures 3.13** and **3.14** show the average erosion depth and mass loss of unmasked areas in western red cedar specimens exposed to artificial accelerated weathering. The size of the unmasked area and the erosion of wood during artificial accelerated weathering were positively correlated. In other words, the average mass loss or erosion depth was the smallest in the smallest unmasked area of 31.7 mm^2 and increased as the unmasked area increased in size from 126.6 mm^2 , 284.9 mm^2 to 506 mm^2 for all exposure times. However, the increase in erosion of the smallest unmasked areas differed from those of the two largest areas. This trend explains the significant interaction of time x size of unmasked area on erosion (**Table 3.4**).

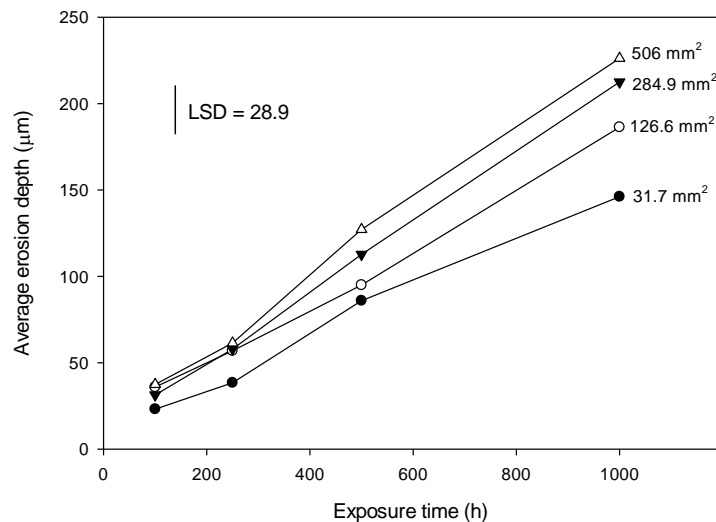


Figure 3.13 Average erosion depth of unmasked areas in western red cedar specimens exposed to artificial accelerated weathering for 100, 250, 500 and 1000 hours (results averaged across samples exposed to weathering in xenon-arc and QUV weatherometers)

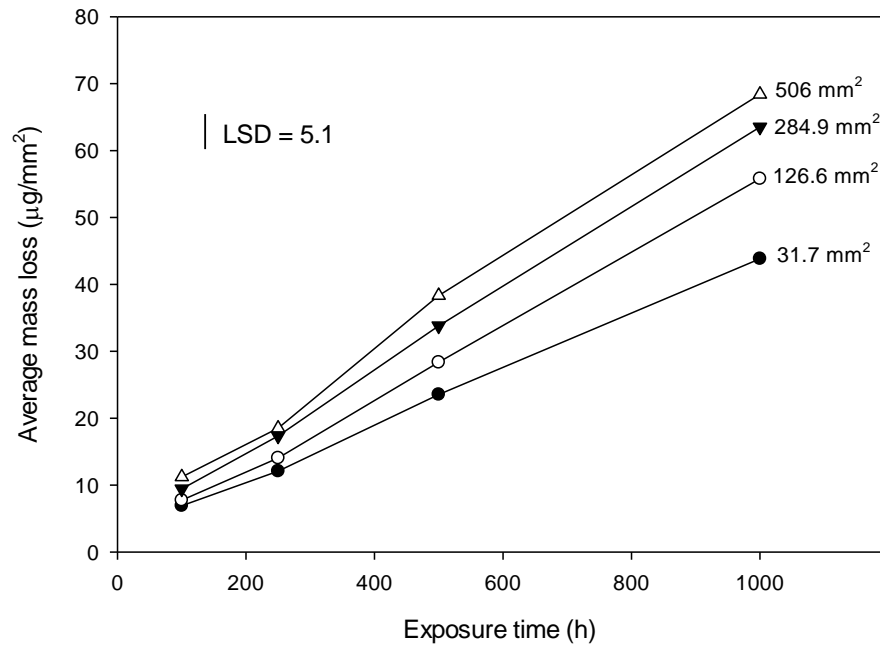


Figure 3.14 Average mass loss of unmasked areas in western red cedar specimens exposed to artificial accelerated weathering for 100, 250, 500 and 1000 hours (results averaged across samples exposed to weathering in xenon-arc and QUV weatherometers)

Comparing **Figures 3.13** and **3.14**, it is clear that the mass loss parameter is better than erosion depth at differentiating between the erosion of wood in the different sized unmasked areas that were exposed to artificial weathering.

3.3.1.3 Micro-structural Changes

SEM images of specimens exposed to artificial weathering in the QUV and Xenon-arc devices show changes to the wood's microstructure. Microstructural changes become more pronounced with increasing exposure time, and they are also more pronounced in earlywood than in latewood. Specimens exposed in the Xenon-arc weatherometer show more severe microstructural changes than those of specimens exposed in the QUV weatherometer.

Figures 3.15 to **3.19** show the micro-structural changes in specimens exposed in the QUV weatherometer for different periods of time. **Figure 3.15** shows that the texture of the western

red cedar specimen exposed in the QUV weatherometer became rough, and the apertures of some bordered pits checked and became larger. Large longitudinal checks formed after specimens were exposed in the QUV weatherometer for 100 hours.

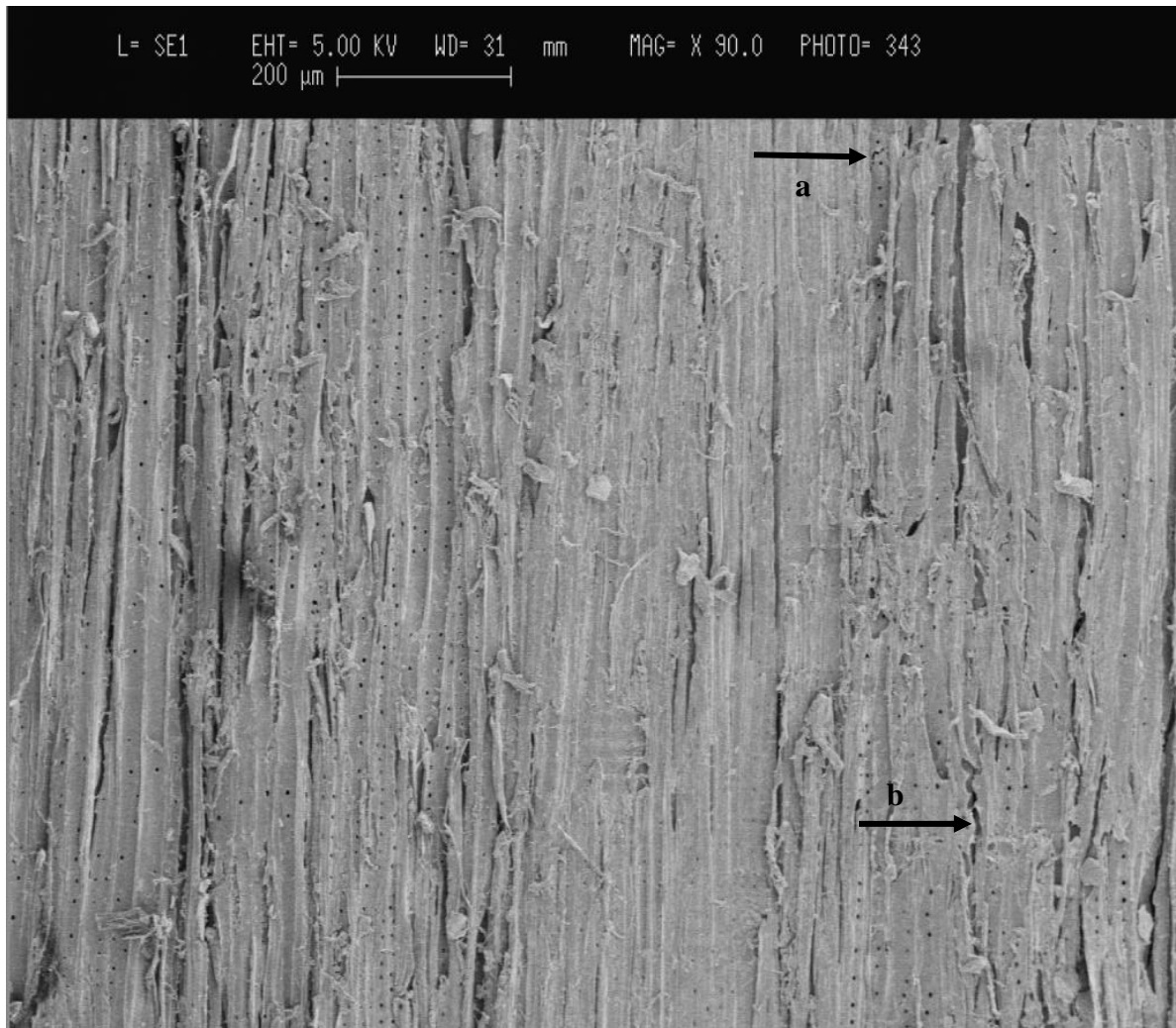


Figure 3.15 Micro-structural changes at the surface of a western red cedar specimen exposed in a QUV weatherometer for 100 hours (a = Microchecking and enlargement of the aperture of a bordered pit; b = Longitudinal check)

After 250 hours of exposure in the QUV device, the apertures of greater numbers of bordered pits became larger. Checks formed in the walls of earlywood tracheids and rays were degraded (**Figure 3.16**).

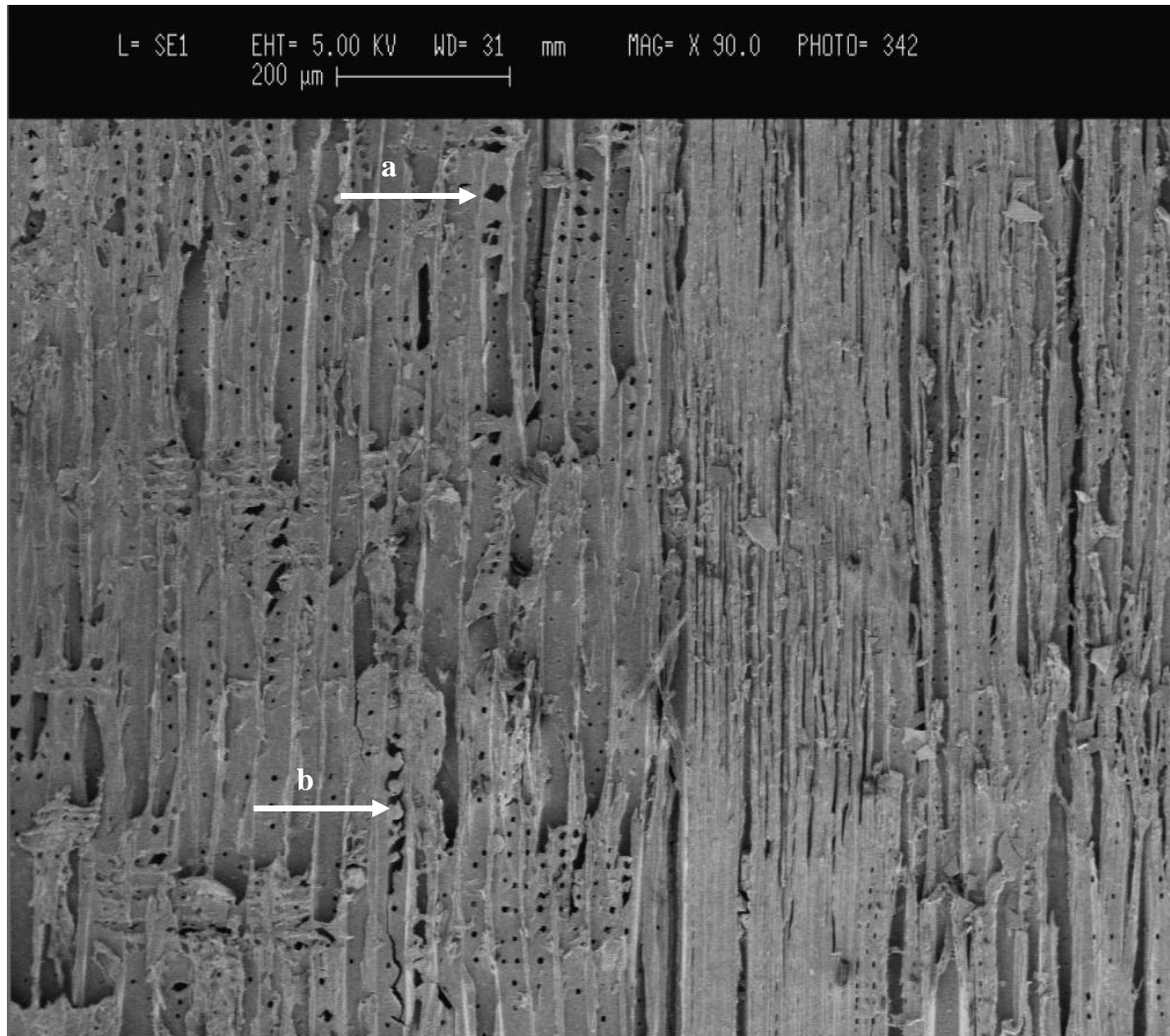


Figure 3.16 Micro-structural changes at the surface of a western red cedar specimen exposed in a QUV weatherometer for 250 hours (a = Enlargement of the aperture of a bordered pit; b = Longitudinal check in earlywood resulting from the enlargement of microcheck in bordered pits)

Vertical checks became more numerous in earlywood and latewood with increasing exposure. Horizontal checks formed in earlywood, but not latewood after western red cedar specimens were exposed to 1000 hours of weathering in QUV weatherometer (**Figures 3.17** and **3.18**).

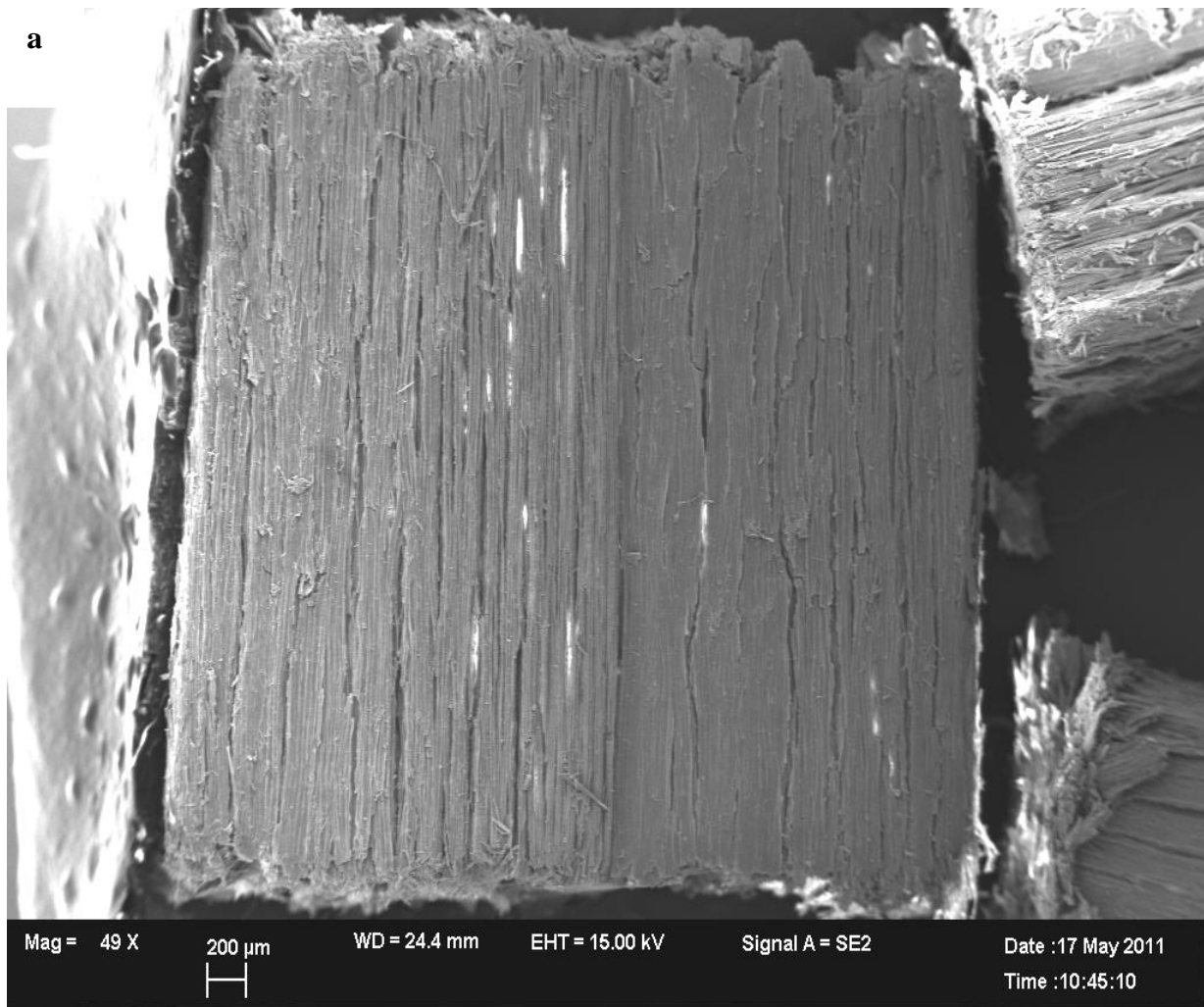


Figure 3.17 Micro-structural changes at the surface of a western red cedar specimen exposed in a QUV weatherometer for 1000 hours. Note the horizontal checks in earlywood (right) and the numerous vertical checks in earlywood and latewood

Figures 3.18 and **3.19** shows two higher magnification SEM pictures of western red cedar specimens exposed in a QUV weatherometer for 1000 hours. These higher magnification photographs reveal that erosion of cellular material from latewood is due to the formation of longitudinal checks and detachment of slivers of cell wall material lying between such checks (**Figure3.18**). In contrast, erosion of earlywood appears to result from the creation of horizontal cell wall checks and detachment of ‘plates’ of cell wall material (**Figure 3.19**).

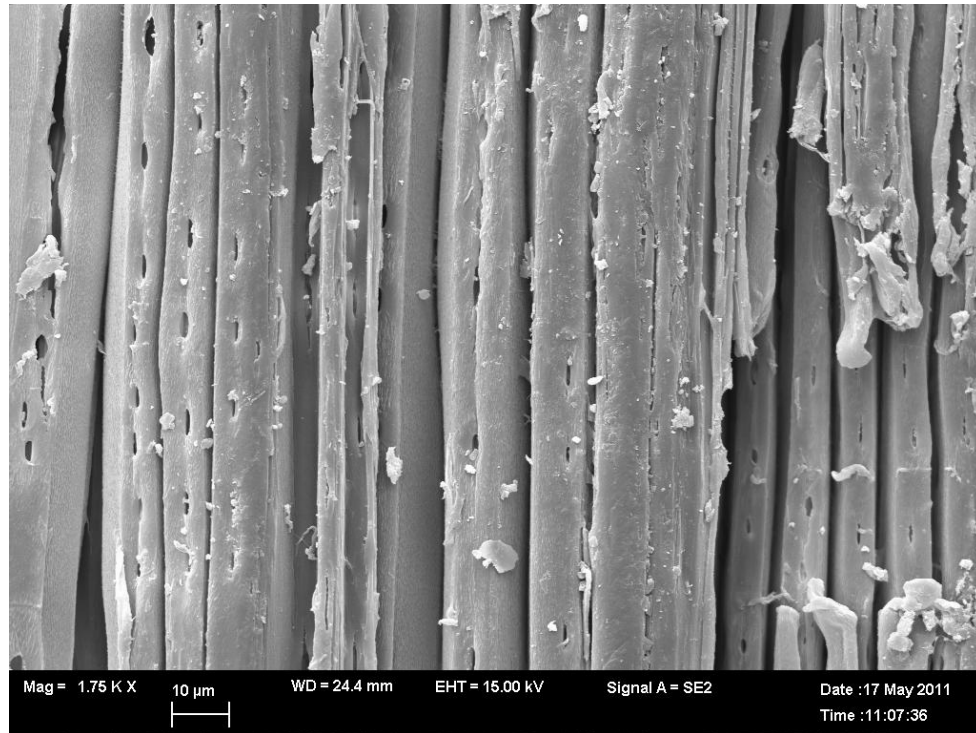


Figure 3.18 Micro-structural changes in latewood at the surface of a western red cedar specimen exposed in a QUV weatherometer for 1000 hours. Note the formation of longitudinal checks as a result of separation of latewood tracheids and detachment of slivers of wall material (right)

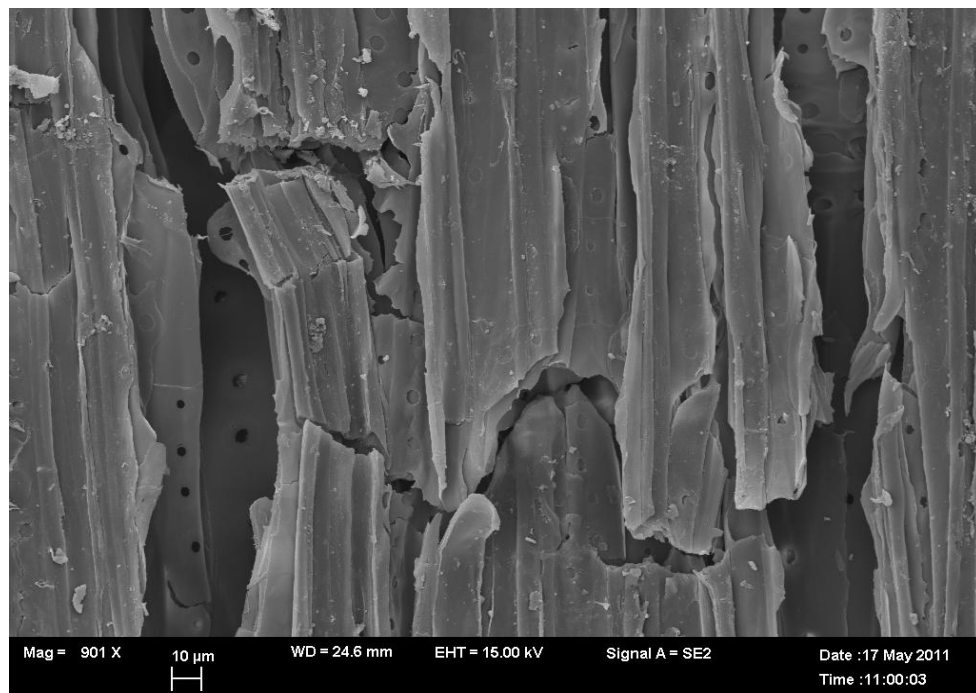


Figure 3.19 Micro-structural changes in earlywood at the surface of a western red cedar specimen exposed in a QUV weatherometer for 1000 hours. Note the detachment of small plates of cell wall material formed as a result of the intersection of vertical and horizontal checks

Figures 3.20 to 3.23 show the micro-structural changes at the surface of western red cedar specimens exposed in xenon-arc weatherometer for different period of times. **Figure 3.20** shows part of the surface of a specimen exposed in the xenon-arc weatherometer for 100 hours. Longitudinal checks developed in earlywood and latewood, partially as a result of the enlargement and micro-checking of bordered pits.

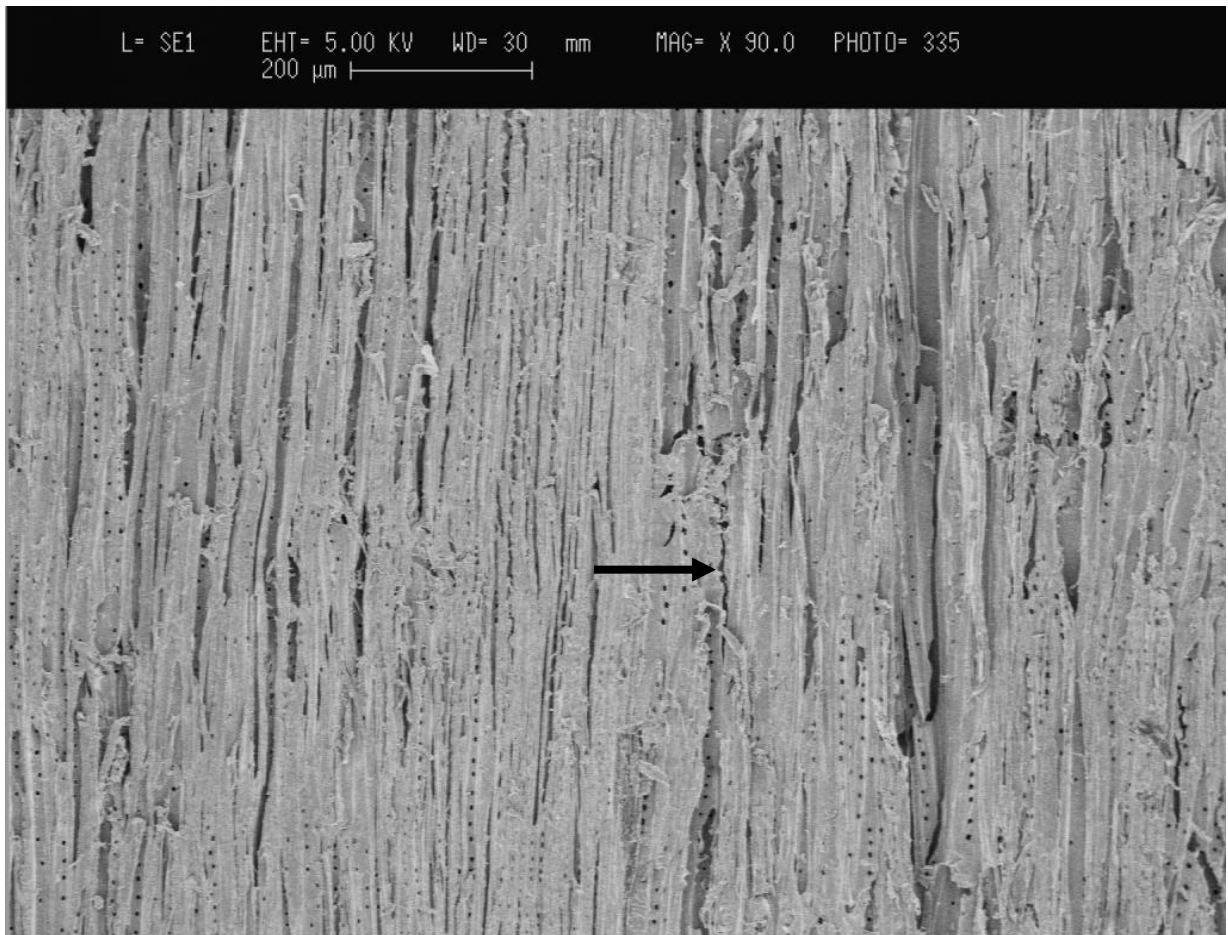


Figure 3.20 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 100 hours. Note the check in earlywood

Large and deep horizontal and vertical checks formed in earlywood in specimens exposed for 250 hours in the xenon-arc weatherometer (**Figure 3.21**). More numerous longitudinal checks developed in latewood (**Figure 3.21**).

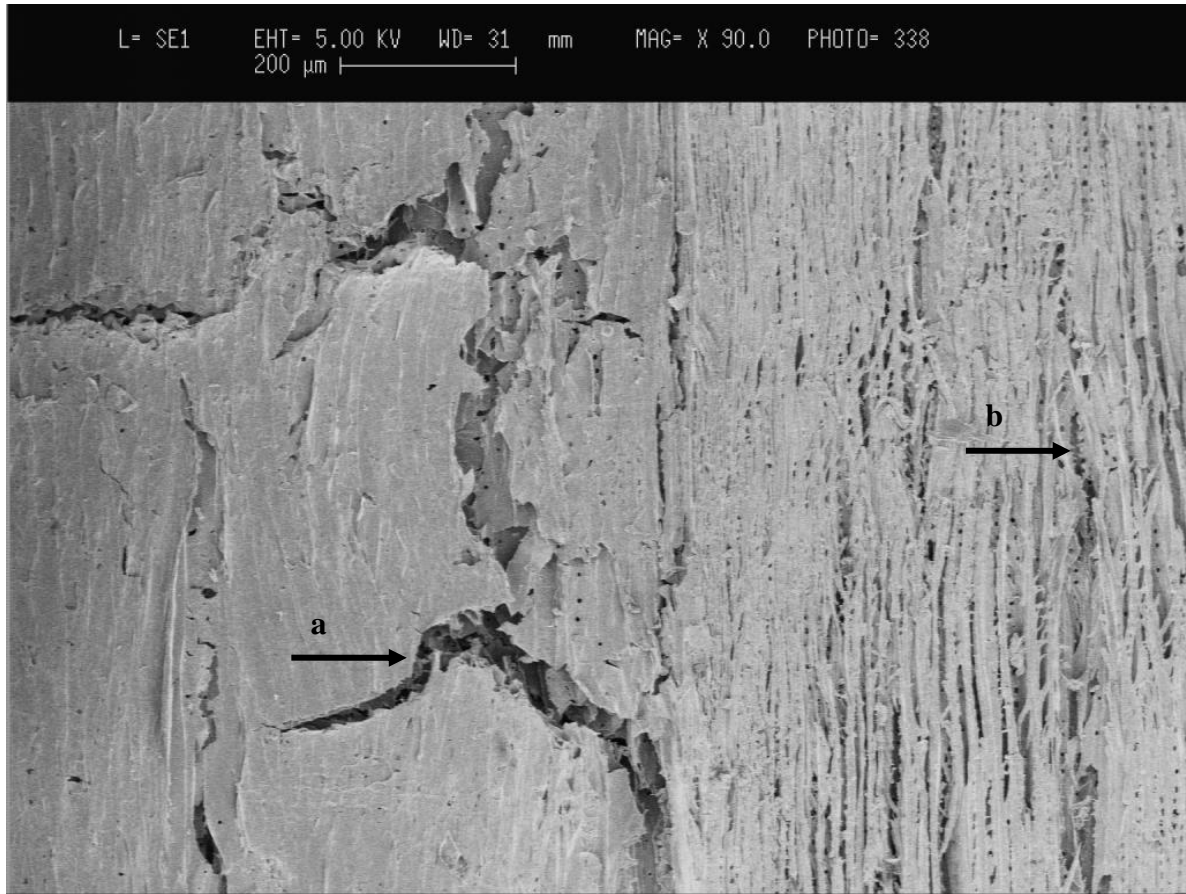


Figure 3.21 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 250 hours (a = Horizontal check in earlywood; b = Vertical check in latewood)

More prolonged exposure of specimens to accelerated weathering in the xenon-arc weatherometer (500 and 1000 hours) resulted in deepening of vertical and horizontal checks in both earlywood and latewood and detachment of large ribbons of cell wall materials from the wood surface (**Figures 3.22** and **3.23**).



Figure 3.22 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 500 hours

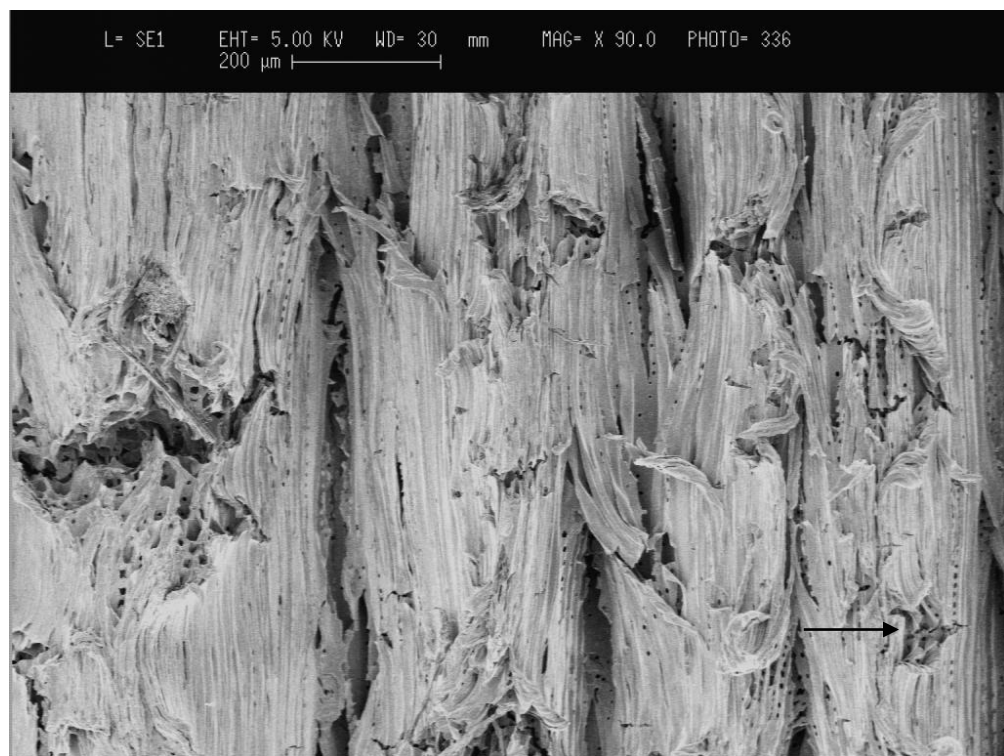


Figure 3.23 Micro-structural changes at the surface of a western red cedar specimen exposed in a xenon-arc weatherometer for 1000 hours. Note that horizontal check extend into latewood (arrowed, right)

3.3.2 Erosion of Wood during Natural Weathering

3.3.2.1 Changes in the Appearance of Specimens

The color of unmasked areas changed from brown to a light grey after specimens were exposed outdoors for 1000 hours. The exposed areas became silvery grey after 5000 hours exposure and finally blue-grey after 10000 hours exposure (**Figure 3.24**).

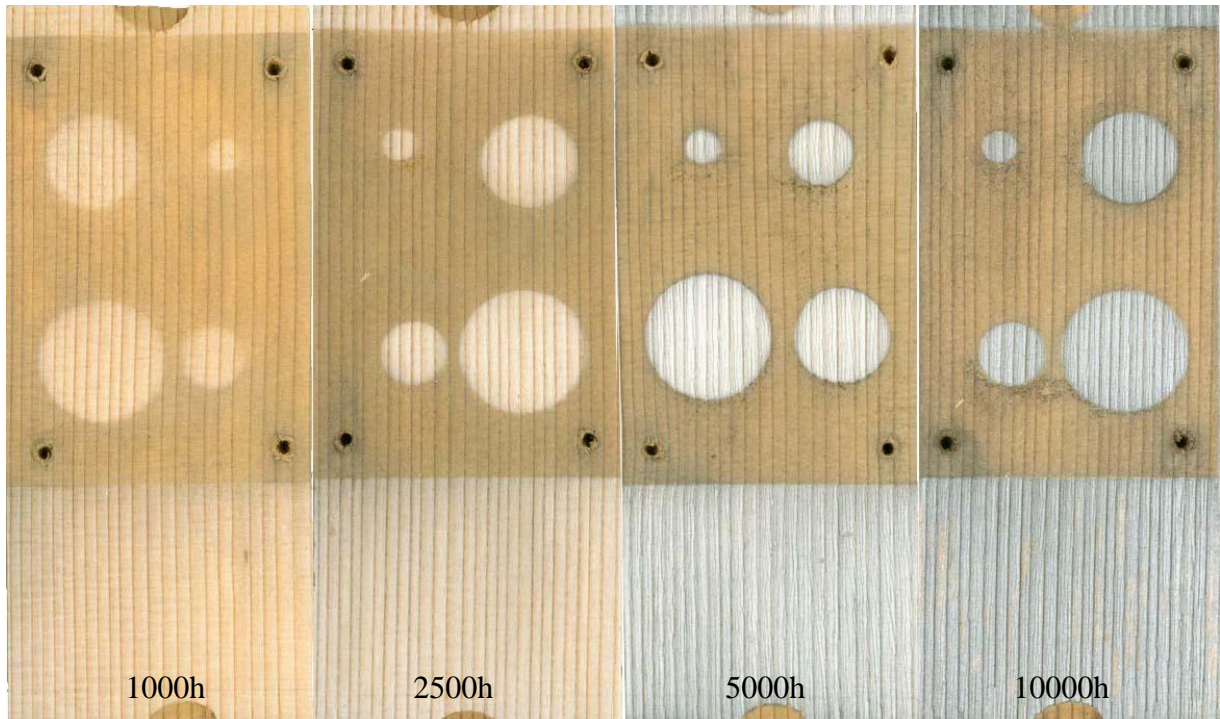


Figure 3.24 Appearance of western red cedar specimens exposed to natural weathering for different periods of time

3.3.2.2 Erosion of Wood

There were highly significant ($p < 0.001$) effects of exposure time and size of unmasked area on the erosion of western red cedar specimens during natural weathering (**Table 3.5**). There were also significant interactions of time and size of unmasked areas on erosion of specimens during natural weathering.

Table 3.5 Statistical significance (p-values) of experimental factors on erosion of western red cedar specimens exposed to natural weathering

Factor	Parameter	
	Average erosion depth	Average mass loss
Exposure time (T)	<0.001	<0.001
Size of unmasked area (S)	<0.001	<0.001
T x S	0.018	<0.001

3.3.2.2.1 Effect of Time on Erosion

Erosion of samples exposed to natural weathering showed similar trends to those of specimens exposed to artificial accelerated weathering. Hence, erosion was positively correlated with exposure time, as expected. Initially erosion increased slowly with exposure time (from 1000h to 2500h). Thereafter it increased more rapidly from 2500h to 5000h, but the rate of erosion decreased from 5000h to 10000h (**Figures 3.25 and 3.26**).

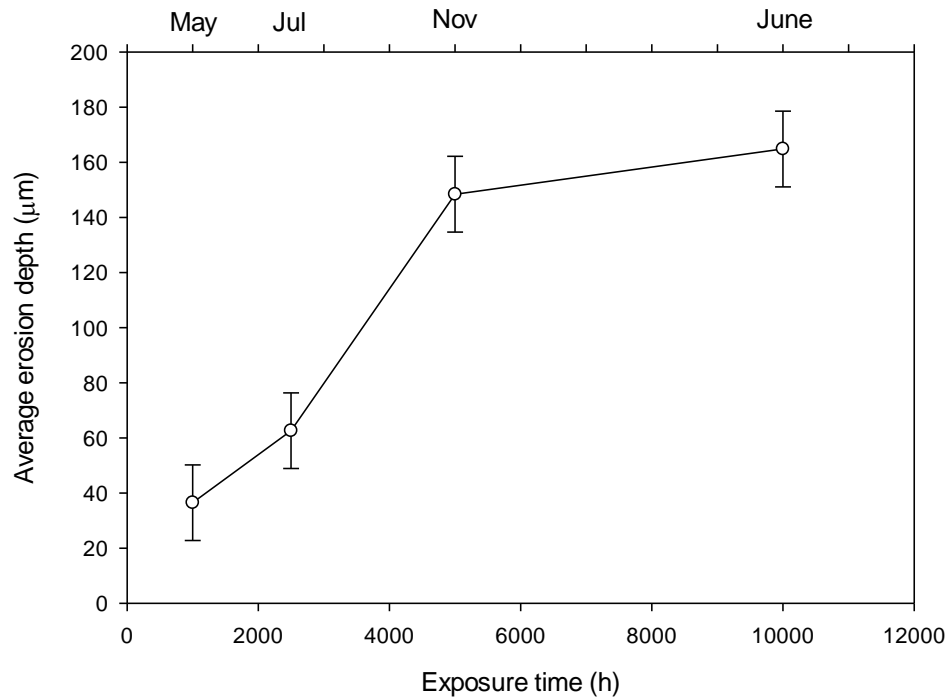


Figure 3.25 Average erosion depths of western red cedar specimens exposed to natural weathering for different periods of time (results averaged across samples containing unmasked areas of different sizes)

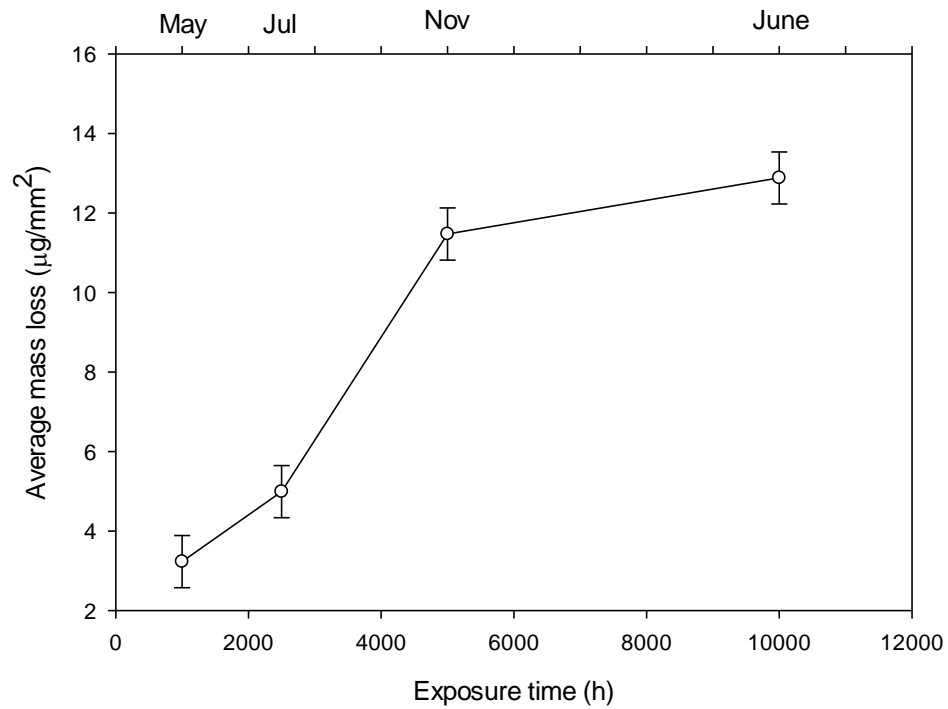


Figure 3.26 Average mass losses of western red cedar specimens exposed to natural weathering for different periods of time (results averaged across samples containing unmasked areas of different sizes)

Two dimensional erosion depth profiles of the specimens also show that erosion increased with exposure time and they also show the differential erosion of earlywood and latewood. Such differences became more pronounced with increasing exposure time (**Figure 3.27**).

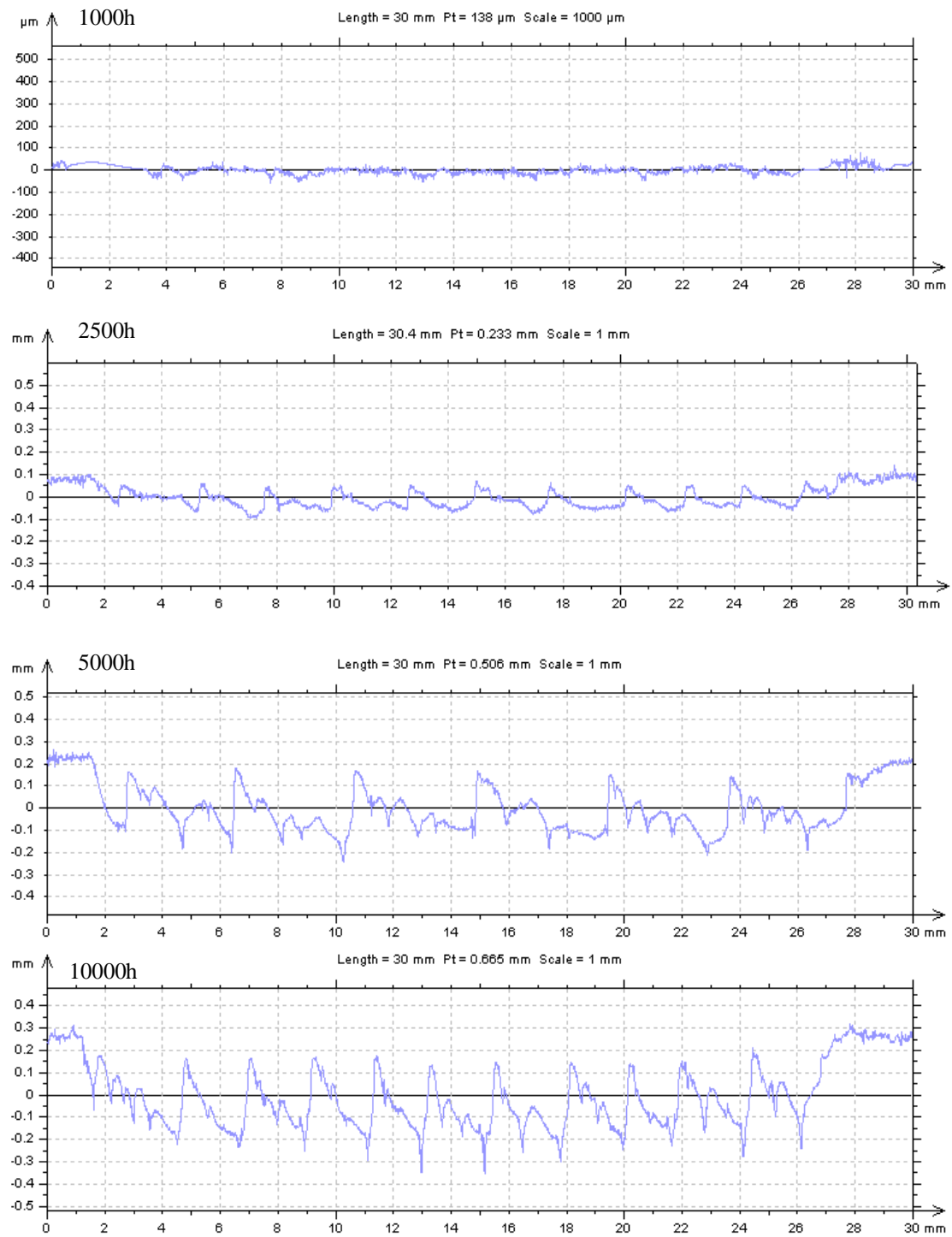


Figure 3.27 Erosion depth profiles of 30 mm diameter unmasked areas in western red cedar specimens exposed to natural weathering for different periods of time

Three dimensional topographic images of specimens exposed to natural weathering provide additional evidence that erosion increased with exposure time and they also clearly show differential erosion of earlywood and latewood (**Figure 3.28**).

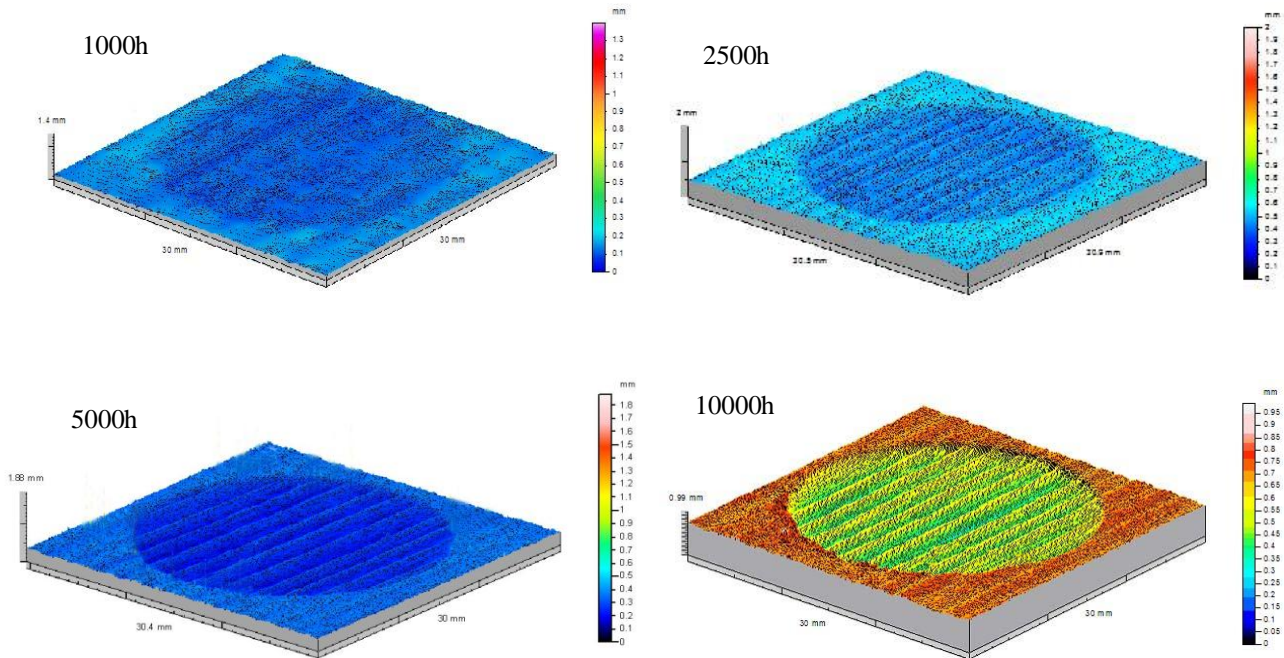


Figure 3.28 Topographic images of unmasked western red cedar specimens exposed to natural weathering for different periods of time

3.3.2.2.2 Effect of Mask Size on the Erosion of Wood during Natural Weathering

The erosion of specimens during natural weathering was also affected by the size of the unmasked area on specimens. **Figures 3.29** and **3.30** show the average erosion depth and average mass loss of unmasked areas in western red cedar specimens exposed to natural weathering. There was a positive correlation between the size of the unmasked areas and the erosion of wood during natural weathering. The average mass loss or erosion depth was the smallest in smallest unmasked area (31.7 mm^2) and increased as the unmasked area increased in size from 126.6 mm^2 , 284.9 mm^2 to 506 mm^2 . However, differences in the erosion of unmasked areas of different

diameters varied over time, which explains the significant interaction of time x size of unmasked area on erosion (**Table 3.5**). Comparing graphs in **Figures 3.29** and **3.30**, it is clear that the mass loss parameter is better than erosion depth at differentiating between erosion in unmasked areas of different sizes.

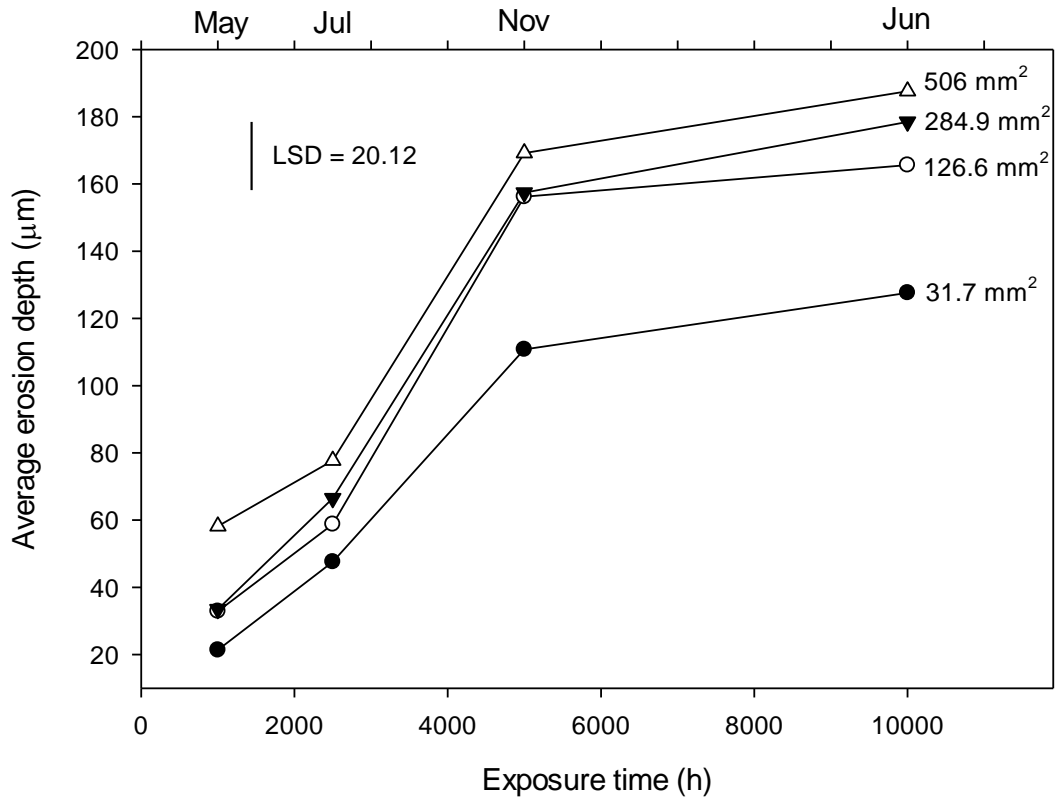


Figure 3.29 Average depth of erosion of unmasked areas in western red cedar samples exposed to natural weathering for 1000, 2500, 5000 and 10000 hours

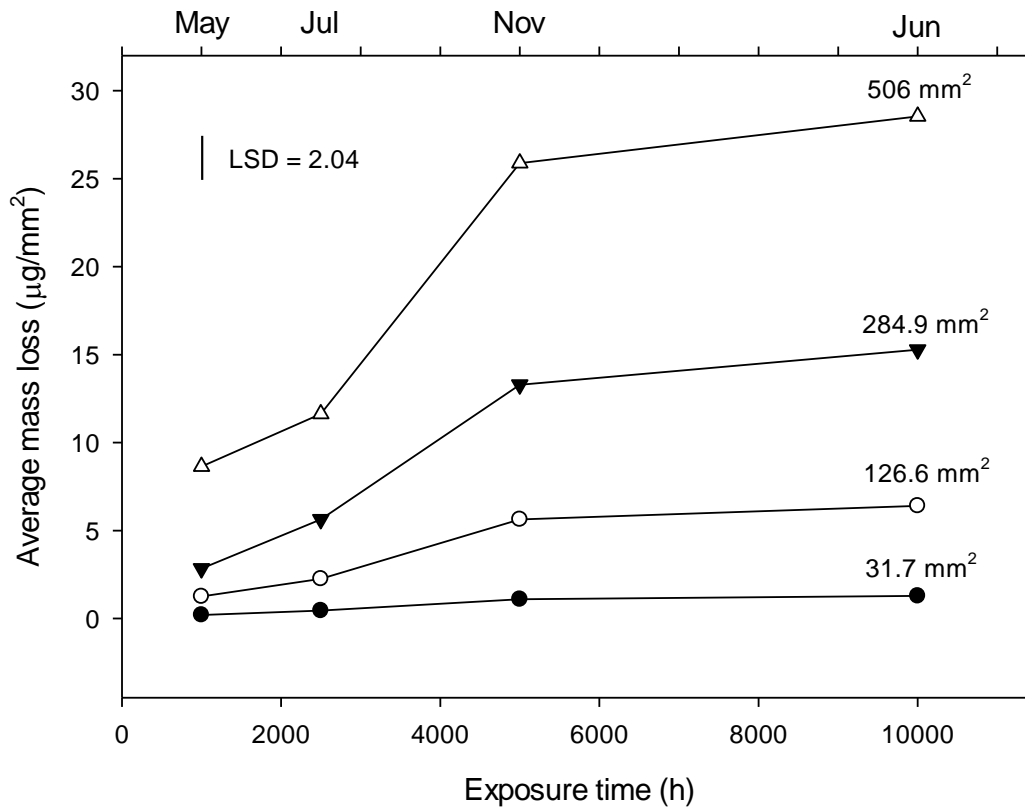


Figure 3.30 Average mass loss of unmasked areas in western red cedar samples exposed to natural weathering for 1000, 2500, 5000 and 10000 hours

3.3.2.3 Micro-structural Changes

SEM images of specimens exposed to natural weathering show that micro-structural changes increased with exposure time. However, such changes were not as severe as those in specimens exposed to artificial weathering.

Figures 3.31 and **3.32** shows that checks developed in earlywood in western red cedar specimens exposed to natural weathering for 1000 hours. These checks deepened with increasing exposure and transverse checks also developed. Checking was less pronounced in latewood, but small checks were present in the latewood of specimens.

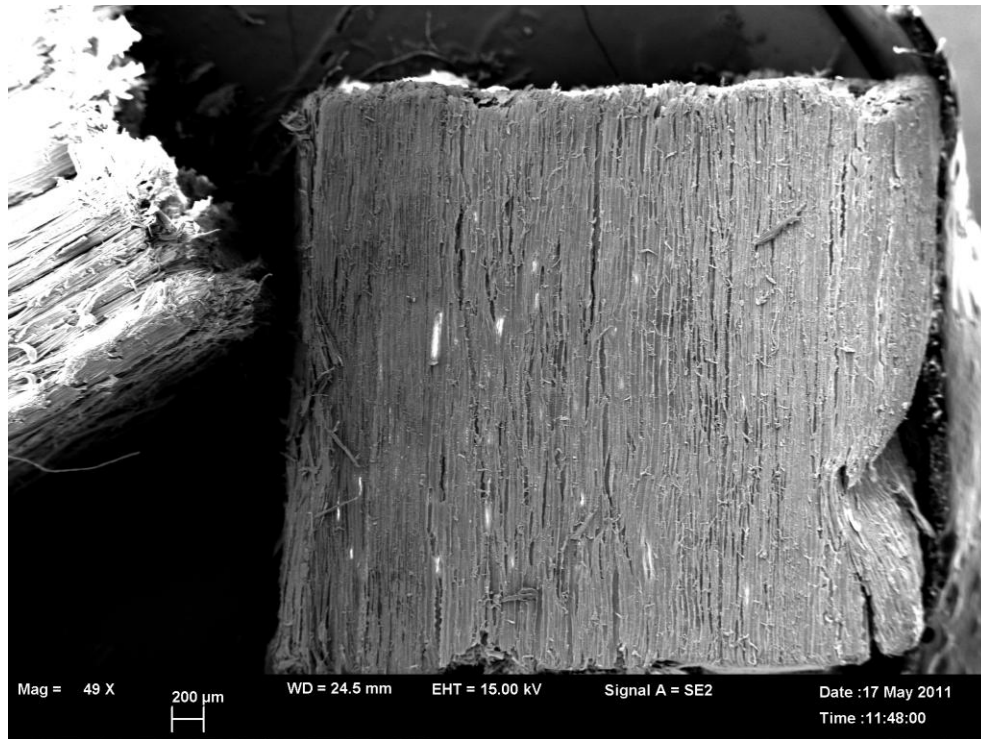


Figure 3.31 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 1000 hours

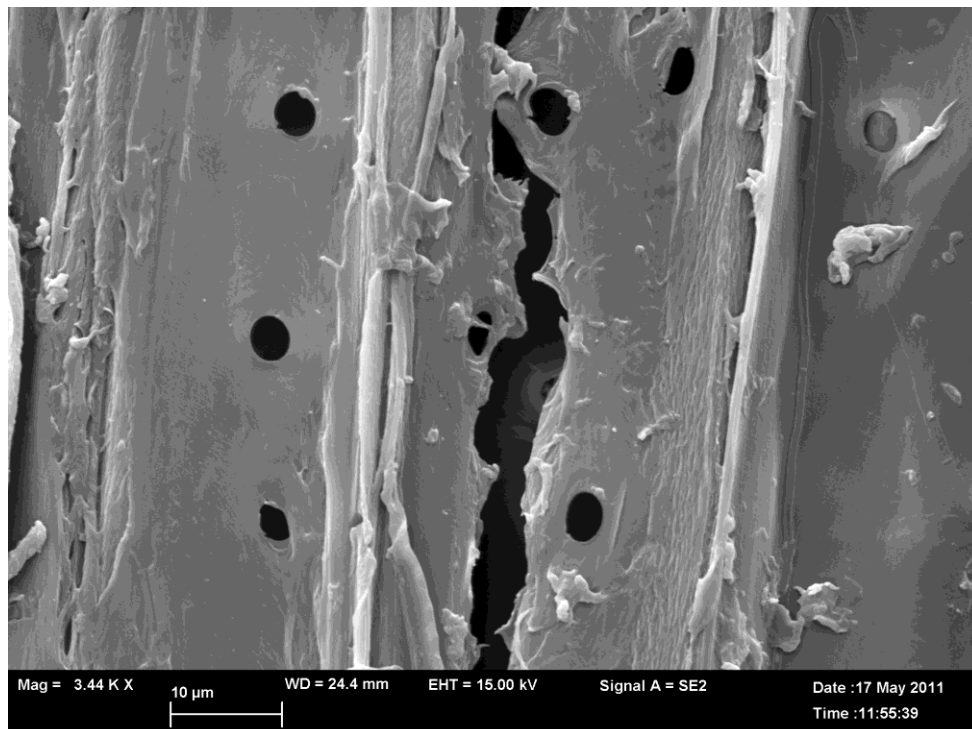


Figure 3.32 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 1000 hours. Note check in earlywood and evidence of fungal colonisation (right)

Numerous vertical checks were present in samples exposed to natural weathering for 10000 hours and there was extensive colonisation of the wood surface by fungi (**Figure 3.33**). The intersection of vertical checks and small horizontal checks created slivers of cell wall material that were not strongly bonded to the wood surface (**Figure 3.34**).

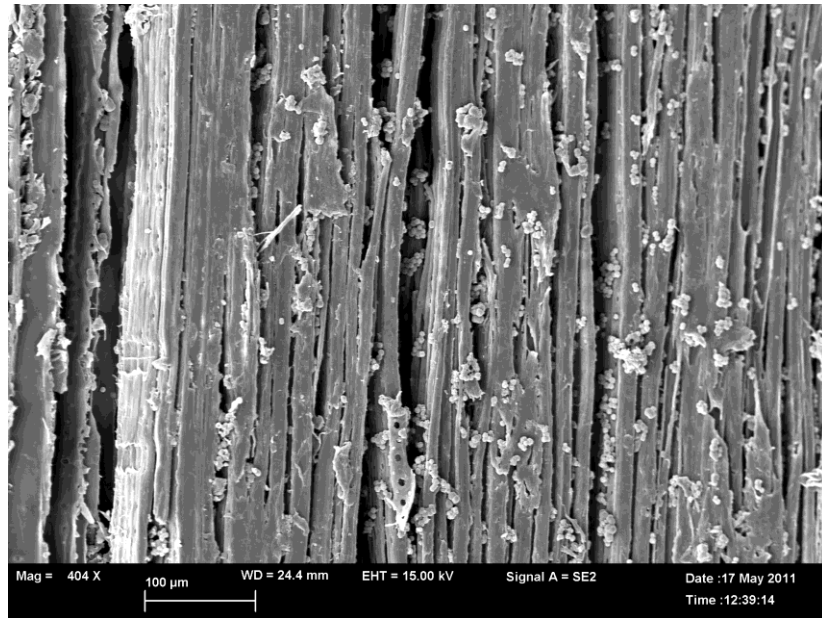


Figure 3.33 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 10000 hours. Note numerous vertical checks and colonisation of surface by fungi

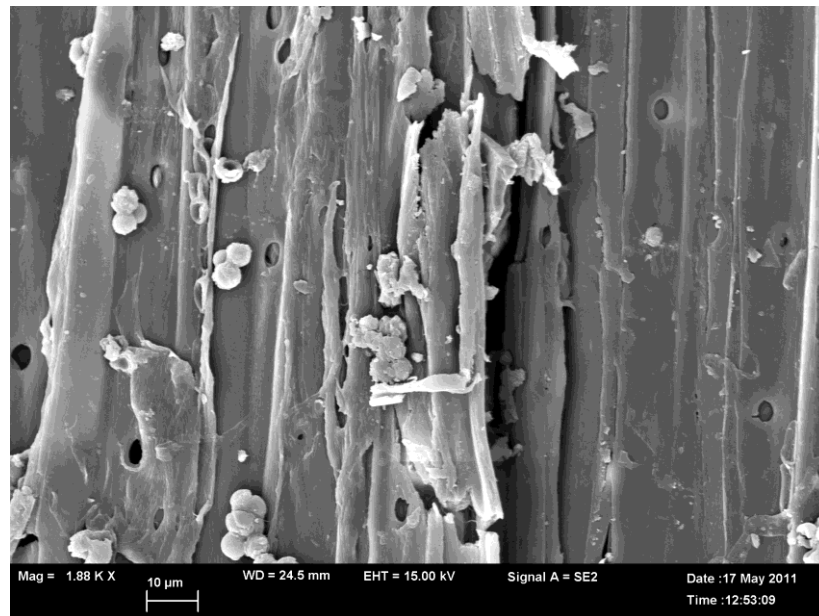


Figure 3.34 Micro-structural changes in a western red cedar specimen exposed to natural weathering for 10000 hours. Note detachment of a small sliver of cell wall material

3.3.3 Comparison of the Erosion of Specimens Exposed to Artificial Accelerated Weathering and Natural Weathering

Artificial weatherometers accelerate the weathering of wood. The extent to which the QUV and xenon-arc weatherometers accelerated the erosion of western red cedar specimens varied (Figures 3.8 and 3.9). Table 3.6 compares erosion depths and mass losses of specimens exposed in the two artificial weatherometers with those of specimens exposed to natural weathering for the same time (1000 h). It is clear that the xenon-arc weatherometer accelerated the erosion of wood to a much greater extent than the QUV weatherometer.

Table 3.6 Comparison of average erosion of western red cedar specimens exposed to artificial weathering (QUV or xenon-arc) or natural weathering for 1000 hours (XA: Xenon-arc; NW: Natural weathering)

Weathering type	Erosion depth (μm)	Acceleration rate	Mass loss (μg/mm ²)	Acceleration rate
QUV	70.3	1.9	15.9	4.9
XA	315.2	8.6	52.3	16.2
NW	36.5		3.2	

Table 3.7 compares the times taken for specimens exposed to artificial weathering and natural weathering to erode to similar depths. Low levels of erosion of 36.5 to 40.5 μm were produced by 100, 250 and 1000 hours of exposure in the xenon-arc, QUV weatherometers or natural weathering, respectively. As weathering proceeded, the degree of acceleration produced by exposing samples in the QUV weatherometer dropped, whereas that arising from exposing samples in the xenon-arc weatherometer increased.

Table 3.7 Comparison of times to reach similar average erosion depths (μm) of western red cedar specimens exposed to artificial weathering or natural weathering (XA: Xenon-arc; NW: Natural weathering)

Erosion depths (μm)	Weathering Time (h)			Ratio	
	XA	QUV	NW	NW/XA	NW/QUV
36.5-40.5	100	250	1000	10	4
62.6-70.6	250	1000	2500	10	2.5
164.8-165.6	500		10000	20	

Table 3.8 compares times for specimens to reach similar levels of mass losses when they were exposed to artificial or natural weathering. The extent to which artificial weathering accelerated erosion of samples is greater when erosion is expressed using mass losses than when it is expressed as erosion depth.

Table 3.8 Comparison of times to reach similar average mass losses ($\mu\text{g}/\text{mm}^2$) of western red cedar specimens exposed to artificial or natural weathering (XA: Xenon-arc; NW: Natural weathering)

Mass losses ($\mu\text{g}/\text{mm}^2$)	Weathering Time (h)			Ratio	
	XA	QUV	NW	NW/XA	NW/QUV
10.7-12.1	100	500	5000	50	10

3.4 Discussion

My results show that optical confocal profilometry can detect significant erosion in western red cedar specimens exposed for 100 hours in a xenon-arc weatherometer. Erosion of specimens exposed in the QUV weatherometer was also detected after 100 hours, but erosion in the smallest unmasked areas of some samples was very low. Hence, tests employing a QUV weatherometer to accelerate the weathering of untreated wood prior to erosion measurements should expose specimens for more than 100 hours. Previous studies of the erosion of wood during accelerated weathering have exposed specimens for a minimum of 600 hours, as mentioned earlier (Arnold *et al.* 1991; Williams *et al.* 2001d). My results suggest that it is possible to shorten this time

when exposing a low density species such as western red cedar to accelerated weathering, and still obtain levels of erosion that can be accurately and reproducibly measured using a confocal profilometer. Erosion measurements made using a profilometer are based on intensive measurements of the eroded area and depend on the machine parameters used, whereas erosion measurements employing optical microscopy have generally used only 3 to 6 measurements per sample (Sell and Feist 1986, Arnold *et al.* 1991, Williams *et al.* 2001a, b, c, d). Furthermore, the profilometer can be programmed to measure erosion on multiple samples, potentially allowing less labor intensive assessment of samples.

A previous study found that the erosion of wood in fluorescent ultraviolet and xenon-arc weathering chambers was similar (Arnold *et al.* 1991). The erosion of western red cedar samples exposed in a xenon-arc weatherometer here was significantly greater than that of specimens exposed in a QUV ultraviolet fluorescent weatherometer. Arnold *et al.* (1991) found that the rate of erosion of western red cedar earlywood exposed in xenon-arc and fluorescent ultraviolet weatherometer were 0.184 $\mu\text{m}/\text{h}$ and 0.213 $\mu\text{m}/\text{h}$, respectively. Comparable figures for the rate of erosion of latewood were 0.028 $\mu\text{m}/\text{h}$ for samples exposed in both types of weatherometers (Arnold *et al.* 1991). The average rate of erosion of western red cedar samples exposed in a xenon-arc weatherometer here was 0.315 $\mu\text{m}/\text{h}$, which is greater than that found by Arnold *et al.* (1991). The reason for the discrepancies between our results and those of Arnold *et al.* (1991) is not known, but they may be related to differences in the weatherometers or weathering cycles employed by Arnold *et al.* (1991) and those used here. Feist and Mraz (1978) compared erosion of softwood in artificial weathering and natural weathering. They reported that erosion of softwood in a carbon arc weatherometer for 6-9 weeks was equivalent to one year of natural

weathering. In my experiment, erosion in xenon-arc weatherometer for 4 weeks was equivalent to one year of natural weathering.

Previous studies have found that the rate of erosion of wood during weathering is related to wood density (Feist and Mraz 1978; Anderson *et al.* 1991a, 1991b). In this study, mass loss due to erosion of wood was calculated by multiplying erosion volume by the density of wood. The use of mass loss, rather than erosion depth, as a measure of erosion was better at differentiating between erosion occurring in unmasked areas of different sizes. It is possible that this parameter might be able to detect differences in the erosion of wood during weathering that is related to the wood's structure rather than to its density. However, further research would be needed to confirm this suggestion.

It is possible that reduced erosion next to the edges of unmasked areas, which would represent a smaller proportion of the large unmasked areas than the smaller ones, may explain the positive correlation between average mass loss and the size of unmasked areas.

Erosion measurements made using the confocal profilometer depended on clear demarkation of eroded (unmasked) and uneroded (masked) areas. Measurement errors could have occurred if the boundary between the masked and unmasked areas was not clear, because masked (unweathered) areas would have been scanned and identified as weathered areas. The erosion of samples exposed to artificial weathering in the QUV weatherometer for 100 hours was not sufficient to produce distinct erosion at the edges of the unmasked areas. Even when exposure times were extended to 250 hours in the QUV or 1000 hours in the case of natural weathering, it was difficult to detect a clear boundary between eroded (unmasked) and uneroded (masked) areas. Hence, measurement errors could have occurred in samples exposed for short periods of time (100-250h) to artificial weathering in the QUV weatherometer or natural

weathering (1000h). In addition, the confocal profilometer was sensitive to the altitude of samples. Noise occurred during scanning if the sample was not flat. As a result, height (z-axis) adjustments had to be made for each sample, and a black calibration also had to be performed before scanning the samples.

The color changes of specimens exposed to artificial and natural weathering varied. Samples exposed to artificial accelerated weathering became a silvery grey after prolonged exposure. The same color change occurred in specimens exposed to natural weathering for up to 5000 hours. However, specimens exposed to 10,000 hours of natural weathering were an unusual metallic blue-grey color. This color was even and consistent in all specimens exposed to natural weathering. The reason for this color change is not clear. It is possible that some metal ions such as Fe or Cr were washed from the stainless steel mask by rain and these ions reacted with the wood to form a blue-grey complex (Farmer 1962; Krilov and Gref 1986). Further experiments would be needed to confirm this hypothesis.

SEM images of specimens exposed to artificial weathering and natural weathering show that the process of erosion was different for specimens exposed in the two different weathrometers and also to natural weathering. Erosion was more pronounced in artificial weathering especially for specimens exposed in the xenon-arc device because degradation of the woods microstructure occurred more rapidly and the changes to the microstructure, particularly checking extended deeper into the wood.

3.5 Conclusions

I conclude that confocal profilometry is a more accurate and less labour-intensive way of measuring the erosion of untreated (western red cedar) wood exposed to accelerated or natural

weathering than optical microscopy. The exposure time required to produce erosion that can be measured using the profilometer is much lower than that needed using an optical microscope. Erosion measurements may provide a more realistic way of assessing the weathering of wood and the ability of chemicals to photostabilize wood because they can be made on large dimension specimens that more closely resemble treated wood than the thin wood strips that have been used in the past to screen photoprotective chemicals for wood (Evans and Schmalzl 1989; Schmalzl and Evans 2003; Jebrane *et al.* 2009). Mass loss of samples exposed to weathering, which can be calculated from erosion data produced by a confocal profilometer, is a useful parameter for quantifying the weathering of wood exposed to artificial or natural weathering.

CHAPTER 4: ASSESSING THE ABILITY OF PHENOL FORMALDHYDE RESIN TO PHOTOSTABILIZE WOOD

4.1 Introduction

Wood is susceptible to degradation by light, water and other environmental factors when used outdoors (Feist & Hon 1984). Modifying the molecular structure of wood is one way of making wood less susceptible to environment factors, and therefore it can be used to increase the service life of wood products (Williams 2005). Chemical modification systems used to improve the photostability of wood include inorganic chemicals, esterification and other chemical modification systems, grafting of UV stabilizers and impregnation of wood with polymerizable monomers (Evans 2009). Hexavalent chromium is the most effective inorganic chemical at photostabilizing wood. However, it is carcinogenic and the treated wood is green (Hon *et al.* 1985; Evans and Schmalzl 1989). Esterification of wood with benzoyl chloride or vinyl benzoate is much more effective at photostabilizing wood (including lignin) (Evans *et al.* 2002; Jebrane *et al.* 2009). However, chemical modification of wood is not cost-effective because large weight gains are required to photostabilize wood. Hence, no chemical modification systems are being used commercially specifically to photostabilize wood (Williams 2005; Evans 2009). Grafting of UV stabilizers to wood cell walls can photostabilize lignin at exposed wood surfaces (Grelier *et al.* 1997; Kiguchi & Evans 1998). Grafting treatments require high temperature and a catalyst (Evans 2009).

Polymerizable monomers can protect wood from weathering to various degrees by forming a stable layer of polymer at exposed wood surfaces (Hawkins 1984; de la Caba *et al.* 2007; Evans 2009). Xie *et al.* (2005) found that 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) was effective at restricting weight and tensile strength losses of treated Scots pine

veneers exposed to artificial weathering, but treatment with DMDHEU did not prevent delignification, and also high weight gains were required for the treatment to be effective (Xie *et al.* 2005; Evans 2009). Low molecular weight PF resin was superior to other polymerizable monomers at restricting discoloration, surface checking, weight loss and decay of treated wood exposed outdoors (Stamm and Baechler 1960; Sudiyani *et al.* 1999). It has been found that PF resin replaces hydroxyl groups on cellulose and lignin with less hygroscopic groups, and forms chemical bonds with wood's polymeric components (Stamm and Seborg 1939; Seborg *et al.* 1962; Stamm and Seborg 1962; Kamke and Lee 2007). Low molecular weight water-soluble PF resin easily penetrates into wood cell walls. Such PF resin is inexpensive, easily applied to wood, and it is not toxic after curing (Stamm 1975; Furuno *et al.* 2004). Treatment of wood with PF resin is promising as a method of protecting wood used outdoors. However, most research to-date has focused on the ability of PF resin to improve the dimensional stability and decay resistance of treated wood. The ability of PF resin to photostabilize wood has received little attention. PF resin treatment deposits aromatic groups in wood cell walls like benzoylation and esterification with vinyl benzoate. Therefore it may be able to photostabilize lignin.

Additives have been used to impart some specific characteristics to PF resins, such as ease of penetration, durability and also to reduce the cost of PF resins (Martin 1956; Knop and Scheib 1979; Marra 1992; Jiang *et al.* 2007). It may be possible to use additives to improve the ability of PF resins to photostabilize wood.

I hypothesize that PF resins will be able to photostabilize wood, and the addition of photostabilizers to PF resin may further improve the ability of PF resin to photostabilize wood. This hypothesis was tested here using measurements of mass and tensile strength losses of treated wood veneers and erosion of veneer-type wood composites exposed to natural weathering.

Losses of weight and tensile strength and color changes of wood veneers, and erosion and color changes of wood composites after weathering were compared to examine whether confocal profilometry can be used to screen chemicals for their ability to photostabilize wood. In order to optimize PF resin treatments, the effects of different concentrations of PF resin and various photostabilizers (HALS, polyethylene glycol, iron oxide and lignin) on the photostability of treated wood were examined. These additives were chosen because they are highly soluble in water and previous research had shown that each of them could photostabilize wood (Chang *et al.* 1998; Ohkoshi 2002; Amin, A.A.H. *et al.* 2005; Ciba 2005; Aloui *et al.* 2007; Forsthuber and Gröll 2010).

4.2 Materials and Methods

4.2.1 Experimental Designs and Statistical Analyses

Four different factorial experiments were designed to examine my hypotheses. The first experiment examined the effects of different concentrations of PF resins (12%, 24%, 36%, 48%) on their own or containing a wax additive (2.5%) on the photostability of wood veneers exposed to 50 days natural weathering. The second experiment examined the ability of different additives on their own to photostabilize wood veneers exposed to natural weathering for 35 days. The third experiment examined the ability of 12% PF resin in combination with different additives to photostabilize wood veneers exposed to natural weathering for 50 days. The final experiment examined the effects of different concentrations of PF resin (10%, 20%, 30%) on their own and in combination with different additives on the erosion and color of a veneer-type wood composite exposed to natural weathering for 2000 hours.

The design of the first three (veneer) experiments accounted for random variation between wood blocks and variation between and within batches of veneers. Veneers cut from four

different yellow cedar wood blocks provided higher level replication for each experiment. Batches of twenty veneers cut from each block were randomly assigned to each treatment (including untreated controls). The design of the experiment on the photostability of wood composites treated with PF resin accounted for random variation between wood boards, variation between wood blocks and variation between and within specimens. Specimens cut from eight different boards provided replication at the higher level. Each of these boards was cut into seven blocks, which were randomly allocated to seven different chemical treatments.

Analyses of variance were used to examine the effect of fixed and random factors on the different response variables in each experiment (1-4). The significance of experimental factors (p-values) on response variables is tabulated allowing the reader to explore significant ($p < 0.05$) effects and their interactions. Statistical computation was done using Genstat (version 12) (VSN International 2009). Statistically significant results are plotted on graphs and least significant difference (lsd) bars ($p < 0.05$) or 95% confidence intervals on graphs can be used to compare differences between individual means.

4.2.2 Preparation of Specimens

4.2.2.1 Preparation of Wood Veneers

Four small blocks measuring 85 mm (longitudinal) x 25 mm (tangential) x 20 mm (radial) were cut from four different defect free yellow cedar wood boards. Wood blocks were vacuum-impregnated (-90 kPa) with distilled water and left to soak overnight in water (under vacuum). Wood veneers measuring 85 mm (length) x 20 mm (width) x 80-85 μm (thickness) were cut from radial surfaces of the four water-saturated yellow cedar blocks using a sledge microtome (Spencer Lens Co. Buffalo, N.Y. U.S.A) and a steel microtome blade holder containing a

disposable microtome blade (**Figure. 4.1**).

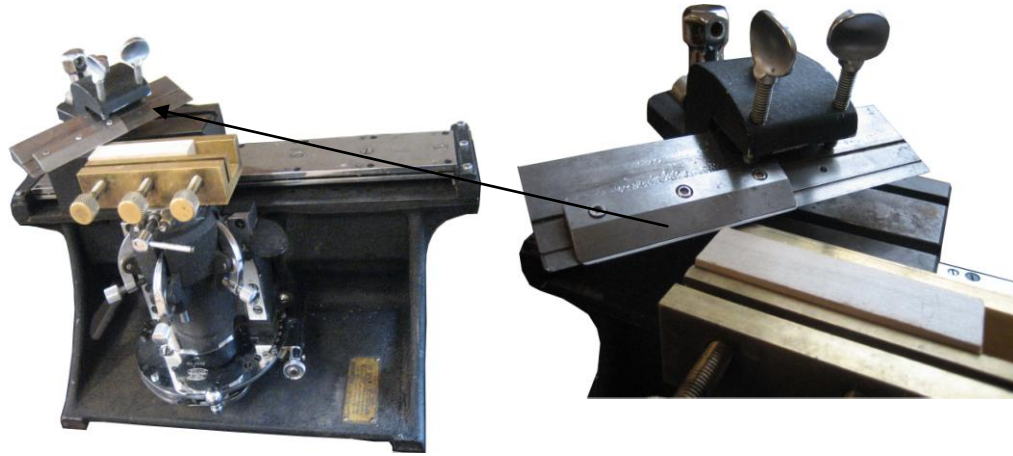


Figure 4.1 Sledge microtome and steel microtome blade used to cut thin wood veneers from a parent wood block (Left: Sledge microtome; Right: A close-up view of steel microtome blade holder and disposable blade)

The dimensions of the wood board, blocks and veneers are shown in **Figure 4.2**. Wet veneers were placed under restraint on glass plates and air-dried for 4 hours. Veneers were conditioned at $20 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ relative humidity (r.h.) for 60 days.

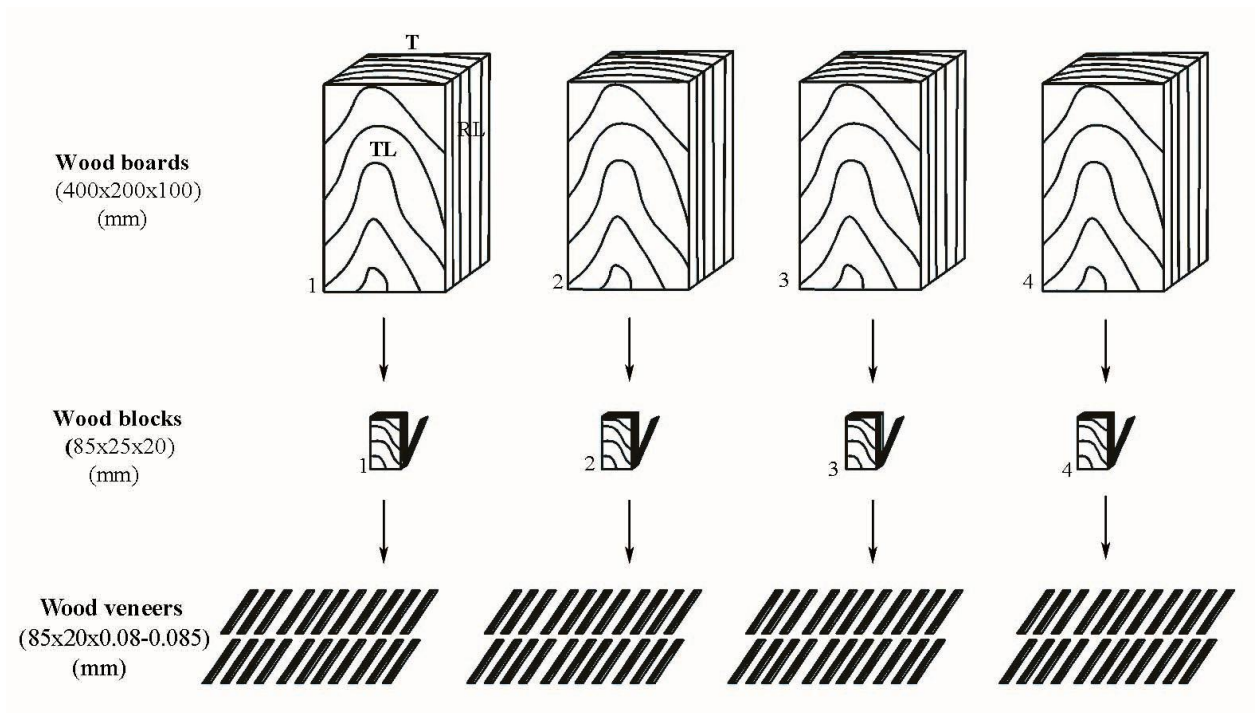


Figure 4.2 Dimensions of parent wood boards, blocks and wood veneers

The thickness of each veneer was measured using HWS 5781 digital micrometer (AB Lorentzen & Wettre, Sweden) (**Figure 4.3**).



Figure 4.3 Digital micrometer used to measure the thickness of individual wood veneers

4.2.2.2 Preparation of Wood Composites from Sawn Veneers

Eight different radiata pine boards measuring 800 mm x 400 mm x 200 mm and eight western red cedar boards measuring 800 mm x 60 mm x 20 mm were used to make laminated wood composites. Radiata pine was used for the upper and lower faces of the composite and western red cedar was used for the core. Boards were planed using a Martin T44 planer and they were then each sawn into seven (4mm) thick veneers using a Altendorf® F45 table saw. Two veneer specimens measuring 50.0 mm x 50.0 mm x 3.0 mm were cut from each of the larger radiata pine veneers using an Omega T55300 chop saw. One thick veneer specimen measuring 50.0 mm x 50.0 mm x 4.0 mm was cut from each of the larger western red cedar veneers. The method used to prepare the radiata pine veneers is shown in **Figure 4.4**, below.

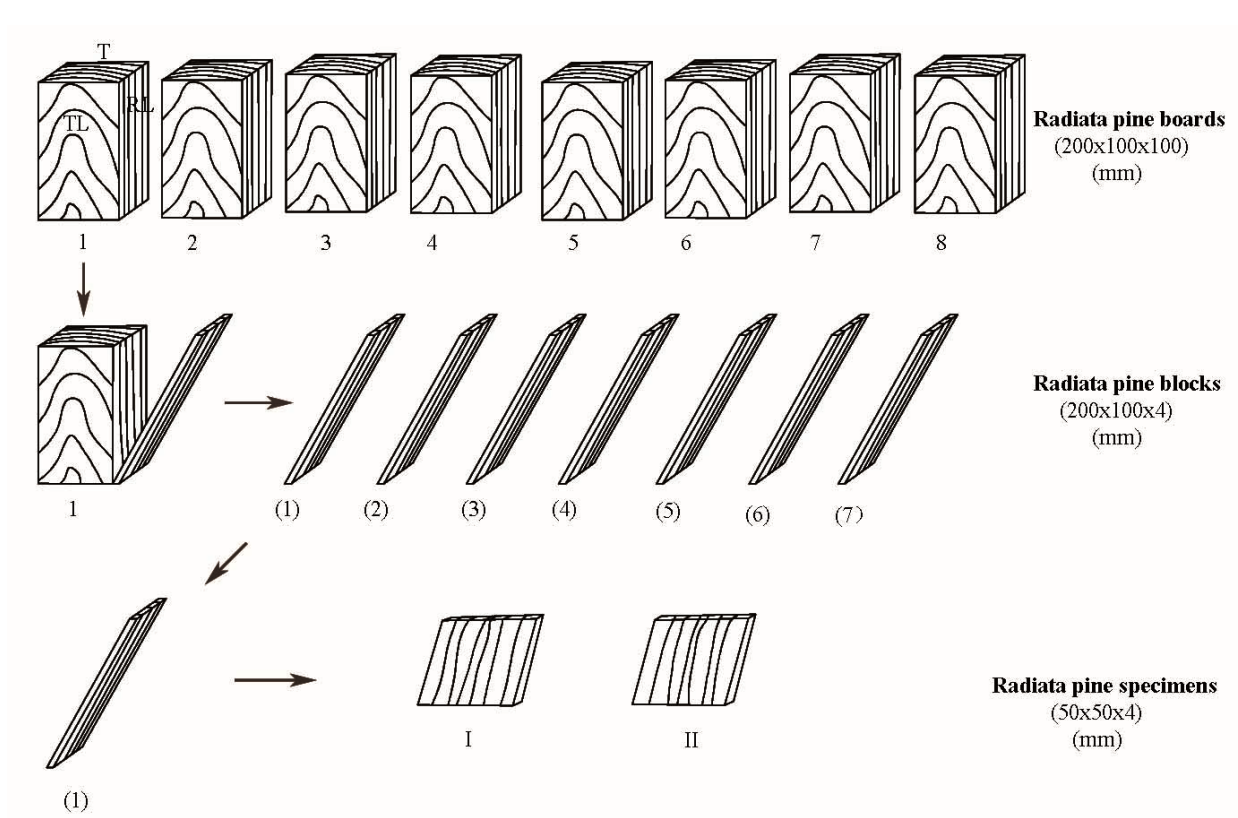


Figure 4.4 Dimensions and process of preparing sawn radiata pine veneers used to make treated composites

Radiata pine was chosen for the face veneers because it is very permeable and easy to treat with PF resin (Bootle 1983). Furthermore, radiata pine is one of the world's most important commercially grown wood species (Koehler 1924, Bootle 1983). Western red cedar was chosen for the core of the composite because it is light, naturally durable and large volumes of second-growth western red cedar are available in North America (Gonzalez 1997).

The densities and rates of growth of the radiata pine boards from which veneers were sawn are shown in **Table 4.1**, below. The densities and rates of growth of western red cedar samples are shown in **Table 3.1**, in Chapter 3.

Table 4.1 Density and growth ring width of radiata pine boards used to make wood composites

Board number	Growth rings/cm	Density (g/cm ³)
1	0.20	0.30
2	0.80	0.44
3	0.68	0.43
4	0.60	0.42
5	0.28	0.38
6	0.68	0.39
7	0.48	0.43
8	0.28	0.36
Average	0.50	0.39

Treated radiata pine veneers were placed with their grain oriented perpendicular to the western red cedar veneers (**Figure 4.5**). The veneers were glued together using a phenol-resorcinol formaldehyde adhesive (Arclin 4001 / 5830) supplied by Arclin USA Inc. (Springfield, Oregon). The adhesive included a resin and a hardener. The resin and hardener were mixed in a ratio of 2.5:1 by weight. The adhesive was spread evenly on the surface of veneers using a stainless steel blade and exposed to air for 10 minutes. The three pieces of veneers were assembled by pressing the glued veneers together for 6 hours at room temperature using a clamping pressure of 861 kPa.

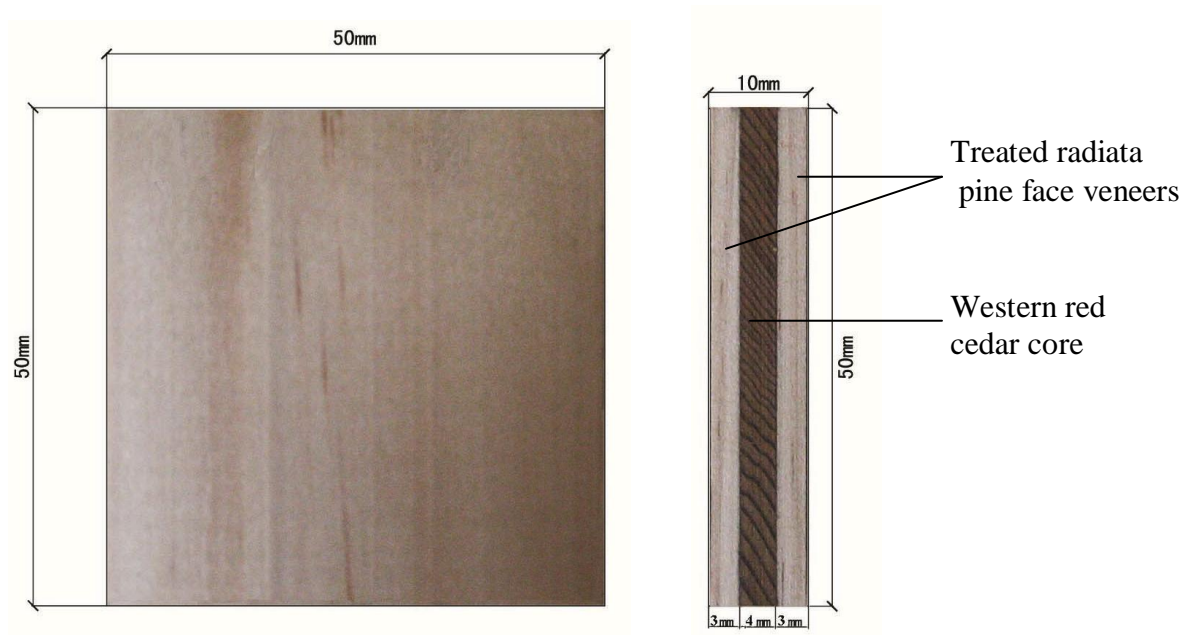


Figure 4.5 Dimensions and construction of the wood composites exposed to natural weathering

Sixteen gauge (0.795 mm thick) stainless steel metal masks measuring 95.2 mm x 63.5 mm employed for the experiment described in Chapter 3 were used to mask the veneer-type composites. The metal masks were fixed to treated wood specimens using stainless steel screws, making sure that the largest circular hole (506 mm²) in the mask was fully underlaid by treated veneer (**Figure 4.6**). The treated wood composites were kept in a constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for 10 days before they were exposed to natural weathering.

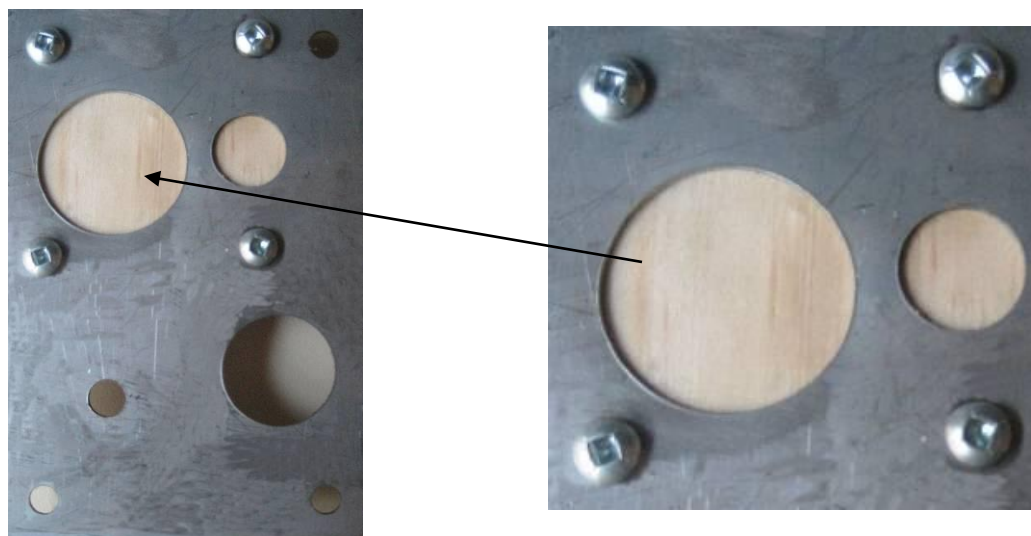


Figure 4.6 Wood composite overlaid with a stainless steel metal mask (left) and a close-up of the wood composite with the stainless steel metal mask (right)

4.2.3 Chemical Treatments

4.2.3.1 Treatment of Yellow Cedar Wood Veneers with PF Resin or PF Resin and Wax

Low molecular water-soluble PF resin (368–3B; 48% solid content) provided by Arclin USA Inc. (Springfield, Oregon) was diluted into different concentrations using distilled water. A wax emulsion (UW5F; 40% solids content) supplied by Viance LCC (Charlotte, North Carolina) was added to the different PF resin solutions to create solutions containing 2.5% wax. Distilled water containing 2.5% wax and distilled water on its own were used as controls. The chemical solutions used to treat wood veneers are shown in **Table 4.2**. Dilution of parent PF resin into lower concentration solutions used the formula below:

$$M_{\text{dilution}} \times V_{\text{dilution}} = M_{\text{parent}} \times V_{\text{parent}}$$

where, M = Concentration (%); V= Volume (ml)

The steps used to treat veneers involved: (1) Impregnation: impregnating the veneers with PF resin solution at room temperature of 20-25 °C. The veneers were soaked with PF resin for 15

minutes; (2) Drying: veneers were removed from the solution, and excess solution was squeezed from both sides of the veneers using a plastic roller. Veneers were clamped at their ends and suspended on a rack for 20 minutes to allow them to air-dry; (3) Curing: Veneers were cured in an oven with an opening to a fume hood at 150 °C for 20 minutes.

Table 4.2 Solvent and concentrations of PF resin and wax (W) used to treat wood veneers

Treatment	Solvent	Concentration (w/w)	Symbol
1. Control	Water	-	Con
2. PF resin	Water	12%	12P
3. PF resin	Water	24%	24P
4. PF resin	Water	36%	36P
5. PF resin	Water	48%	48P
6. Wax	Water	2.5%	W
7. PF resin + wax	Water	12% PF, 2.5% W	12PW
8. PF resin + wax	Water	24% PF, 2.5% W	24PW
9. PF resin + wax	Water	36% PF, 2.5% W	36PW
10. PF resin + wax	Water	48% PF, 2.5% W	48PW

The dry weight and color of veneers were measured after treatment and the treated veneers were kept in constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for seven days before they were exposed to natural weathering.

4.2.3.2 Wood Veneers Treated with Aqueous Solutions Containing Different Additives

Lignostab[®] 1198, a water soluble hindered amine light stabilizer was provided by CIBA Specialty Chemicals Corp (Tarrytown, New York). Micronized iron oxide (PW601, Yellow) was purchased from Johnson Matthey Ceramics. Inc (Downingtown, Pennsylvania). PEG 1000 was purchased from Sigma-Aldrich, Inc (Saint Louis, Missouri). Lignosulphonate (DP 518) was provided by Borregaard LignoTech HQ (Sarpsborg, Norway). These additives were dissolved in distilled water (**Table 4.3**).

Table 4.3 Solvent and concentrations of additives in aqueous solutions used to treat wood veneers

Treatment	Solvent	Concentration (w/w)	Symbol
1. Control	Water	-	Con
2. PEG	Water	10%	PEG
3. Iron oxide	Water	1%	IO
4. Lignostab 1198	Water	2%	Lstab
5. Lignosulphonate	Water	10%	Lig

The processes used to treat wood veneers with aqueous solutions containing additives only included impregnation and drying steps without curing. These were described above for Experiment 1. Dry weight and color of treated veneers were measured after treatment, as above, and the treated veneers were kept in a constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for two days before they were exposed to natural weathering.

4.2.3.3 Wood Veneers Treated with PF Resin and Different Additives

Low molecular weight water-soluble PF resin (SKG-113-09; 50% solid content) was provided by Arclin USA Inc. (Springfield, Oregon). The additives used were the same as those described above for Experiment 2. The concentrated PF resin solution (50% w/w) was diluted with distilled water to produce solutions containing 12% (w/w) of PF resin. The different additives were dissolved into solutions containing 12% PF resin (**Table 4.4**).

The processes used to treat wood veneers with aqueous solutions containing PF resin and different additives were the same as those used in Experiment 1. Dry weight and color of treated wood veneers were measured and they were then kept in a constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for 5 days before they were exposed to natural weathering.

Table 4.4 Solvent and concentrations of PF resin and additives used to treat wood veneers

Treatment	Solvent	Concentration (w/w)	Symbol
1. Control	Water	-	Con
2. PF resin	Water	12% PF	PF
3. PF resin + PEG	Water	12% PF, 10% PEG	PFPEG
4. PF resin + Iron oxide	Water	12% PF, 1% IO	PFIO
5. PF resin + Lignostab 1198	Water	12% PF, 2% Lstab	PFLstab
6. PF resin + Lignosulphonate	Water	12% PF, 10% Lig	PFLig

4.2.3.4 Wood Composites Treated with PF Resin or PF Resin and Different Additives

PF resin and additives used to treat wood composites were the same as those described above for Experiment 3. **Table 4.5** shows the chemicals and concentrations of aqueous solutions used to treat sawn radiata pine veneers.

Table 4.5 Solvent and concentrations of PF resin and additives used to treat sawn radiata pine veneers

Treatment	Solvent	Concentration (w/w)	Symbol
1. Control	Water	-	Con
2. PF resin	Water	10%	10PF
3. PF resin	Water	20%	20PF
4. PF resin	Water	30%	30PF
5. PF resin + PEG	Water	10% PF, 10% PEG	PFPEG
6. PF resin + Iron oxide	Water	10% PF, 1% IO	PFIO
7. PF resin + Lignostab 1198	Water	10% PF, 2% Lstab	PFLstab
8. PF resin + Lignosulphonate	Water	10% PF, 10% Lig	PFLig

Sawn radiata pine wood veneers were vacuum (-90kPa) pressure (689kPa) impregnated with resin solutions for 2 hours at a room temperature of 20-25 °C. Then the veneers were air-dried for 2 hours, placed in an oven with an opening to a fume hood at 150 °C and cured for 2 hours.

The color of the treated radiata pine specimens was measured after curing. The treated wood composites were kept in a constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for 10 days before they were exposed to natural weathering.

4.2.4 Weathering

4.2.4.1 Weathering of Wood Veneers

The groups of treated and conditioned yellow cedar veneers from each batch were placed on glass backing plates and clamped at their ends. The specimens were exposed horizontally to natural weathering in Vancouver, Canada (Latitude: $49^{\circ}11'42.000''$ N; Longitude: $123^{\circ}10'55.000''$; Elevation: 04.30 m) (**Figure 4.7**). All the controls (treated and untreated, unweathered specimens) were kept in a constant climate room at 20 ± 1 °C and $65 \pm 5\%$ relative humidity (r.h.) for the duration of the exposure trial.

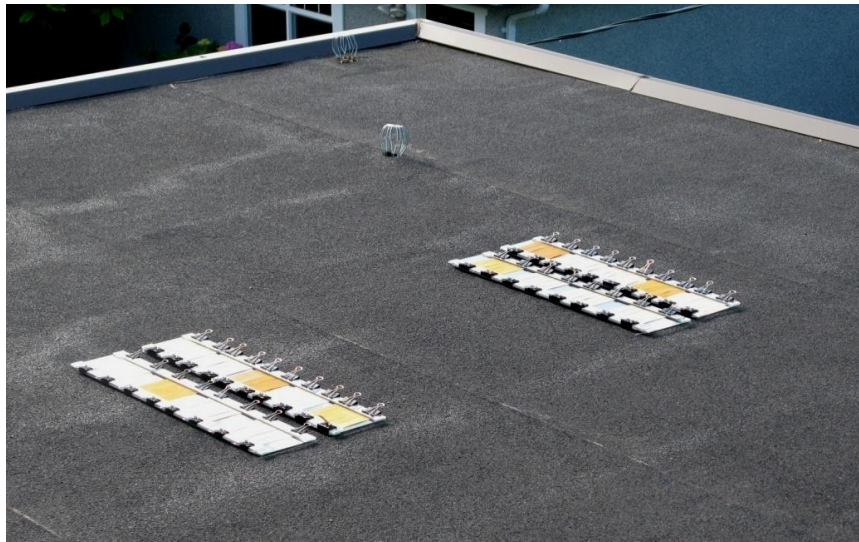


Figure 4.7 Glass plates containing treated wood veneers during a natural weathering trial

The veneers treated with PF resin or PF resin containing wax were exposed to weathering for 50 days from Sept. 27th, 2008 to Nov. 17th, 2008. The meteorological conditions during this period are shown in **Table 4.6**.

Table 4.6 Meteorological conditions in Vancouver from September 2008 to November 2008

Month	Mean Max Temp (°C)	Mean Temp (°C)	Mean Min Temp (°C)	Highest Temp (°C)	Lowest Temp (°C)	Total Precip (mm)	Total Sunshine (h/m)	Mean Sunshine (h/d)
Sep.	18.2	14.6	10.8	24.5	6.9	30.6	210.9	7.0
Oct.	13.3	10.0	6.6	22.2	0.9	99.6	123.1	4.0
Nov.	10.7	8.1	5.5	14.6	-0.3	177.0	56.9	1.9
Ave.	14.1	10.9	7.6	20.4	2.5	102.4	130.3	4.3

(Source: Environment Canada. <http://www.weatheroffice.gc.ca>)

The veneers treated with modified PF resin containing different additives were exposed to natural weathering for 50 days from July 11th 2009 to August 29th 2009. The veneers treated with different additives were exposed to weathering for 35 days from September 3rd 2009 to October 6th 2009. The climatic conditions during these periods are shown in **Table 4.7**.

Table 4.7 Meteorological conditions in Vancouver from July 2009 to October 2009

Month	Mean Max Temp (°C)	Mean Temp (°C)	Mean Min Temp (°C)	Highest Temp (°C)	Lowest Temp (°C)	Total Precip (mm)	Total Sunshine (h/m)	Mean Sunshine (h/d)
Jul.	24.1	19.6	15.0	34.4	10.6	20.0	330.2	10.7
Aug.	22.0	18.0	14.0	26.7	10.4	26.6	265.7	8.6
Sep.	19.8	15.7	11.6	27.8	5.0	65.6	220.1	7.3
Oct.	13.4	10.0	6.7	17.6	0.4	168.0	115.6	3.7
Ave.	19.8	15.8	11.8	26.6	6.6	70.1	232.9	7.6

(Source: Environment Canada. <http://www.weatheroffice.gc.ca>)

4.2.4.2 Weathering of Wood Composites

The treated plywood-type wood composites were randomly placed on a weathering rack at an inclination of 45 °C facing south and exposed to 2000 hours (83.3 days) of natural weathering from August 7th 2009 to October 31st 2009 (**Figure 4.8**). The test site was located on UBC's

Point Grey campus in Vancouver, Canada. The meteorological conditions during this period are shown in **Table 4.7**.



Figure 4.8 Weathering rack containing treated wood composite specimens

4.2.5 Measurement of Physical Changes in Wood Veneers and Composites as a Result of Treatment and Exposure to Natural Weathering

4.2.5.1 Dry Weight Gains and Losses of Veneers

The untreated and conditioned wood veneers were oven dried at $105 \pm 5^{\circ}\text{C}$ for 90 minutes and their initial oven-dry weights (W_i) were measured using a digital analytical balance (GR-200; A&D Company, Limited. Japan). After chemical treatment, the veneers were reconditioned for 7 days and oven dried. Their dry weights were remeasured (W_t) as above. Weight gain (W_g) of veneers is the difference between their initial, untreated, dry weights (W_i) and their dry weights after treatment (W_t). Veneers were removed from the glass plates after natural

weathering and reconditioned for 7 days once again and oven dried. Their dry weights after weathering (W_w) were then remeasured, as above. Weight loss (W_l) of veneers is the difference between veneers' dry weights after treatment (W_t) and after weathering (W_w). The equations used to calculate (1) percentage weight gains ($W_g\%$) and (2) percentage weight losses ($W_l\%$) is as follows:

$$(1) W_g (\%) = [(W_t - W_i) / W_i] \times 100$$

$$(2) W_l (\%) = [(W_t - W_w) / W_t] \times 100$$

4.2.5.2 Tensile Strength of Veneers

Untreated veneers were kept in a conditioning room for the duration of the exposure trial. Weathered veneers were reconditioned for 7 days after they were weathered. The tensile strength of untreated and unweathered controls, treated and unweathered veneers, and weathered veneers was measured using a Pulmac paper tester (HWS5786) at zero-span (Evans and Schmalzl 1989) (Figure 4.9).



Figure 4.9 Pulmac TS 100 paper testing machine used to measure the zero-span tensile strength of thin wood veneers (left) and a close-up of the jaws of the testing device (right)

The clamping pressure used during testing was 550 kPa. The tensile strength of veneers was calculated using the following equation:

$$TS \text{ (kg/mm}^2\text{)} = (P - P_0) \times K / S_w \times S_t \times 0.001$$

Where, P = Failure load (psi)

P_0 = 1.9 psi (zero pressure values required to unload jaws)

K = 0.375 (instrument constant provided by the manufacturer)

S_w = 15 mm (specimen effective width)

S_t = Specimen thickness (μm)

4.2.5.3 Color Changes during Weathering

The color of each yellow cedar veneer and the face veneers of each composite wood specimen were measured after treatment (L_t) and re-measured after weathering (L_w) using a Minolta CM-2600D spectrophotometer. This machine is capable of simultaneous measurement of SCI (specular component included)/SCE (specular component excluded) parameters. Each average color measurement is the average of three measurements. Zero calibration and white calibration were performed before measurement. Color is expressed using the CIE 1976 $L^*a^*b^*$ Space system, which uses three parameters to describe color: (1) L^* is luminance (hereafter called lightness) [0 = black; 100 = white]; (2) a^* is greenness/redness [-60 = green; 60 = red]; and (3) b^* is blueness/yellowness [-60 = blue; 60 = yellow] (ISO 11664-4:2008(E)/CIE S 014-4/E:2007).

4.2.5.4 Erosion of Composite Specimens during Weathering

Erosion of radiata pine composite specimens after 2000 hours of natural weathering was measured using a non-contact confocal white light profilometer (AltiSurf[®] 500). Measurement of the erosion of treated samples was difficult because little erosion occurred after 2000 hours (83.3 days) of natural weathering. In addition, warping of some of the specimens occurred

because the uppermost veneer exposed to natural weathering delaminated from the underlying western red cedar core. Furthermore, checks sometimes developed in exposed face veneers. Warping and checking of specimens made it more difficult to measure erosion. Two methods were used to reduce the influence of warping on erosion measurements. Firstly, I separated the uppermost veneer of some specimens from the underlying western red cedar core and sanded the back to make the specimens flat before scanning. Secondly, I increased scanning areas to adjust the reference point to a flat area.

4.3 Results

4.3.1 Effects of PF resin and Wax on Weight Losses, Tensile Strength and Color Stability of Wood Veneers Exposed to Natural Weathering

4.3.1.1 Percentage Weight Losses

There was a significant effect ($p < 0.05$) of chemical treatment on weight losses of veneers exposed to natural weathering (**Figure 4.10**), but there was no significant effect ($p > 0.05$) of concentration of PF resin on weight losses of treated veneers during weathering. The wax additive had no significant ($p > 0.05$) effect on weight losses of veneers treated with PF resin, but the weight losses of wax treated controls (W) were significantly ($p < 0.05$) lower than those of untreated exposed controls (Con) (**Figure 4.10**).

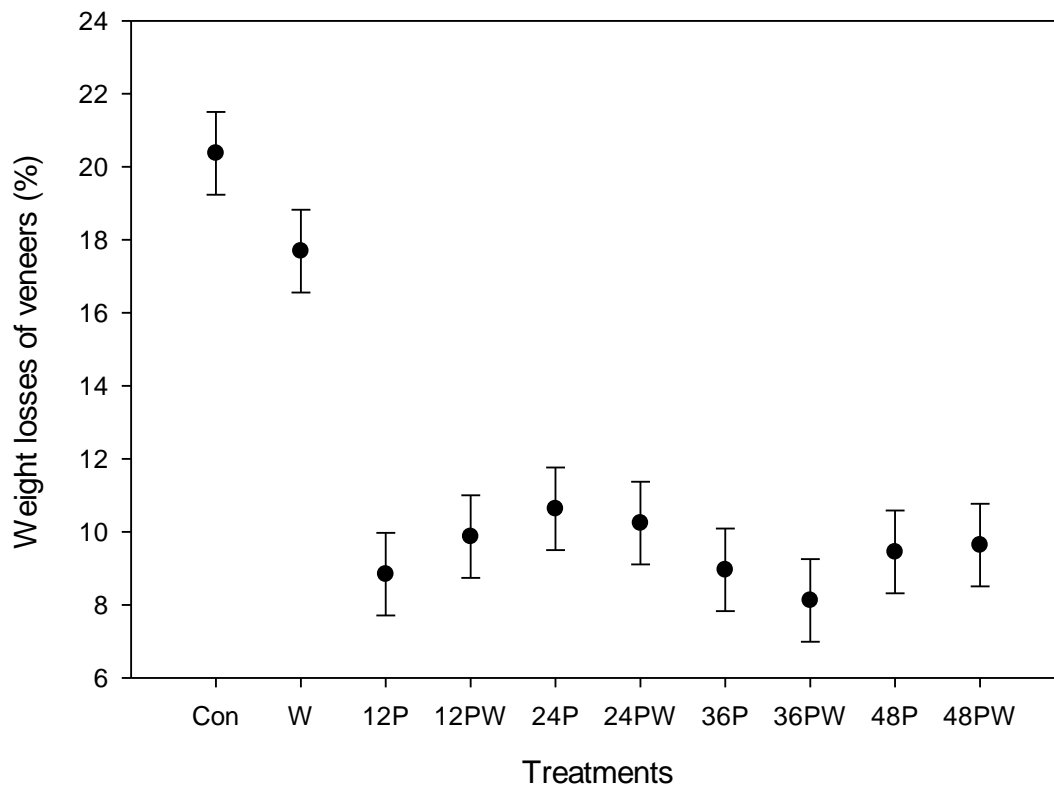


Figure 4.10 Percentage weight losses of treated veneers after 50 days natural weathering (Con = Control; W = 2.5% Wax; 12 P = 12% PF resin; 12 PW = 12% PF resin containing 2.5% wax; 24 P = 24% PF resin; 24 PW = 24% PF resin containing 2.5% wax; 36 P = 36% PF resin; 36 PW = 36% PF resin containing 2.5% wax; 48 P = 48% PF resin; 48 PW = 48% PF resin containing 2.5% wax). Error bars represent 95% confidence intervals

The percentage weight gain of treated wood veneers significantly increased with an increase in the concentration of PF resin used to treat veneers. However, these increased weight gains were not reflected in the weight losses of treated veneers during natural weathering. For example, there was no significant correlation between weight gains due to treatment and weight losses during weathering ($R^2=0.4891$) (**Table 4.8**).

Table 4.8 Percentage weight gains of veneers after treatment and percentage weight losses of veneers after weathering

Treatment	Weight Gain (WG) %	Weight Loss (WG) %
Control	0	20.4
Wax (2.5%)	5.0	17.7
12% PF resin	36.5	8.8
12% PF +2.5% Wax	44.7	9.9
24% PF resin	73.1	10.6
24% PF +2.5% Wax	68.7	10.2
36% PF resin	110.2	9.0
36% PF +2.5% Wax	110.3	8.1
48% PF resin	161.7	9.5
48% PF +2.5% Wax	146.1	9.6

(Con = Control; W = 2.5% Wax; 12 P = 12% PF resin; 12 PW = 12% PF resin containing 2.5% wax; 24 P = 24% PF resin; 24 PW = 24% PF resin containing 2.5% wax; 36 P = 36% PF resin; 36 PW = 36% PF resin containing 2.5% wax; 48 P = 48% PF resin; 48 PW = 48% PF resin containing 2.5% wax)

4.3.1.2 Tensile Strength

Veneers treated with higher concentrations of PF resin (>24%) were generally significantly stronger after natural weathering than the controls, or veneers treated with 12% PF resin, with the exception of veneers treated with 48% PF resin. The tensile strength of veneers treated with 12% PF resin was not significantly ($p < 0.05$) greater than that of the controls. The addition of wax to the PF resin did not produce positive effects on tensile strength of veneers treated with 12%, 24% or 36% PF resin. However, the tensile strength of veneers treated with 48% PF resin containing wax and exposed to weathering was significantly ($p = 0.007$) greater than that of similarly exposed veneers that had been treated with 48% PF resin (**Figure 4.11**).

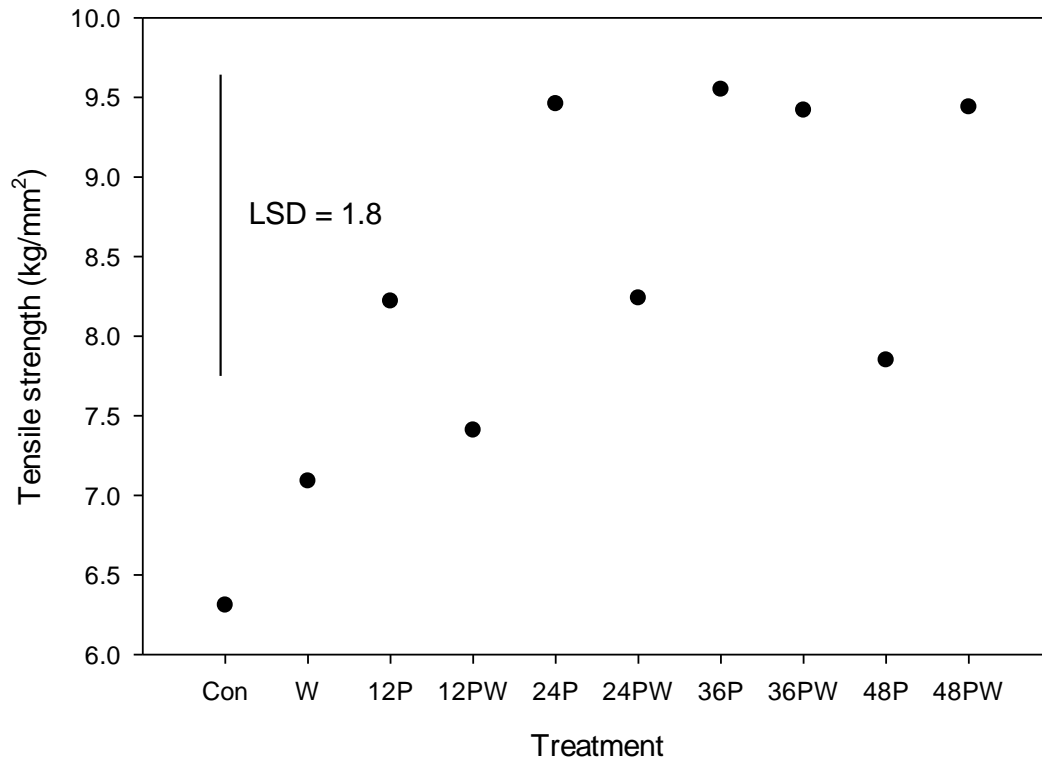


Figure 4.11 Zero-span tensile strength of treated veneers after 50 days natural weathering (Con = Control; W = 2.5% wax; 12 P = 12% PF resin; 12 PW = 12% PF resin containing 2.5% wax; 24 P = 24% PF resin; 24 PW = 24% PF resin containing 2.5% wax; 36 P = 36% PF resin; 36 PW = 36% PF resin containing 2.5% wax; 48 P = 48% PF resin; 48 PW = 48% PF resin containing 2.5 % wax)

All treatments had a positive effect on losses of tensile strength of veneers during natural weathering (**Table 4.9**). Treatment solutions containing 24% and 36% PF resin were better at restricting tensile strength losses during natural weathering than treatment solutions containing 12% or 48% PF resin. Wax significantly increased the ability of PF resin to restrict tensile strength losses during weathering except the treatment containing 24% PF resin.

Table 4.9 Tensile strength and tensile strength losses of veneers after weathering

Treatment	Tensile strength (kg/mm ²)		Tensile strength losses %
	Before weathering	After weathering	
Control	10.11	6.31	37.6
Wax (2.5%)	10.36	7.09	31.6
12% PF resin	10.21	8.22	19.5
12% PF resin +2.5% Wax	8.68	7.41	14.6
<u>24% PF resin</u>	10.81	9.46	<u>12.5</u>
24% PF resin +2.5% Wax	10.16	8.24	18.9
36% PF resin	10.99	9.55	13.1
<u>36% PF +2.5% Wax</u>	9.85	9.42	<u>4.4</u>
48% PF resin	10.15	7.85	22.7
<u>48% PF resin +2.5% Wax</u>	9.93	9.44	<u>5.0</u>

4.3.1.3 Color Changes

Untreated veneers were light yellow. They became a straw color after 50 days natural weathering. Veneers treated with PF resin were yellow. Their yellow color deepened during weathering and they became redder. The wax additive slightly decreased the yellowing of treated veneers both before and after weathering. **Figure 4.12** shows the appearance of veneers after treatment and after weathering.

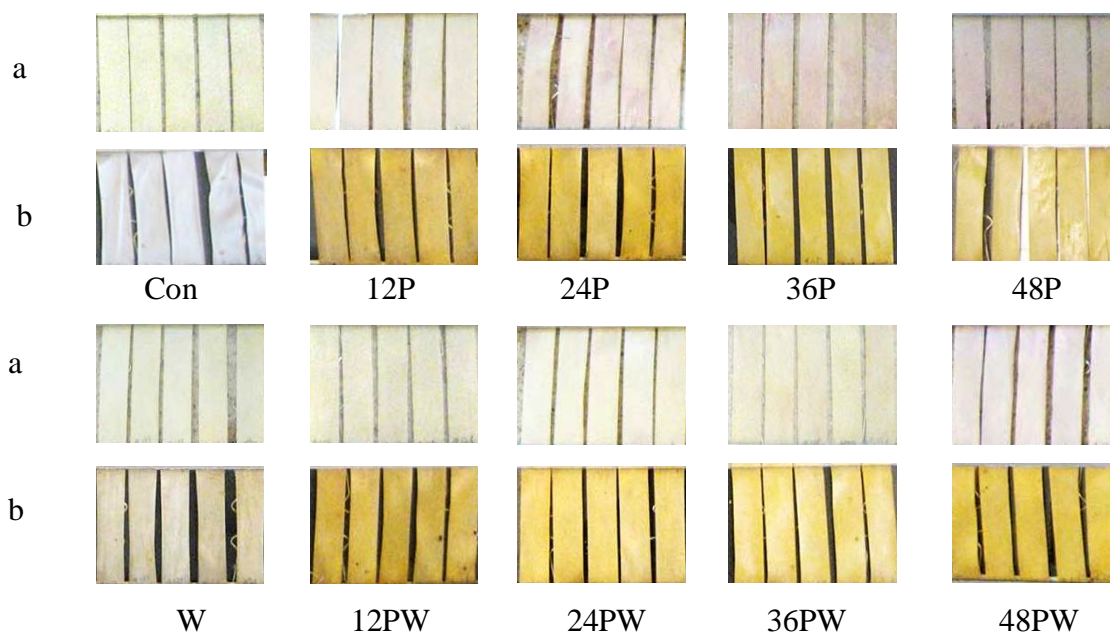


Figure 4.12 Appearance of treated wood veneers before and after weathering (a = Veneers without weathering; b = Veneers weathered. Con = Control; 12 P = 12% PF resin; 24 P = 24% PF resin; 36 P = 36% PF resin; 48 P = 48% PF resin; W = 2.5% Wax; 12 PW = 12% PF resin containing 2.5% wax; 24 PW = 24% PF resin containing 2.5% wax; 36 PW = 36% PF resin containing 2.5% wax; 48 PW = 48% PF resin containing 2.5% wax)

Table 4.10 shows the ratio of the lightness (ΔL^*), yellowness (Δb^*) and redness (Δa^*) of veneers after weathering to their lightness, yellowness and redness before weathering. A ratio closer to 1 indicates that less discoloration of veneers occurred during weathering. PF resin treatments at higher concentration reduced the darkening (ΔL^*) of veneers exposed to natural weathering. But these increases in color stability were small and not statistically significant ($p < 0.05$), except for the 36% PF resin treatment that contained wax. In general, the influence of the wax additive on the darkening of PF resin treated veneers was negative. However, the wax additive reduced the darkening of veneers treated with 36% PF resin. Untreated controls became yellower during weathering (Δb^* became smaller), (**Table 4.10**). The wax additive increased yellowing of treated samples. The PF resin treatments reduced yellowing, but veneers became bluer. The 12% PF resin treatment was the best at restricting yellowing of treated veneers during

weathering. Treated veneers and untreated controls became redder during weathering, but PF resin treatments restricted reddening of veneers during weathering, particularly the 24% PF resin treatment.

Table 4.10 Color changes of veneers after 50 days natural weathering

Treatment	Ratio of L*, b* or a* (after weathering/ before weathering)		
	ΔL^*	Δb^*	Δa^*
Control	0.85	0.85	4.18
Wax (2.5%)	0.83	0.77	3.95
<u>12% PF resin</u>	0.82	<u>1.09</u>	2.94
12% PF resin + 2.5% Wax	0.80	1.21	4.02
<u>24% PF resin</u>	0.88	1.16	<u>1.83</u>
24% PF resin + 2.5% Wax	0.81	1.22	3.22
36% PF resin	0.87	1.33	2.08
<u>36% PF resin + 2.5% Wax</u>	<u>0.99</u>	1.36	2.00
48% PF resin	0.88	1.19	2.00
48% PF resin + 2.5% Wax	0.85	1.28	2.33

4.3.2 Effects of Additives on Weight Losses, Tensile Strength and Color Stability of Wood Veneers Exposed to Natural Weathering

4.3.2.1 Percentage Weight Losses

None of the additives on their own, except for iron oxide (IO) restricted weight losses of veneers during natural weathering. Indeed the weight losses of veneers treated with lignosulphonate (Lig) or polyethylene glycol (PEG) were significantly ($p < 0.001$) greater than those of the untreated (exposed) controls (Con), (**Figure 4.13**).

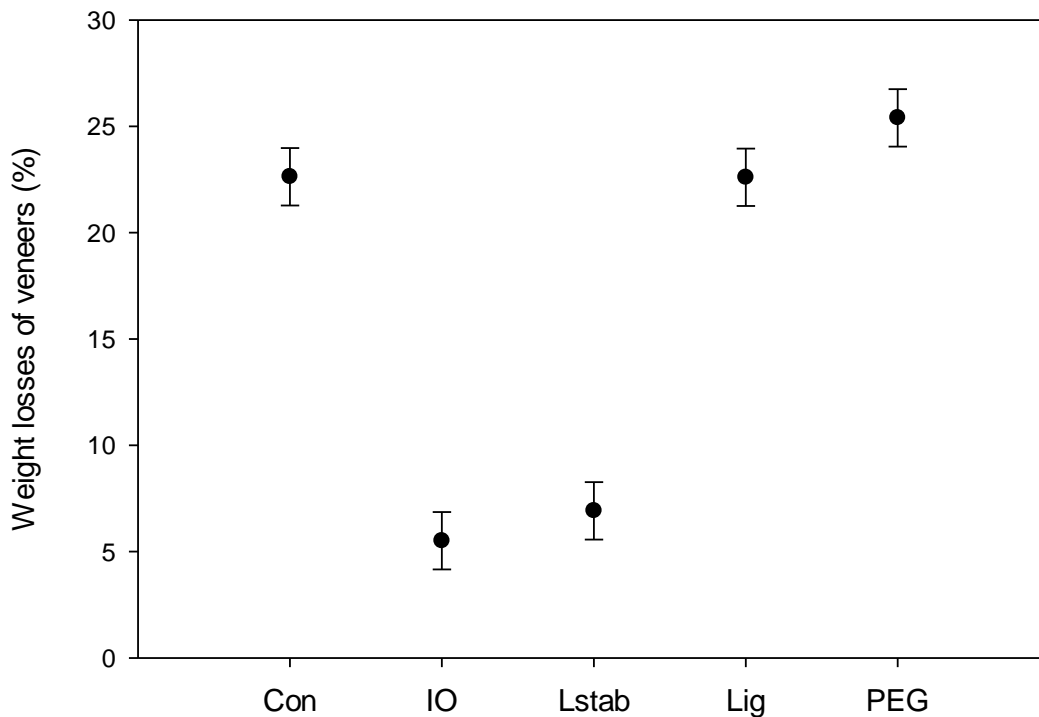


Figure 4.13 Percentage weight losses of veneers treated with different additives after 35 days natural weathering (Con = Control; IO = 1% Iron oxide; Lstab = 2% Lignostab 1198; Lig = 10% Lignosulphonate; PEG = 10% Polyethylene glycol). Error bars represent 95% confidence intervals

4.3.2.2 Tensile Strength

Figure 4.14 plots the tensile strength of treated veneers after natural weathering. Veneers treated with iron oxide were significantly stronger ($p < 0.05$) than the untreated controls (Con) or veneers treated with the other additives (Lstab, Lig or PEG). There was no significant difference ($p > 0.05$) in the tensile strength of veneers treated with lignostab, lignosulphonate or PEG after the veneers were exposed to natural weathering.

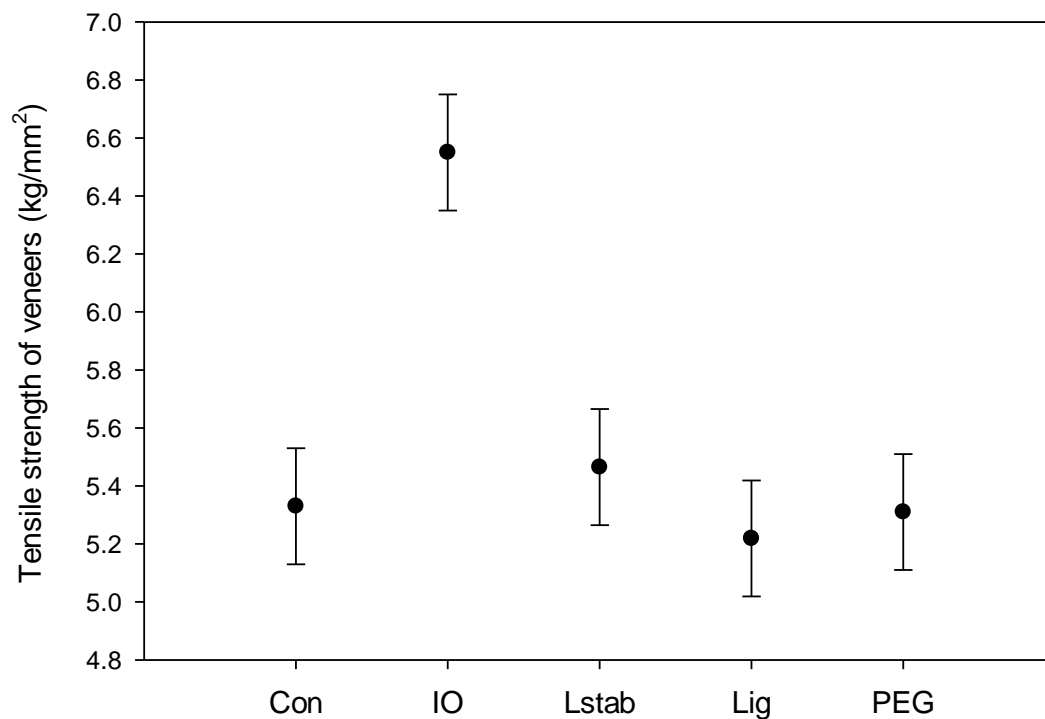


Figure 4.14 Zero-span tensile strength of treated veneers after 35 days natural weathering (Con = Control; IO = 1% Iron oxide; Lstab = 2% Lignostab; Lig = 10% Lignosulphonate; PEG = 10% Polyethylene glycol). Error bars represent 95% confidence intervals

Table 4.11 shows the tensile strength of veneers before and after weathering and the percentage tensile strength losses due to weathering. Iron oxide restricted tensile strength losses, whereas the other treatments were ineffective.

Table 4.11 Tensile strength of veneers before and after weathering and tensile strength losses after weathering

Treatment	Tensile strength (kg/mm ²)		Tensile strength loss (%)
	Before weathering	After weathering	
Control	9.89	5.33	46.1
<u>1% Iron oxide</u>	9.52	6.55	<u>31.2</u>
2% Lignostab 1198	11.62	5.47	53.0
10% Lignosulphonate	10.87	5.22	52.0
10% Polyethylene glycol	9.93	5.31	46.5

4.3.2.3 Color Changes

Figure 4.15 shows the appearance of veneers after treatment with the additives (on their own) and after weathering. Untreated veneers were light yellow. They became a straw color after weathering. Veneers treated with an aqueous solution containing liginosulphonate were dark brown. They became light yellow after weathering. Veneers treated with PEG were whitish. They became a washed-out straw color after weathering. Veneers treated with lignostab were yellow. They became a deep straw color after weathering. Finally, veneers treated with iron oxide were a deep yellow color. They became light brown after weathering.

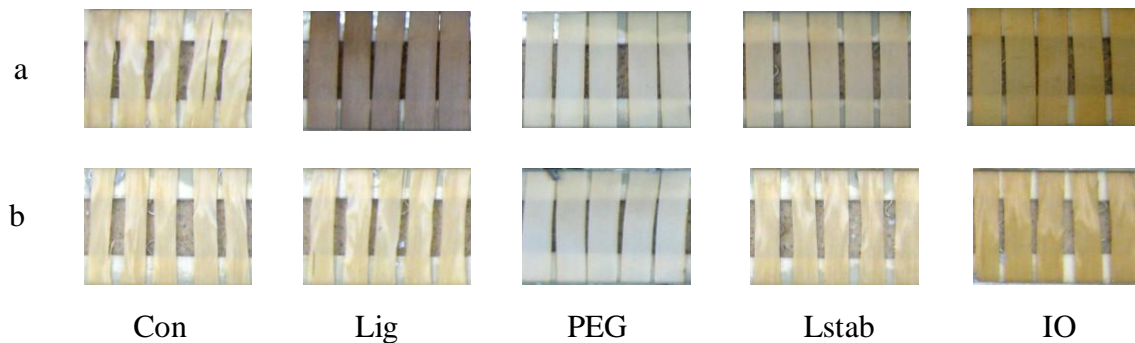


Figure 4.15 Appearance of treated wood veneers before and after weathering
(a = Veneers without weathering; b = Veneers after weathering) (Con = Control; Lig = 10% Liginosulphonate; IO = 1% Iron oxide; Lstab = 2% Lignostab 1198; PEG = 10% Polyethylene glycol)

The changes in lightness and yellow color of veneers treated with liginosulphonate during weathering are reflected in significantly higher ($p < 0.05$) lightness and yellowness ratios (**Table 4.12**). The darkening of untreated controls (Con) or treated veneers during weathering is reflected in lightness ratios that are less than 1 (**Table 4.12**). The lightness ratio of veneers treated with lignostab is closest to 1 indicating that this treatment was the most effective one at restricting darkening of veneers during natural weathering. The b-ratios of veneers are less than 1 indicating that veneers became yellow during weathering, except those treated with liginosulphonate.

Table 4.12 Color changes of veneers exposed to 35 days natural weathering

Treatment	Ratio of L* or b* (after weathering/ before weathering)	
	ΔL^*	Δb^*
Control	0.94	0.95
1% Iron oxide	0.85	0.75
<u>2% Lignostab 1198</u>	<u>0.97</u>	0.93
10% Lignosulphonate	1.30	1.14
10% Polyethylene glycol	0.93	0.89

4.3.3 Effects of PF Resin and Additives on Weight Losses, Tensile Strength and Color Stability of Wood Veneers Exposed to Natural Weathering

4.3.3.1 Percentage Weight Losses

The 12% PF resin treatment (PF) was very effective at restricting weight losses of treated wood veneers exposed to natural weathering (**Figure 4.16**). The additives when incorporated into the PF resin did not increase the ability of the PF resin to restrict weight losses of treated veneers during natural weathering (**Figure 4.16**). In fact weight losses of veneers treated with 12% PF resin containing lignosulphonate (PFLig) or polyethylene glycol (PFPEG) during natural weathering were significantly greater ($p < 0.05$) than those of veneers treated with PF resin alone or PF resin containing iron oxide (PFIO) or lignostab (PFLstab). The weight losses of treated veneers after weathering were not significantly correlated ($R^2 = 0.62$) with weight gains due to treatment.

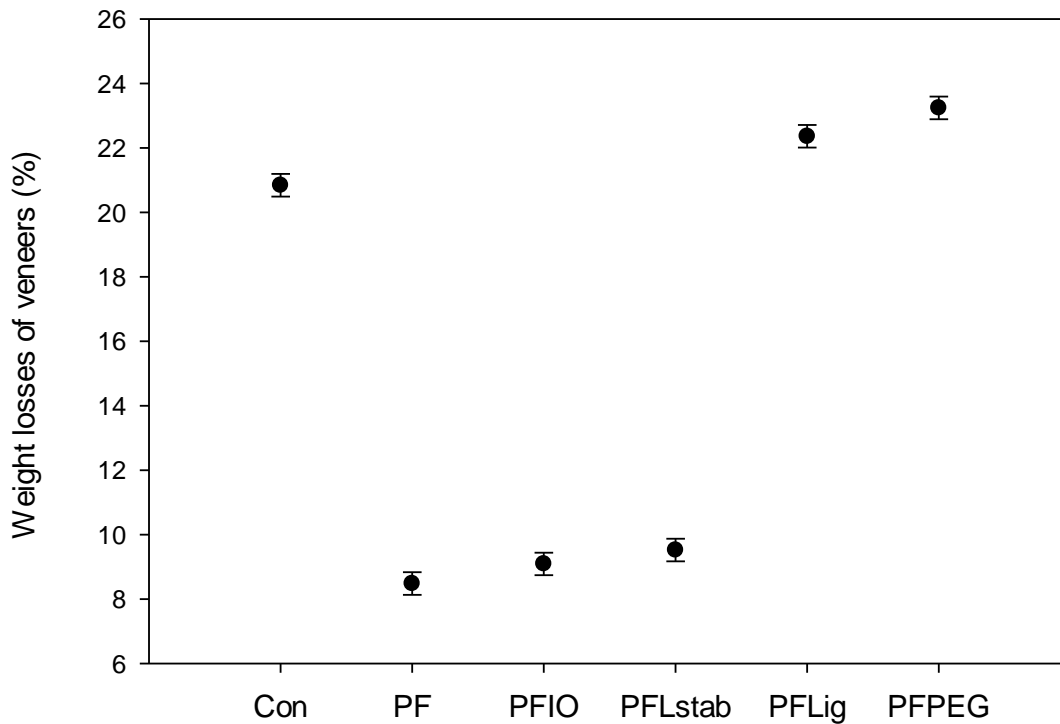


Figure 4.16 Percentage weight losses of treated wood veneers after 50 days natural weathering (Con = Control; PF = 12% PF resin; PFIO = 12% PF resin + 1% Iron oxide; PFLstab = 12% PF resin + 2% Lignostab; PFLig = 12% PF resin + 10% Lignosulphonate; PFPEG = 12% PF resin + 10% Polyethylene glycol). Error bars represent 95% confidence intervals

4.3.3.2 Tensile Strength

Veneers treated with 12% PF resin and 12% PF resin containing the different additives and exposed to natural weathering were significantly stronger ($p < 0.001$) than the untreated weathered controls (**Figure. 4.17**).

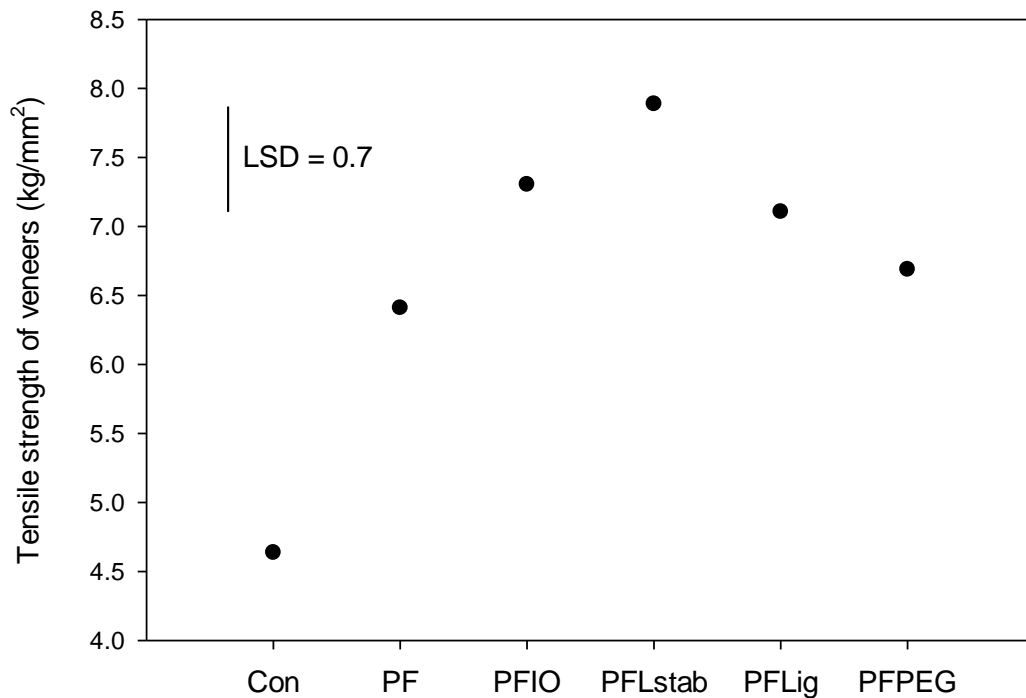


Figure 4.17 Zero-span tensile strength of treated veneers after 50 days natural weathering (Con = Control; PF = 12% PF; PFIO = 12% PF+ 1% Iron oxide; PFLstab = 12% PF+2% Lignostab; PFLig = 12% PF+10% Lignosulphonate; PFPEG = 12% PF+10% Polyethylene glycol). Error bars represent 95% confidence intervals

The lignostab and iron oxide additives increased the ability of PF resin to restrict tensile strength losses of treated wood veneers exposed to natural weathering. However, the opposite was the case for the lignosulphonate and PEG additives (**Table 4.13**).

Table 4.13 Tensile strength of veneers and tensile strength losses after weathering

Treatment	Tensile strength (kg/mm ²)		Tensile strength loss (%)
	Before weathering	After weathering	
Control	10.07	4.63	54.0
12% PF resin	10.03	6.41	36.1
<u>12% PF + 1% Iron oxide</u>	9.32	7.30	<u>21.6</u>
12% PF + 10%Lignosulphonate	12.18	7.10	41.6
12% PF + 10% Polyethylene glycol	11.61	6.68	42.4
<u>12% PF + 2% Lignostab 1198</u>	9.90	7.88	<u>20.3</u>

4.3.3.3 Color Changes

Untreated veneers were light yellow. They became a straw color after 50 days natural weathering. Veneers treated with PF resin were purplish yellow. They became a deep yellow color after weathering. Veneers treated with PF resin containing lignin were dark brown. They became brown after weathering. Veneers treated with PF resin containing PEG were yellowish. They became brown after weathering. Veneers treated with PF resin containing lignostab were purplish in color. They became brown after weathering. Finally, veneers treated with PF resin containing iron oxide were deep yellow in color. They became brown after weathering. **Figure 4.18** shows the appearance of veneers after treatment and after weathering.

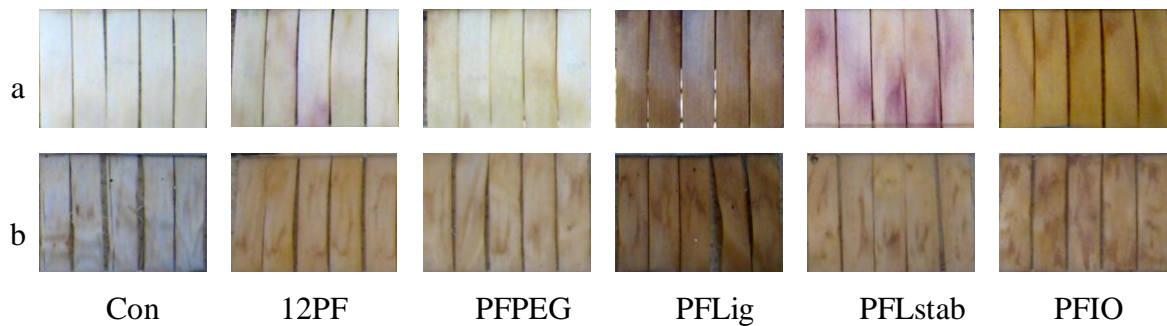


Figure 4.18 Appearance of treated veneers before and after natural weathering
(a = Treated veneers without weathering; b = Treated veneers after weathering. Con = Control; P = 12% PF resin; PFPEG = 12% PF resin + 10% Polyethylene glycol; PFLig = 12% PF resin + 10% Lignosulphonate; PFLstab = 12% PF resin + 2% Lignostab; PFIO = 12% PF resin + 1% Iron oxide)

The PF resin did not restrict the darkening of treated wood veneers exposed to natural weathering, because there was no significant ($p > 0.05$) difference in the L-ratio of the veneers treated with 12% PF resin and the untreated controls. Veneers treated with PF resin and iron oxide (PFIO) showed the largest change in L-ratio during weathering, whereas the change in the L-ratio of veneers treated with PF resin and lignosulphonate (PFLig) or lignostab (PFLstab) were the smallest. The L-ratio of veneers treated with PF resin and polyethylene glycol (PFPEG) was

similar to that of the untreated control. All the treatments either increased yellowness or blueness except PEG.

Table 4.14 Color changes of veneers exposed to 50 days natural weathering

Treatment	Ratio of L* or b* (after weathering/ before weathering)	
	ΔL^*	Δb^*
Control	0.79	0.98
12% PF resin	0.78	1.30
12% PF resin + 1% Iron oxide	0.75	0.88
<u>12% PF resin + 2% Lignostab 1198</u>	<u>0.93</u>	1.45
12% PF resin + 10% Lignosulphonate	1.04	1.52
<u>12% PF resin + 10% Polyethylene glycol</u>	0.80	<u>1.00</u>

4.3.4 Effects of PF Resin and Additives on Color Stability and Erosion of Radiata Pine Veneer-Based Composites Exposed to Natural Weathering

4.3.4.1 Color Changes

Untreated veneer-based composite specimens were light brown. They became grey after 2000 hours (83.3 days) of natural weathering. Specimens treated with PF resin became purplish brown. They became yellow-brown after weathering. The color of specimens after treatment was related to the concentration of PF resin used to treat specimens. The higher the concentration of PF resin, the deeper the purplish-brown color of treated specimens. Specimens treated with PF resin containing PEG were light purplish and they became yellow after weathering. Specimens treated with PF resin containing iron oxide were brown and they became dark brown after weathering. Specimens treated with PF resin containing lignostab were purplish brown and they became yellow after weathering. **Figure 4.19** shows the appearance of treated veneer-based wood composites after 2000 hours (83.3 days) of natural weathering.



Figure 4.19 Appearance of treated radiata pine specimens after 2000 hours of natural weathering (The circular areas inside the specimens were exposed to natural weathering, whereas the areas outside the circles were covered by metal masks. Con = Control; 10PF = 10% PF resin; 20PF = 20% PF resin; 30PF = 30% PF resin; PFPEG = 10% PF resin + 10% Polyethylene glycol; PFIO = 10% PF resin + 1% Iron oxide; PFLstab = 10% PF resin + 2% Lignostab)

A 10% PF resin treatment significantly restricted discoloration of radiata pine veneer-based composites exposed to natural weathering for 2000 hours (**Table 4.15**). The lignostab additive was particularly effective at restricting discoloration of PF-treated specimens exposed to natural weathering. Iron oxide was also effective at restricting yellowing of PF-treated specimens. However, increasing the concentrations of PF resin did not improve the color stability of the radiata pine specimens. Similarly, the PEG additive did not improve the ability of PF resin to restrict discoloration of radiata pine specimens.

Table 4.15 Color changes of radiata pine veneer-based composite specimens exposed to 2000 hours of natural weathering

Treatment	Ratio of L, b, or a (after weathering/before weathering)		
	ΔL^*	Δb^*	Δa^*
Control	0.77	0.68	0.77
<u>10% PF resin</u>	<u>0.84</u>	1.33	2.37
20% PF resin	0.77	1.39	2.99
30% PF resin	0.75	1.40	3.14
<u>10% PF resin + 2% Lignostab 1198</u>	<u>0.97</u>	1.55	1.59
<u>10% PF resin + 1% Iron oxide</u>	0.83	<u>1.02</u>	1.43
10% PF resin + 10% Polyethylene glycol	0.84	1.33	2.39

4.3.4.2 Erosion

Originally I intended to expose treated specimens to 1000 hours of natural weathering, but there was almost no erosion of treated specimens after 1000 hours exposure. Therefore the exposure time was increased to 2000 hours (83.3 days). Nevertheless, even after 2000 hours exposure the erosion of treated specimens was small and some specimens warped and cracked, which made it difficult to measure erosion. **Figures 4.20 and 4.21** show that the PF resin treatment significantly reduced the mass loss and mean erosion depth of radiata pine specimens exposed to natural weathering. There was a positive effect of PF resin concentration (10, 20 and 30%) on the ability of the PF resin treatments to restrict mass losses of samples during natural weathering.

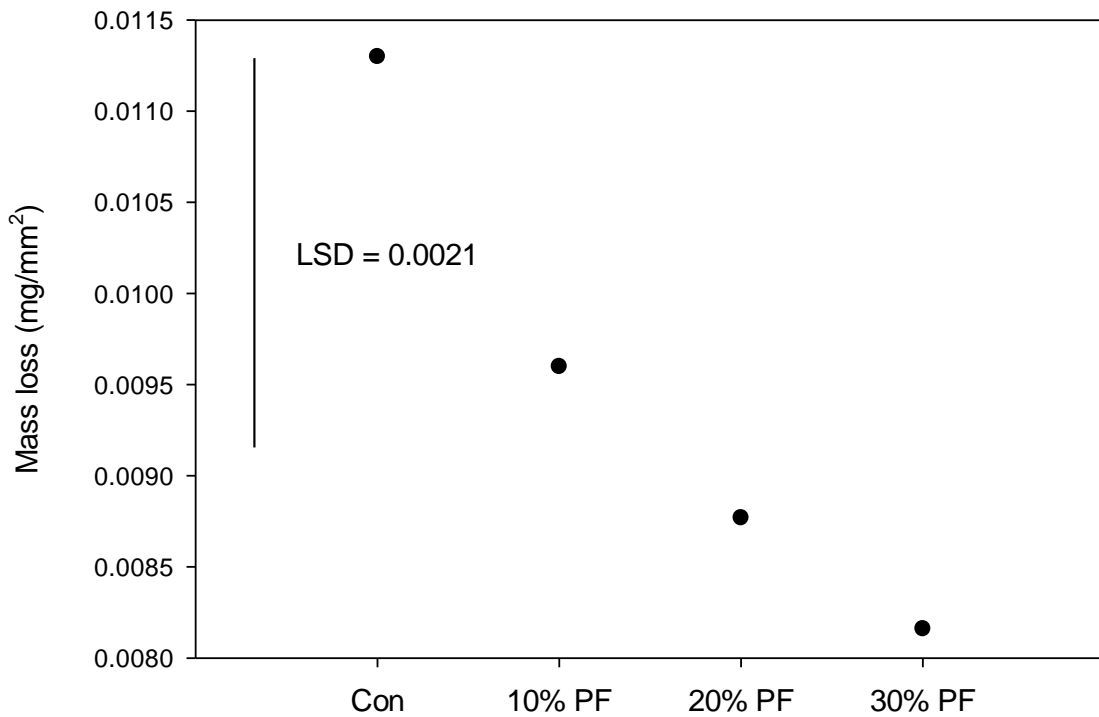


Figure 4.20 Mass losses of treated radiata pine specimens exposed to 2000 hours of natural weathering (Con = Control; 10PF = 10% PF resin; 20PF = 20% PF resin; 30PF = 30% PF resin)

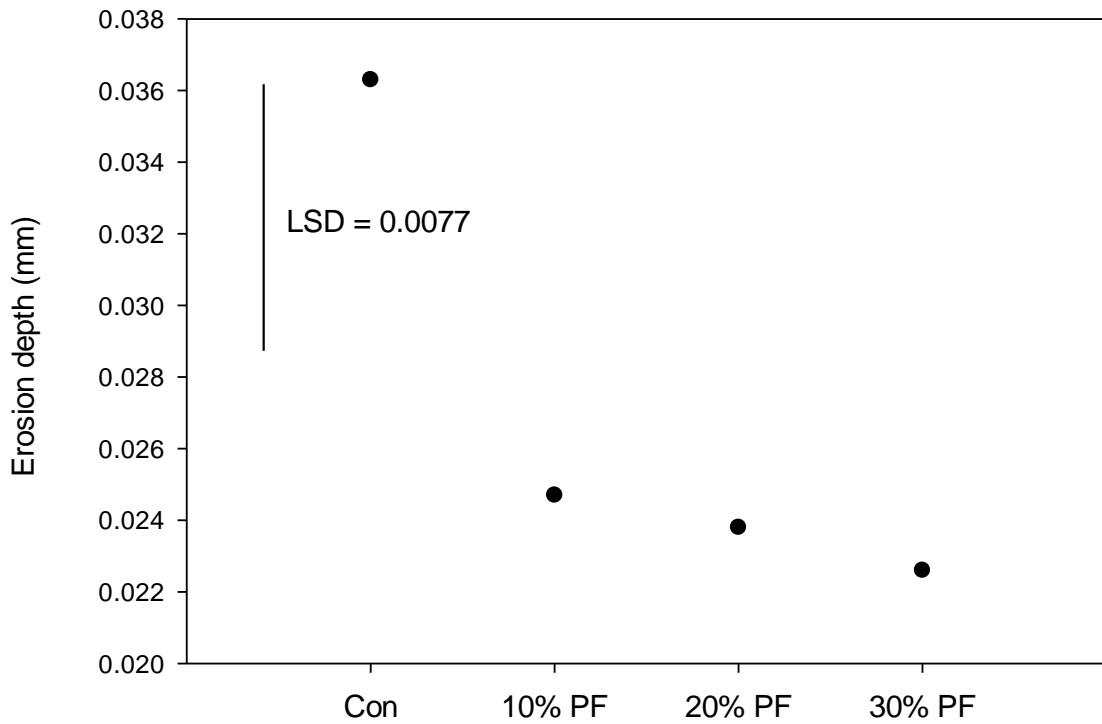


Figure 4.21 Erosion depth of treated radiata pine specimens exposed to 2000 hours of natural weathering (Con = Control; 10PF = 10% PF resin; 20PF = 20% PF resin; 30PF = 30% PF resin)

The iron oxide and lignostab additives had positive effects on the ability of the PF resin treatments to restrict the erosion of treated radiata pine specimens exposed to natural weathering, although the differences between the treatments were not statistically significant ($p > 0.05$). However, treated samples showed significantly ($p < 0.05$) less erosion than that of the untreated controls (**Figure 4.22**).

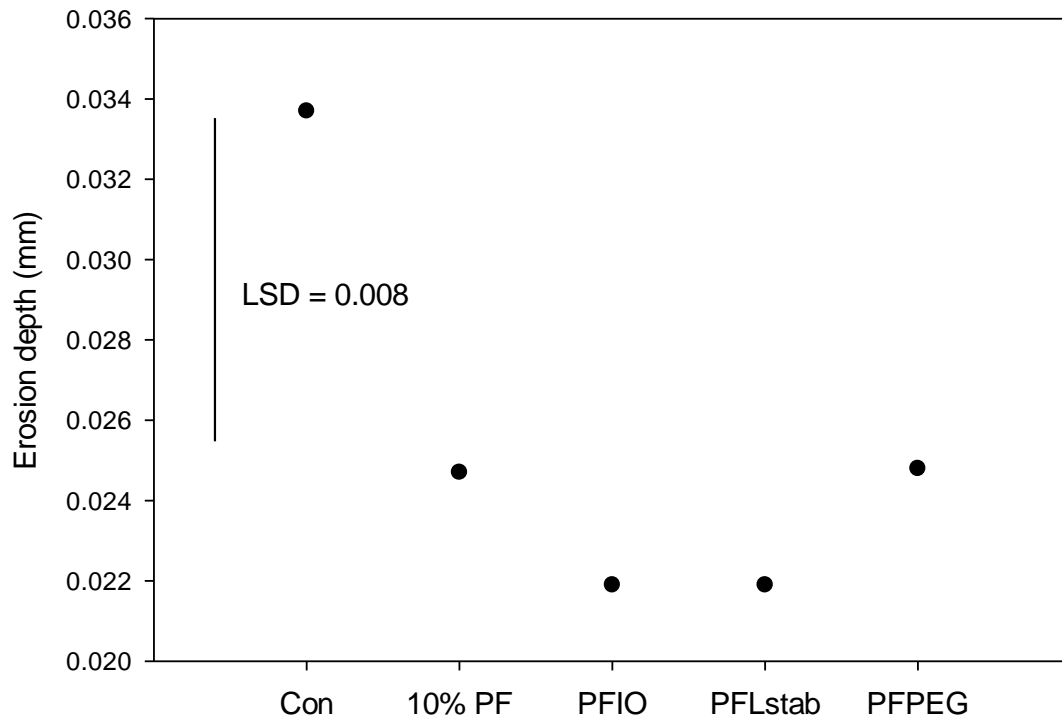


Figure 4.22 Mean erosion depths of treated radiata pine specimens exposed to 2000 hours of natural weathering (Con = Control; 10PF = 10% PF resin; PFIO = 10% PF resin + 1% Iron oxide; PFLstab = 10% PF resin + 2% Lignostab 1198; PFPEG = 10% PF resin + 10% Polyethylene glycol)

4.4 Discussion

This work demonstrated that PF resin treatment significantly reduced the erosion of radiata pine specimens exposed to natural weathering for 2000 hours. The erosion of the treated radiata pine veneer composites during natural weathering was very small because the PF resin treatment was effective at photostabilizing wood.

However, it was difficult to measure the erosion of treated specimens using confocal profilometry for three reasons. Firstly, very little erosion of treated specimens occurred during the 2000 hour (83.3 days) weathering trial. Secondly, checks developed in the specimens during weathering particularly in the corners where metal masks were fixed to the underlying wood.

These cracks sometimes extended into unmasked (weathered) areas of the specimens. Voids in the unmasked areas created by checks artificially inflated erosion measurements. Thirdly, specimens warped, possibly because they were made from different wood species with different water absorption characteristics. These differences may have created unbalanced stresses in specimens and caused delamination at glue lines. I tried to minimize the effect of warping on measurements by separating the outer radiata pine veneer from the underlying western red cedar veneer and sanding the back of the radiata pine veneer to create a flat specimen. Nevertheless, measurement errors were still large. As a result, it was difficult to detect significant differences in the erosion of samples treated with the various PF resin formulations. It is possible that greater differences may have emerged if the exposure time had been extended.

My results clearly show that PF resin can increase the photostability of wood, which would explain why studies have shown that PF resin treatment can reduce the surface cracking of plywood, and maintain the mechanical properties and reduce discoloration of wood exposed to weathering (Stamm and Seborg 1939; Lloyd and Stamm 1958; Stamm and Seborg 1962; Sudiyani *et al.*, 1999; Imamura 2007).

My experiment that examined the effects of different concentrations of PF resin on the photostability of wood veneers found that a 12% PF resin treatment was as effective as treatments that contained higher concentrations of PF resin at restricting weight losses of wood veneers exposed to natural weathering. However, treatments that contained higher concentrations of PF resin (24% and 36%) were generally more effective at restricting tensile strength losses of wood veneers exposed to natural weathering. The treatment containing a low (12%) concentration of PF resin had low viscosity, which may have allowed the PF resin solutions to more easily penetrate wood cell walls than the solutions that contained higher concentrations of

PF resin. Treatments containing higher concentrations of PF resin may deposit some resin in the coarse capillary structure of wood (lumens of tracheids and ray parenchyma), which is less effective at stabilizing wood (Stamm and Seborg 1962). This suggestion may explain why solutions containing 12% PF resin were equally effective as solutions containing higher concentration of PF resin at restricting weight losses of treated veneers exposed to natural weathering. On the other hand, high concentrations of PF resin may have reinforced veneers by creating a highly cross-linked resin network in treated wood (Marra 1992). This suggestion may explain why the tensile strength of treated veneers after weathering was higher for veneers treated with 24% or 36% solutions of PF resin than that of veneers treated with solutions containing 12% PF resin (Stamm and Baechler 1960). Considering all results, the most effective treatment was the one that contained 36% PF resin. The experiment on the weathering resistance of veneer-based wood composites showed that the 30% PF resin treatment was more effective than the 10% PF resin treatment at restricting erosion of treated radiata pine specimens exposed to 2000 hours (83.3 days) of natural weathering. This finding is consistent with the results of other researchers who found that solutions containing 30 to 40% PF resin were the most effective at restricting surface checking and cracking of plywood exposed to natural weathering (Stamm and Baechler 1960; Stamm and Seborg 1962).

Experiments were carried out to try to improve the performance of the PF resin by adding different types of additives, either wax or different photostabilizers. The wax additive was a water-based wax emulsion. This emulsion additive has been shown to be very effective at restricting the checking of wood exposed outdoors (Zahora 2000; Evans *et al.* 2009). However, when the wax emulsion was added to the PF resin it did not greatly improve the ability of the PF resin treatments to photostabilize wood veneers, possibly because it was degraded and washed

away by rain during the weathering trial. The wax emulsion reduced tensile strength losses of wood veneers treated with 36% and 48% PF resin after they were exposed to natural weathering, possibly because it reduced the embrittlement of veneers during weathering. The wax increased the color stability of wood veneers treated with 36% PF resin possibly because it reduced the leaching of PF resin or photo-degraded wood from weathered wood surfaces. Further research, however, would be needed to confirm both these suggestions.

Wood veneers treated with photostabilizers lost more weight than untreated veneers, except for veneers treated with the iron oxide additive. The iron oxide treatment contained a polymer binder, whereas the other treatments contained no binder. Therefore it's likely that the other photostabilizers (lignostab, lignosulphonate and polyethylene glycol) were washed from veneers surfaces during weathering. This suggestion would explain why veneers treated with these additives all lost more weight during weathering than the untreated controls. However, when the lignostab (HALS) was incorporated into 12% PF resin, weight losses of treated veneers during weathering were similar to those of veneers treated with PF resin on its own. This observation suggests that the PF resin can reduce leaching of photostabilizers from exposed wood surfaces. PF resin penetrates into cell walls and forms secondary chemical bonds with the cell wall's polymeric components (Kamke and Lee 2007). This network formed in and on the wood surface may have helped the HALS additive to bond to wood. Amongst all the additives that were added to PF resin, Lignostab 1198 was the most effective at enhancing the ability of the PF resin to photostabilize wood veneers exposed to natural weathering. Lignostab 1198 was also the most effective additive at restricting discoloration of PF resin-treated radiata pine specimens exposed to 2000 hours (83.3 days) of natural weathering. Lignostab[®] 1198 is a hindered amine light stabilizer. Such additives restrict photo-degradation by scavenging free radicals (Ciba Specialty

Chemicals 2005). The ability of the PF/HALS treatment to increase the photostability of wood probably arises because the PF resin absorbs UV light and the lignostab terminates free radicals formed from the photo-oxidation of lignin. Synergistic effects of UV absorbers and HALS on the photostability of polymers have been observed previously (Kurumada *et al.* 1987; Ávár and Bechtold 1999; George *et al.* 2005; Muasher and Sain 2006; Schaller 2007) and it is possible that such an effect accounts for the effectiveness of PF/HALS treatment at photostabilizing wood here. However, further research would be needed to confirm this hypothesis. Iron oxide also improved the ability of PF resin to restrict weight and tensile strength losses of wood veneers exposed to natural weathering. However, increased discoloration of wood veneers treated with PF resin and iron oxide exposed to natural weathering, was noted. Lignosulphonate and PEG were ineffective at improving the ability of PF resin to photostabilize wood veneers even though they are both UV stabilizers (Alexy *et al.* 2000; El-Salamouny *et al.* 2002; Ohkoshi 2002; Bardet *et al.* 2007b; Jeremic *et al.* 2007). Lignosulphonates are very water-soluble and PEG is easily leached from treated wood (Stamm 1974; Ohkoshi 2002). It's possible that PEG and lignosulphonate were washed from PF resin treated veneers, which explains why they were less effective than lignostab and iron oxide at photostabilizing veneers.

4.5 Conclusions

PF resin was effective at restricting weight and tensile strength losses and color changes of yellow cedar wood veneers exposed to natural weathering. PF resin treatments also restricted the erosion and color changes of radiata pine specimens exposed to natural weathering. Therefore my results confirm the hypothesis posed at the start of this chapter and provide further evidence

that creating cross-linked aromatic groups in wood cell walls is an effective route to photostabilizing wood.

There was some evidence that the effectiveness of the PF resin treatment could be improved by increasing the concentration of the PF resin solution. For example, the treatment containing 36% PF resin was very effective at restricting weight and tensile strength losses and color changes of wood veneers exposed to weathering. Furthermore, the 30% PF resin treatment was very effective at restricting the erosion of radiata pine composite-veneer specimens exposed to natural weathering. Therefore, I recommended that future research and trials should focus on treatment solutions that contain 30% PF resin.

The addition of a photostabilizer to PF resin was a more effective way of increasing the ability of the PF resin to photostabilize wood than increasing the concentration of PF resin. The hindered amine light stabilizer lignostab 1198 in particular, and to a lesser extent iron oxide were effective photostabilizing additives for the PF resin. Incorporating additives into PF resin provides a cost-effective way of improving the ability of PF resin to photostabilize wood. Instead of looking for new resin systems to protect wood from weathering, future research should identify synergistic combinations of UV absorbers and HALS to add to low molecular weight PF resins.

Measurement of erosion of treated wood using confocal profilometry is not effective if the treatment is very effective at restricting erosion and the exposure time is relatively short, and the measurement process can be confounded by warping and cracking of specimens during weathering.

CHAPTER 5: GENERAL DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

5.1 General Discussion

This study demonstrated that erosion of untreated western red cedar wood could be accurately quantified by combining confocal profilometry and artificial weathering. I was able to quantify the erosion of western red cedar in a xenon-arc weatherometer after only 100 hours, whereas previously a minimum time of 600 hours of artificial weathering was needed before erosion could be quantified using optical microscopy (Arnold *et al.* 1991, Williams *et al.* 2001d). Numerous measurements were made within eroded areas using confocal profilometry. The erosion values I obtained from the profilometer were the average of 6944 measurements per mm². In comparison, optical microscopy relies on far fewer measurements. The mean erosion values that previous studies obtained using optical microscopy were averages of 40 measurements (Feist and Mraz 1978, Sell and Feist 1986, Arnold *et al.* 1991, Williams *et al.* 2001d). In addition, the confocal profilometer can be programmed to measure erosion on multiple samples, which makes it less labour intensive to use. Furthermore, software associated with the device is able to automatically calculate maximum erosion depth, mean erosion depth and volume eroded from a defined area and it can visualize erosion in both 2-D and 3-D. Results from an experiment described in Chapter 3 showed that confocal profilometry was clearly able to discern the effects of exposure time, weathering type and area of unmasked wood on erosion. A previous study found that the erosion of wood in fluorescent ultraviolet and xenon-arc weathering chambers was similar (Arnold *et al.* 1991). My results showed that the rate of erosion of western red cedar was much faster in a xenon-arc weatherometer than that in a QUV weatherometer. Furthermore, the rate of erosion of western red cedar samples exposed in a xenon-arc weatherometer here was

greater than that found by Arnold *et al.* (1991). The latter discrepancy may be due to differences in the weatherometers or weathering cycles employed by Arnold *et al.* (1991) and those used here. The degree to which the xenon-arc weatherometer accelerated erosion of samples here was greater than that reported for a carbon arc light weatherometer by Feist and Mraz (1978). This discrepancy may also be related to differences in the weatherometers or weathering cycles employed by Feist and Mraz (1978) and those used here. My results also showed that there was a positive correlation between the size of the unmasked area and the erosion of wood during artificial accelerated weathering and also natural weathering. It is possible that reduced erosion next to the edges of unmasked areas, which represents a smaller proportion of the large unmasked areas than the smaller ones, may explain the positive correlation between erosion and size of unmasked areas. Nevertheless, some factors limit the speed and accuracy of erosion measurements made using confocal profilometry. For example, there has to be a distinct difference in erosion between unmasked areas and masked areas. If the boundary between the eroded (unmasked) and uneroded (masked) area is not clear then it is difficult to accurately calculate erosion area and volume of wood removed. Furthermore, erosion depth measurements could include measurement on masked area, which would affect the accuracy of mean values for erosion depth.

Confocal profilometry was less effective at differentiating between the ability of chemical treatments to restrict the erosion of wood. Experiments in Chapter 4 used the thin strip technique and confocal profilometry measurements of the erosion of solid wood samples to evaluate the ability of phenol formaldehyde resin treatments to photostabilize wood. The thin strip technique was able to discern differences between treatments, and also between treated veneers and untreated controls. In contrast, confocal profilometry was only able to discern significant

($p < 0.05$) differences in the erosion of treated specimens and untreated controls, because the differences in erosion of specimens impregnated with various PF resin were very small, on the order of 22 microns.

A further difficulty encountered when using confocal profilometry to measure the erosion of treated wood was the sensitivity of the device to the form of the wood surface. Vacuum impregnation, drying and curing processes were involved in the treatment of sawn radiata pine veneers with PF resin. Then adhesive was applied to veneers and mechanical pressure was used to bond treated veneers to a western red cedar core. The resulting composites tended to distort during weathering, possibly because they were made of veneers from two different species that have different water absorption characteristics. Failure of the glueline between different layers of veneers in some of the composites also contributed to the distortion of specimens. Furthermore, cracks developed at the surface of the composites particularly around the screw holes that were used to fix the metal mask to the surface of the treated veneer. Both the distortion of composite samples and cracking of surface veneers confounded the process of measuring erosion using confocal profilometry. Distortion of wood samples changed the reference point for measurements. Cracking of wood samples created voids at the wood surface. The depth and volume of these voids were measured by the profilometer, which artificially inflated erosion depth and volume parameters for samples that contained cracks. In contrast, the conventional thin strip method proved to be a faster and more effective method of ranking various PF resin treatments for their ability to photostabilize wood.

This thesis also examined the ability of various PF resin treatments to photostabilize wood. Results in Chapter 4 showed that a low molecular weight, water-soluble, PF resin was able to photostabilize wood. For example, the PF resin restricted weight and tensile strength losses and

increased color stability of wood veneers exposed to natural weathering. The PF resin also restricted erosion and discoloration of veneer-based wood composites exposed to natural weathering. These positive effects of the PF resin on the photostability of wood might be explained as follows: (1) PF resin in the wood cell wall may have absorbed UV radiation and protected lignin and wood's other chemical constituents from photodegradation; (2) PF resin deposited in the wood cell wall had a bulking effect and replaced hydroxyl groups on cellulose and lignin with less hygroscopic groups, which also improves the photostability of wood (Feist *et al.* 1991); (3) Bonds formed between the PF resin and wood's cellular and molecular constituents reinforced the wood and reduced the erosion and weight losses of treated samples (Feist *et al.* 1991). The ability of PF resin to photostabilize wood was improved when the UV stabilizers, Lignostab or iron oxide were added to the PF resin. Adding these compounds to the PF resin was a more effective way of improving the ability of the resin to increase the photostability of wood than increasing the concentration of the resin in the treatment solution. Lignostab can scavenge free radicals, and iron oxides can reflect and screen UV light (Ciba 2005; Blackburn and Meldrum 1991; Hocken *et al.* 1999). These photoprotective effects may explain why the additives improved the performance of the PF resin. UV stabilizers are easily leached from wood, but PF resin forms a cross-linked polymer after curing and this probably reduced such leaching. Incorporating a UV absorber, in addition to HALS in the PF resin might further improve the photostability of wood treated with PF resin because UVA and HALS in combination are known to have synergistic effects on the photostability of polymers (Hayoz *et al.* 2003; de la Caba *et al.* 2007). A range of other additives (wax, PEG, lignosulphonate) was tested to see if they improved the ability of PF resin to photostabilize wood. None of these additives were as effective as

lignostab or iron oxide possibly because they were degraded by UV radiation or leached from treated specimens during weathering (Stamm 1974; Ohkoshi 2002).

5.2 General Conclusions

I conclude that confocal profilometry is a more accurate and less labour-intensive way of measuring the erosion of untreated western red cedar wood during accelerated weathering or natural weathering than optical microscopy. As a result shorter exposure periods are needed to produce levels of erosion that can be measured by the confocal profilometer. However, longer outdoor exposure times in Vancouver are needed to produce erosion of treated wood that can be detected using confocal profilometry. Therefore I conclude that treated specimens should be subjected to artificial weathering to accelerate the erosion of treated wood and reduce the time required to produce levels of erosion that can be accurately quantified using confocal profilometry. Distortion and checking of wood specimens during weathering reduced the accuracy of erosion measurements obtained using confocal profilometry. Therefore, I conclude that treated specimens whose weathering resistance will be assessed using confocal profilometry should be thicker than those tested here so they are less susceptible to distortion. Checking of specimens reduced the accuracy of profilometry measurements. These checks were absent from some areas of the specimens. Hence, it would be possible to reduce their effects on profilometry measurements by using larger specimens and overlaying such specimens with a metal mask that contained multiple unmasked areas and assessing erosion in areas that are free of checks.

Measurement of weight and tensile strength losses of thin, treated wood strips is a faster and easier method than confocal profilometry for screening large numbers of chemicals for their ability to photostabilize wood. Therefore I conclude the use of confocal profilometry to measure

the erosion of treated wood is more suited to the evaluation of smaller numbers of treatments that have undergone preliminary screening using the thin strip technique.

PF resin was effective at restricting weight and tensile strength losses and color changes of wood veneers, and erosion and color changes of veneer-based wood composites exposed to natural weathering. Therefore, I conclude that a low molecular weight, water-soluble PF resin shows promise as a practical method of photostabilizing wood. Finally, I conclude that incorporating UV stabilizing additives into PF resin is a cost-effective way of improving the ability of PF resin to photostabilize wood. The development of a cost-effective PF resin treatment that can photostabilize wood could be important to industry because it could allow for increased use of wood in exterior applications such as cladding, windows and doors.

5.3 Suggestions for Future Research

The use of confocal profilometry to screen chemicals for their ability to photostabilize wood is a new approach and is in its infancy. Research is needed to further investigate and optimize the method as follows. Firstly, as alluded to in the conclusions section above, research is needed to examine whether increasing the number of masked areas and thickness of specimens will reduce the confounding effects that checking and warping had on profilometry measurements, respectively. Secondly, it is possible that solid wood rather than veneer-based wood composites may be more suited to profilometry measurement because solid wood will not delaminate during weathering. Research would be needed to test this hypothesis. Finally, weatherometer trials are needed to determine the exposure times needed to produce measurable levels of erosion in specimens treated with chemicals such as chromic acid and PF resin that are very effective photoprotective treatments for wood.

Low molecular weight PF resin treatments show promise as photostabilizing treatments for wood. However, the mechanism behind the ability of PF resin to photostabilize wood is not clear. Furthermore, we don't know whether PF resins can photostabilize lignin, or how the additives tested here improved the ability of PF resin to photostabilize wood. The chemical changes in wood treated with PF resin systems, both before and after weathering need to be investigated to better understand how PF resin systems can photostabilize wood.

In this thesis, I only examined four water-soluble additives. Research is needed to test different water soluble or emulsifiable additives to see if they can further improve PF resin treatments. In particular, it would be worthwhile to add both a UV absorber and HALS to PF resin because together these additives act synergistically to photostabilize polymers. It would also be interesting to combine inorganic UV absorbers (metal oxides), organic UV absorbers and HALS and add them to PF resin because this combination of UV stabilizers is much more effective than a single UV stabilizer at photostabilizing polymers and wood composites (Hayoz *et al.* 2003; Muasher and Sain 2006; de la Caba *et al.* 2007).

REFERENCES

- Amin, A.A.H., Khattab, M.M., El-Sheikh, M.A.K, El-Salamony, S. 2003. Screening of four lignin additives as UV protectants to baculovirus. *Bulletin of the Entomological Society of Egypt. Economic series*, 29,165-178.
- Alexy, P., Košíková, B., Podstránska, G. 2000. The effect of blending lignin with polyethylene and polypropylene on physical properties. *Polymer*, 41(13), 4901-4908.
- Allen, N.S., Edge, M., Ortega, A., Liauw, C.M., Stratton, J., McIntyre, R.B. 2002. Behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilisers on the photooxidative stability of water based acrylic and isocyanate based acrylic coatings. *Polymer Degradation and Stability*, 78(3), 467-478.
- Aloui, F., Ahajji, A., Irmouli, Y., George, B., Charrier, B., Merlin, A. 2007. Inorganic UV absorbers for the photostabilisation of wood-clearcoating systems: comparison with organic UV absorbers. *Applied Surface Science*, 253(8), 3737-3745.
- Anderson, E.L., Pawlak, Z., Owen, N.L., Feist, W.C. 1991a. Infrared studies of wood weathering. Part I: Softwoods. *Applied Spectroscopy*, 45(4), 641-647.
- Anderson, E.L., Pawlak, Z., Owen, N.L., Feist, W.C. 1991b. Infrared studies of wood weathering. Part II: Hardwoods. *Applied Spectroscopy*, 45(4), 648-652.
- Anikin, L.T., Kraretskii, G.T., Kuzina, O.A. 1992. Heat-resistant adhesive for joining of carbon materials. *Plaste Kautsch*, 39(2), 54-56.
- Arnold, M., Lemaster, R.L., Dost, W.A. 1992. Surface characterization of weathered wood using a laser scanning system. *Wood and Fiber Science*, 24(3), 287-293.
- Arnold, M., Sell, J., Feist, W.C. 1991. Wood weathering in fluorescent ultraviolet and Xenon-arc chambers. *Forest Products Journal*, 41(2), 40-44.
- Avar, L., Bechtold, K. 1999. Studies on the interaction of photoreactive light stabilizers and UV-absorbers. *Progress in Organic Coatings*, 35(1-4), 11-17.
- Bardet, M., Gerbaud, G., Trăn, Q. K., Hediger, S. 2007 b. Study of interactions between polyethylene glycol and archaeological wood components by ¹³C high-resolution solid-state CP-MAS NMR. *Journal of Archaeological Science*, 34(10), 1670-1676.
- Bauer, D.R., Gerlock, J.L., Mielewski, D.F., Paputa Peck, M.C., Carter III R.O. 1990. Photo-stabilization and photo-degradation in organic coatings containing a hindered amine light stabilizer. Part V: Infrared spectroscopic measurements of hindered amine effectiveness. *Polymer Degradation and Stability*, 28(1), 39-51.

- Black, J.M., Mraz, E.A. 1974. Inorganic surface treatments for weather-resistant natural finishes. FPL232, USDA, Madison, WI, USA.
- Blackburn, S.R., Meldrum, B.J., Clayton, J. 1991. The use of fine particle titanium dioxide for UV protection in wood finishes. *Färg Och Lack Scandinavia*, 37(9), 192-196.
- Boas, I.H. 1947. Chapter X: Improved wood. In *the Commercial Timbers of Australia: Their Properties and Uses*, J.J. Gourlev, Government Printer, Melbourne, Australia.
- Bootle K.R. 1983. Wood in Australia. Types, Properties and Uses. McGraw Hill Book, Sydney, pp.333-335.
- Borgin, K. 1971. The mechanism of the breakdown of the structure of wood due to environmental factors. *Journal of the Institute of Wood Science*, 5(4), 26-30.
- Borgin, K., Corbett, K. 1970. The stability and weathering properties of wood treated with various waxes. *Plastics, Paint and Rubber*, 14(3), 69-72.
- Bortolus, P., Camaioni, N., Flamigni, L., Minto, F., Monti Antonio, S. 1992. Photostabilization mechanisms of hindered amine light stabilizers: interaction of singlet and triplet anthracene with piperidine model compounds. *Journal of Photochemistry and Photobiology A: Chemistry*, 68(2), 239-246.
- Brelid, P.L., Westin, M. 2007. Acetylated wood—results from long-term field tests. In: C.A.S. Hill, D., Jones, H., Militz, G.A. Ormondroyd, Eds. *Proceedings of 3rd European Conference on Wood Modification*, pp.71-78.
- Browne, F.L., Simonson, H.C. 1957. The penetration of light into wood. *Forest Products Journal*, 7(10), 308–314.
- Burr, H.K., Stamm, A.J. 1956. Comparison of commercial water-soluble phenol-formaldehyde resinoids for wood impregnation. FPL 1384, USDA, Madison, WI, USA.
- de la Caba, K., Guerrero, P., Del Rio, M., Mondragon, I. 2007. Weathering behaviour of wood-faced construction materials. *Construction and Building Materials*, 21(6), 1288-1294.
- Carlsson, D.J., Jensen, J.P.T., Wiles, D.M. 1984. Antioxidant mechanisms of hindered amine light stabilizers. *Micromolecular Chemistry and Physics*, 8(8), 79-88.
- Chang, S.T., Chang, H.T. 2001. Comparisons of the photostability of esterified wood. *Polymer Degradation and Stability*, 71(2), 261-266.
- Chang, S.T., Cheng, S.S. 2001. Effects of environmental factors on the color of sugi (*Cryptomeria Japonica* D. Don) yellowish heartwood. *Holzforschung*, 55(5), 459-463.

- Chang, S.T., Hon, D.N.S., Feist, W.C. 1982. Photodegradation and photoprotection of wood surfaces. *Wood and Fiber*, 14(2), 104-117.
- Chang, S.T., Wang, S.Y., Su, Y.C. 1998. Retention of red color in Taiwania (*Taiwania Cryptomeriodes* Hay.) heartwood. *Holzforschung*, 52(1), 13-17.
- Ciba® LIGNOSTAB® 1198. 2005. Wood photostabilizing additive. Ciba Specialty Chemicals Inc. Switzerland. www.cibasc.com (Accessed May 4th, 2010).
- Clayton, R.H., Sawitowski, T. 2006. The impact of nano-materials on UV-protective coatings. <http://www.nsti.org/Nanotech2006/> (Accessed Oct.15th, 2010).
- Cui, F., Zahora, A. 2000. Effect of a water repellent additive on the performance of ACQ treated decks. *International Research Group on Wood Preservation Document*, IRG/WP 00-40168.
- Davis, A. 1981. Effect of climate on the weathering of polyacetal. *Polymer Degradation and Stability*, 3(3), 187-198.
- Davis, A., Sims, D. 1983. Chapter 2: Ultraviolet radiation. In *Weathering of Polymers*, Elsevier Applied Science Publishers Ltd, New York, U.S.A., pp.20-41.
- DebRoy, T. 2006. Stabilization of coatings. *Ciba Specialty Chemicals 2nd Annual Wood Coatings and Substrates Conference*, Greensboro, NC. USA.
- Deka, M., Saikia, C.N. 2000. Chemical modification of wood with thermosetting resin: effect on dimensional stability and strength property. *Bioresource Technology*, 73(2), 179-181.
- De Paoli Marco-A., Furlan, L.T. 1985. Sugar cane bagasse-lignin as photo-stabilizer for butadiene rubber. *Polymer Degradation and Stability*, 11(4), 327-337.
- Derbyshire, H., Miller, E.R. 1981. The photodegradation of wood during solar irradiation. *Holz als Roh und Werkstoff*, 39(8), 341-350.
- Derbyshire, H., Miller, E.R., Turkulin, H. 1995. Investigations into the photodegradation of wood using microtensile testing. Part I: The application of microtensile testing to measurement of photodegradation rates. *Holz als Roh und Werkstoff*, 53(5), 339-345.
- Derbyshire, H., Miller, E.R., Turkulin, H. 1996. Investigations into the photodegradation of wood using microtensile testing. Part II: An investigation of the changes in tensile strength of different softwood species during natural weathering. *Holz als Roh und Werkstoff*, 54(1), 1-6.
- Donath, S., Militz, H., Mai, C. 2007. Weathering of silane treated wood. *Holz als Roh und Werkstoff*, 65(1), 35-42.

- Edmondson, C.H. 1953. Response of marine borers to chemically treated woods and other products. Occasional Papers of Bernice P. Bishop Museum, Howlulu, Hawaii. 21(7), 87-133.
- El Salamouny, S., Herz, A., Huber, J. 2002. Suitability of three lignin products as UV protectants to baculovirus. *Bulletin Entomological Society Egypt Economic Series*, 28, 103-111.
- El Salamouny S, Shapiro, M., Ling, K.S., Shepard, B.M. 2009. Black tea and lignin as ultraviolet protectants for the beet armyworm nucleopolyhedrovirus. *Journal of Entomological Science*, 44(1), 50-58.
- Erickson, E.C.O., Faulkes, W.F., Jr. 1966. Basic properties of yellow birch laminates modified with phenol and urea resin. FPL1741, *Forest Product Laboratory*, USDA, Madison, WI, USA.
- Evans, P.D. 1988. A note on assessing the deterioration of thin wood veneers during weathering. *Wood and Fiber Science*, 20(4), 487-492.
- Evans, P.D. 1989. Effect of angle of exposure on the weathering of wood surfaces. *Polymer Degradation and Stability*, 24(1), 81-87.
- Evans, P.D. 1996. The Influence of season and angle of exposure on the weathering of wood. *Holz als Roh-und Werkstoff*, 54(3), 200.
- Evans, P.D. 2009. Review of the weathering and photostability of modified wood. *Wood Material Science and Engineering*, 4(1), 2-13.
- Evans, P.D., Chowdhury, M.J., Mathews, B., Schmalzl, K., Ayer, S., Kiguchi, M., Kataoka, Y. 2005. Weathering and surface protection of wood. In *Handbook of Environmental Degradation of Materials*, Myer Kutz, Ed, William Andrew Publishing, Norwich, NY, USA., pp.277-297.
- Evans, P.D., Kiguchi, M. 1998. Weathering and photoprotection of chemically modified wood. *Proceeding of 4th Pacific Rim Biobased Composites Symposium*, Bogor, Indonesia, pp. 271-279.
- Evans, P.D., Michell, A.J., Schmalzl, K.J. 1992. Studies of the degradation and protection of wood surfaces. *Wood Science and Technology*, 26(2), 151-163.
- Evans, P.D., Owen, N.L., Schmid, S., Webster, R.D. 2002. Weathering and photostability of benzoylated wood. *Polymer Degradation and Stability*, 76(2), 291-303.
- Evans, P.D., Schmalzl, K.J. 1989. A quantitative weathering study of wood surfaces modified by Chromium VI and iron III compounds. I: Loss in zero-span tensile strength and weight of thin wood veneers. *Holzforschung*, 43(5), 289-292.

- Evans, P.D., Schmalzl, K.J., Michell, A.J. 1992. Rapid loss of lignin at wood surfaces during natural weathering. *The International Research Group on Wood Preservation*, IRG/WP/2390-92.
- Evans, P.D., Thay, P.D., Schmalzl, K.J. 1996. Degradation of wood surfaces during natural weathering. Effects on lignin and cellulose and on the adhesion of acrylic latex primers. *Wood Science and Technology*, 30(6), 411-422.
- Evans, P.D., Wallis, A.F.A., Owen, N.C. 2000. Weathering of chemically modified wood surfaces, Natural weathering of Scots pine acetylated to different weight gains. *Wood Science and Technology*, 34(2), 155-165.
- Evans, P.D., Wingate-Hill, R., Cunningham, R.B. 2009. Wax and oil emulsion additives: how effective are they at improving the performance of preservative treated wood. *Forest Products Journal*, 59(1-2), 66-70.
- Fairgrieve, S.P., MacCallum, J.R. 1984. Hindered amine light stabilizers: a proposed photo-stabilization mechanism. *Polymer Degradation and Stability*, 8(2), 107-121.
- Farmer, R.H. 1962. Corrosion of metals in association with wood. Part 1. Corrosion by acidic vapours from wood. *Wood* 27, 326-328.
- Farrar, R.R., Ridgway, R.L. 2000. Laboratory evaluation of selected spray adjuvants as ultraviolet light protectants for the nuclear polyhedrosis virus of the celery looper (Lepidoptera: Noctuidae). *Journal of Entomological Science*, 35(3), 239-250.
- Feist, W.C. 1979. Protection of wood surfaces with chromium trioxide. FPL-339, *Forest Product Laboratory*, USDA, Madison, WI, USA.
- Feist, W.C. 1990. Outdoor wood weathering and protection. In *Archaeological Wood: Properties, Chemistry, and Preservation*, R.M. Rowell and R. J. Barbour, Eds. American Chemical Society, Washington, DC., pp.263-297.
- Feist, W.C. 1992. Natural weathering of wood and its control by water-repellent preservatives. *American Painting Contractor*, 69(4), 18-25.
- Feist, W.C., Hon, D.N.S. 1984. Chemistry of weathering and protection. In *Chemistry of Solid Wood*, R.M. Rowell, Ed. American Chemical Society, Washington, DC., pp. 401-454.
- Feist, W.C., Mraz, E.A. 1978. Comparison of outdoor and accelerated weathering of unprotected softwoods. *Forest Products Journal*, 28(3), 38-43.
- Feist, W.C., Rowell, R.M. 1982. Chapter 21: Ultraviolet degradation and accelerated weathering of chemically modified wood. In *Graft Copolymerization of Lignocellulosic Fibers*, A.C.S. Symposium Series, D.N.S. Hon, Ed., Washington, DC., pp. 349-370.

- Feist, W.C., Rowell, R.M., Ellis, W.D. 1991. Moisture sorption and accelerated weathering of acetylated and methacrylated aspen. *Wood and Fiber Science*, 23(1), 128-136.
- Feldman, D. 2002. Lignin and its polyblends, a review. In *Chemical Modification, Properties, and Usage of Lignin*, Thomas Q. Hu, Ed. Kluwer Academic Publishers, New York, pp.81-99.
- Forsthuber, B., Gröll, G. 2010. The effects of HALS in the prevention of photo-degradation of acrylic clear topcoats and wooden surfaces. *Polymer Degradation and Stability*, 95(5), 746-755.
- Fukuta, S., Asada, F., Sasaki, Y. 2008. Manufacture of compressed wood fixed by phenolic resin impregnation through drilled holes. *Journal of Wood Science*, 54(2), 100-106.
- Furuno, T., Imamura, Y., Kajita, H. 2004. The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. *Wood Science and Technology*, 37(5), 349-361.
- Gabrielli, C.P., Kamke, F.A. 2010. Phenol-formaldehyde impregnation of densified wood for improved dimensional stability. *Wood Science and Technology*, 44(1), 95-104.
- Gantz, G.M., Sumner, W.G. 1957. Stable ultraviolet light absorbers. *Textile Research Journal*, 27(3), 244.
- Gare, J. 2000. Comparison of the weathering of sawn and split shingles from Australian timber species. *Professional Practice Report for Conservation of Cultural Materials Program*, University of Canberra, Australia, pp. 49.
- George, B., Suttie, E., Merlin, A., Deglise, X. 2005. Photodegradation and photostabilization of wood-the state of the art. *Polymer Degradation and Stability*, 88(2), 268-274.
- Gijsman, P. 2002. New synergists for hindered amine light stabilizers. *Polymer*, 43(5), 1573-1579.
- Gollob, L., Krahmer, R.L., Wellons, J.D., Christiansen, A.W. 1985. Relationship between chemical characteristics of phenol-formaldehyde resins and adhesive performance. *Forest Products Journal*, 35(3), 42-48.
- Gonzalez J.S. 1997. Growth, Properties and Uses of Western Red Cedar (*Thuja plicata* Donn ex D. Don). Forintec Canada Corp., Western Red Cedar Lumber Association and Western Red Cedar Export Association, Vancouver.
- Gosselink, R.J.A., Snijder, M.H.B., Kranenbarg, A., Keijzers, E.R.P., de Jong, E., Stigsson, L.L. 2004. Characterisation and application of NovaFiber lignin. *Industrial Crops and Products*, 20(2), 191-203.

- Gotô, T., Kadita S. 1956. Studies on the impregnated woods. IX. Relation between the moisture content at time of cure of phenol resin-impregnated wood and the dimensional stability. *Mokuzai Gakkaishi*, 2(2), 85-87.
- Gotô, T., Kadita, S. 1957. Studies on the impregnated woods. XII. The effect of the hardening process of resin upon the tensile-, bending-, and shear strength of water-soluble phenolic resin-impregnated wood. *Mokuzai Gakkaishi*, 3(4), 133-138.
- Grelier, S., Castellan, A., Desrousseaux, S., Nourmamode, A., Podgorski, L. 1997. Attempt to protect wood color against UV/visible light by using antioxidants bearing isocyanate groups and grafted to the materials with microwave. *Holzforchung*, 51(6), 511-518.
- Hansmann, C., Deka, M., Wimmer, R., Gindl, W. 2006. Artificial weathering of wood surfaces modified by melamine formaldehyde resins. *Holz als Roh und Werkstoff*, 64(3), 198-203.
- Hawkins, W.L. 1984. Polymer Degradation and Stabilization. Springer-Verlag, Berlin. pp.119.
- Haygreen, J.C., Gertjejansen, R.O. 1971. Improving the properties of particleboard by treating the particles with phenolic impregnating resin. *Wood and Fiber Science*, 3(2), 95-105.
- Hayoz, P., Peter, W., Rogez, D. 2003. A new innovative stabilization method for the protection of natural wood. *Progress in Organic Coatings*, 48(2-4), 297-309.
- Hon, D.N.S., Chang, Sh-T. 1984. Surface degradation of wood by ultraviolet light. *Journal of Polymer Science*, 22(9), 2227-2241.
- Hon, D.N.S., Chang, Sh-T., Feist, W.C. 1982. Participation of singlet oxygen in the photodegradation of wood surfaces. *Wood Science and Technology*, 16(3), 193-201.
- Hon, D.N.S., Chang, Sh-T., Feist, W.C. 1985. Protection of wood surfaces against photooxidation. *Journal of Applied Polymer Science*, 30(4), 1429-1448.
- Hon, D.N.S., Feist, W.C. 1981. Free radical formation in wood: The role of water. *Wood Science*, 14(1), 41-48.
- Hon, D.N.S., Feist, W.C. 1986. Weathering characteristics of hardwood surfaces. *Wood Science and Technology*, 20(2), 169-183.
- Hon, D.N.S., Ifju, G. 1978. Measuring penetration of light into wood by detection of photo-induced free radicals. *Wood Science*, 11(2), 118-127.
- Hon, D.N.S., Minemura, N. 1991. Color and discoloration. In *Wood and Cellulosic Chemistry*, Hon, Shiraishi, Eds. Marcel Dekker, NY., pp. 395-454.
- Imamura, Y. 2007. Research projects on high-performance utilization of wood for outdoor uses. Laboratory of Innovative Humano-Habitability, Kyoto University (Rapid Report of Wood Industry-Japanese), 3, 11-11.

ISO 11664-4:2008(E)/CIE S 014-4/E:2007: Joint ISO/CIE Standard: CIE Colorimetry Part 4: 1976 L*a*b* Colour Space.

Jackson, N., Goode, J.H., Wstkins, J.B., Greaces, H. 1992. Accelerated weathering comparison of CCA/Oil-, CCA- and CCA/Wax-treated *Pinus radiata* specimens. *CSIRO Forest Products Laboratory Report*. Clayton, Vic., Australia.

Jebrane, M., Sèbe, G. Cullis, I., Evans, P. D. 2009. Photostabilization of wood using aromatic vinyl esters. *Polymer Degradation and Stability*, 94(2), 151-157.

Jemison G.M. 1937. Loss of weight of wood due to weathering. *Journal of Forestry*, 35(5), 460-462.

Jeremic, D., Cooper, P., Brodersen, P. 2007. Penetration of poly (ethylene glycol) into wood cell walls of red pine. *Holzforschung*, 61(3), 272-278.

Jiang, H., Wang, J., Duan, Z., Li, F. 2007. Study on the microstructure evolution of phenol-formaldehyde resin modified by ceramic additive. *Frontiers of Materials Science in China*, 1(1), 35-39.

Johnson, B.R., Gjovik, L.R. 1970. Effect of trichoderma viride and a contaminating bacterium on microstructure and permeability of loblolly pine and Douglas fir. *Proceedings American Wood Preservers' Association*. 66, 234-240.

Kajita, H., Imamura, Y. 1991. Improvement of physical and biological properties of particleboards by impregnation with phenolic resin. *Wood Science and Technology*. 26(1), 63-70.

Kalnins, M.A. 1966. Surface characteristics of wood as they affect durability of finishes. Part II. Photochemical degradation of wood. *FPL 57*: 23-60. USA.

Kalnins, M.A. 1984. Photochemical degradation of acetylated, methylated, phenylhydrazine-modified, and ACC-treated wood. *Journal of Applied Polymer Science*, 29(1), 105-115.

Kalnins, M.A., Feist, W.C. 1993. Increase in wettability of wood with weathering. *Forest Products Journal*, 43(2), 55-57.

Kalnins, M.A., Knaebe, M.T. 1992. Wettability of weathered wood. *Journal of Adhesion Science and Technology*, 6(12), 1325-1330.

Kamke, F.A., Lee, J.N. 2007. Adhesive penetration in wood-a review. *Wood and Fibre Science*, 39(2), 205-220.

Kampmann, D., Stuhlmüller, G., Simon, R., Cottet, F., Leroux, F., Schlosser, M. 2005. A large-scale low-cost access to the lithium 2,2,6,6-tetramethylpiperidide precursor. *Synthesis*, 303(6), 1028-1029.

- Kiefer J.R. Jr. 1967. Ultraviolet light absorbers in clear coatings for wood. *Journal of Paint Technology*, 39(15), 736-751.
- Kiguchi, M., Evans, P.D. 1998. Photostabilisation of wood surfaces using a grafted benzophenone UV absorber. *Polymer Degradation and Stability*, 61(1), 33-45.
- Kiguchi, M., Kataoka, Y., Doi, S., Mori, M., Hasegawa, M., Morita, S., Kaneshiro, M., Kategari, Y., Imamura, Y. 1996. Evaluation of weathering resistance of the commercial pigmented stains by outdoor exposure test in Japan. *Mokuzai Gakkaishi*, 22(3), 150–159.
- Kim, M.G., Pittman, C.U., Nicholas, D.D., Schultz, T.P., Ingram, L.L., Kabir, F.R.A., Wang, L., Wu, Y., Wasson, L., Ivankoe, M. 2001. Wood made decontaminable of chemical warfare agents after sunlight weathering or abrasion. *Journal of Wood Chemistry and Technology*, 21(3), 263-283.
- Kishino, M., Nakano, T. 2004. Artificial weathering of tropical woods. Part II: Color change. *Holzforschung*, 58(5), 558-565.
- Knop, A., Scheib, W. 1979. Chemistry and application of phenolic resins. In *Polymers, Properties and Applications*, Springer-Verlag, New York.
- Knop, A., Pilato, L. 1985. Phenolic Resins: Chemistry, Applications, and Performance: Future Directions. Springer-Verlag, Berlin and New York.
- Koehler, B.S.A. 1924. The Properties and Uses of Wood. Industrial Education Series. McGraw-Hill Book Company, New York and London, pp. 224.
- Košíková, B., Tolvaj, L. 1998. Characterization of lignin fraction isolated from photodegraded wood. *Drevársky Výskum*, 43(2), 19-28.
- Krilov, A., Gref, R. 1986. Mechanism of sawblade corrosion by polyphenolic compounds. *Wood Science and Technology*, 20(4), 369-375.
- Kurumada, T., Ohsawa, H., Yamazaki, T. 1987. Synergism of hindered amine light stabilizers and UV-absorbers. *Polymer Degradation and Stability*, 19(3), 263-272.
- Laborie, M.P.G., Salmen, L., Frazier, C.E. 2006. A morphological study of the wood/phenol-formaldehyde adhesive interphase. *Journal of Adhesion Science and Technology*, 20(8), 729-741.
- Larsson-Brelid, P., Westin, M. 2007. Acetylated wood—results from long-term field tests. In *Proceedings of 3rd European Conference on Wood Modification*, C.A.S. Hill, D. Jones, H. Militz, G.A. Ormondroyd, Eds. Cardiff, UK., pp. 71-78.
- Leary, G.J. 1967. The yellowing of wood by light. *Tappi*, 50(1), 17-19.

- Leary, G.J. 1968. The yellowing of wood by light: Part II. *Tappi*, 51(6), 257-260.
- Liu, C, Ahniyaz, A., Evans, P.D. 2010. Preliminary observations of the photostabilization of wood surfaces with cerium oxide nanoparticles. *International Research Group Wood Protection Documents*, IRG/WP 10-40504.
- Lloyd, R.A., Stamm, A.J. 1958. Effect of resin treatment and compression upon the weathering properties of veneer laminates. *Forest Products Journal*, 8(8), 230-235.
- Loos, W.E., Coppock, W.A. 1964. Measuring wood color with precision. *Forest Products Journal*, 14(2), 85-86.
- Mahltig, B., Böttcher, H., Rauch, K., Dieckmann, U., Nitsche, R., Fritz, T. 2005. Optimized UV protecting coatings by combination of organic and inorganic UV absorbers. *Thin Solid Films*, 485(1-2), 108-114.
- Marra, A.A. 1992. *Technology of Wood Bonding: Principles in Practice*. Van Nostrand Reinhold, New York, pp.75-84.
- Martin, R.W. 1956. *The Chemistry of Phenolic Resins*. Wiley, New York.
- Millett, M.A., Seborg, R.M., Stamm, A.J. 1943. Influence of manufacturing variables on the impact resistance of resin-treated wood. FPL1386. USDA, MI, USA.
- Millett, M.A., Stamm, A.J. 1947. Treatment of wood with urea resin-forming systems: comparison with phenolic resin for making compreg. FPL1676. USDA, MI, USA.
- Miniutti, V.P. 1964. Microscale changes in cell structure at softwood surfaces during weathering. *Forest Products Journal*, 14(12), 571-576.
- Miniutti, V.P. 1967. Microscopic observations of ultraviolet irradiated and weathered softwood surfaces and clear coatings. FPL74, USDA, MI, USA.
- Modzel, G., Kamke, F.A., De Carlo, F. 2011. Comparative analysis of a wood: adhesive bondline. *Wood Science and Technology*, 45(1), 147-158.
- Muasher, M., Sain, M. 2006. The efficacy of photostabilizers on the color change of wood filled plastic composites. *Polymer Degradation and Stability*, 91(5), 1156-1165.
- Müller, U., Rätzsch, M., Schwanninger, M., Steiner, M., Zöbl, H. 2003. Yellowing and IR-changes of spruce wood as result of UV-irradiation. *Journal of Photochemistry and Photobiology B: Biology*, 69 (2), 97-105.
- Murakami, K., Matsuda, H. 1990. Oligoesterified woods based on anhydride and epoxide VIII. resistances of oligoesterified woods against weathering and biodeterioration. *Mokuzai Gakkaishi* 36(7), 538-544.

- Nepotchatykh, O.V., Power, J.F. 2000. Multilayer method as a tool for depth dependent polymer film photodegradation studies. *Polymer Engineering and Science*, 40(8), 1747-1757.
- Ohkoshi, M. 2002. FTIR-PAS study of light-induced changes in the surface of acetylated or polyethylene glycol-impregnated wood. *Journal of Wood Science*, 48(5), 394-401.
- Pandey, K.K., Chandrashekar, N. 2006. Photostability of wood surfaces esterified by benzoyl chloride. *Journal of Applied Polymer Science*, 99(5), 2367-2374.
- Panshin, A.J. 1962. Forest Products, Their Sources, Production and Utilization. McGraw-Hill. New York, pp.538.
- Panshin, A.J., Harrar, E.S., Baker, W.J., Proctor, P.B. 1950. Forest Products, Their Sources, Production and Utilization. McGraw-Hill. New York, pp.164-167.
- Paridah, M.T., Ong, L.L., Zaidon, A., Rahim, S., Anwar, U.M.K. 2006. Improving the dimensional stability of multilayered strand board through resin impregnation. *Journal of Tropical Forest Science*, 18(3), 166-172.
- Pastore, T.C.M., Santos, K.O., Rubim, J.C. 2004. A spectrophotometric study on the effect of ultraviolet irradiation of four tropical hardwoods. *Bioresource Technology*, 93(1), 37-42.
- Patel, A.R., Usilton, J.J. 1978. Chapter 10: Ultraviolet stabilization of polymers: development with hindered-amine light stabilizers. In *Stabilization and Degradation of Polymers*, ACS., pp.116-132.
- Plackett, D.V., Dunningham, E.A., Singh, A.P. 1992. Weathering of chemically modified wood. *Holz als Roh und Werkstoff*, 50(4), 135-140.
- Prakash, G.K., Pandey, K.K., Ram, R.K.D., Mahadevan, K. M. 2006. Dimensional stability and photostability of octanoylated wood. *Holzforchung*, 60(5), 539-542.
- Qayyum, M.M., Davis, A. 1984. Ultraviolet radiation for various angles of exposure at Jeddah and its relation to the weathering of polyacetal. *Polymer Degradation and Stability* 6(4), 201-209.
- Raczkowski, J. 1980. Seasonal effects on the atmospheric corrosion of spruce micro-sections. *Holz als Roh und Werkstoff*, 38(6), 231-234.
- Rapp, A.O., Peek, R.D. 1999. Melamine resin treated as well as varnish coated and untreated solid wood during two years of natural weathering. *Holz als Roh und Werkstoff*, 57(5), 331-339.
- Rowell, R.M., Feist, W.C., Ellis, W.D. 1981. Weathering of chemically modified southern pine. *Wood Science*, 13(4), 202-208.

- Rowell, R.M., Konkol, P. 1987. Treatments that enhance physical properties of wood. FPL-GTR-55, Gen.Tech.Rep., USDA, Madison, WI, U.S.A.
- Ryu, J.Y., Imamura, Y., Takahashi, M., Kajita, H. 1993. Effects of molecular weight and some other properties of resins on the biological resistance of phenolic resin treated wood. *Mokuzai Gakkaishi (Journal of the Japan Wood Research Society)*, 39(4), 481-492.
- Ryu, J.Y., Takahashi, M., Imamura, Y., Sato, T. 1991. Biological resistance of phenol-resin treated wood. *Mokuzai Gakkaishi*, 37(9), 852-858.
- Sandberg, D. 1999. Weathering of radial and tangential wood surfaces of pine and spruce. *Holzforschung*, 53(4), 355-364.
- Sandermann, W., Schlumbom, F. 1962. On the effect of filtered ultraviolet light on wood. Part II: Kind and magnitude of color difference on wood surfaces. *Holz als Roh und Werkstoff*, 20(8), 285-291.
- Saunders, K.J. 1988. Organic Polymer Chemistry, an Introduction to the Organic Chemistry of Adhesives, Fibres, Paints, Plastics and Rubbers. Chapman and Hall, London.
- Schaller, C. 2007. New approaches in wood coating stabilization. *Journal of Coatings Technology and Research*, 4(4), 401-409.
- Schmalzl, K.J., Evans, P.D. 2003. Wood surface protection with some titanium, zirconium and manganese compounds. *Polymer Degradation & Stability*. 82(3), 409-419.
- Seborg, RM, Tarkow, H., Stamm, A.J. 1962. Modified woods. FPL1580, Madison, WI, USA.
- Sell, J., Feist, W.C. 1986. Role of density in the erosion of wood during weathering. *Forest Products Journal*, 36(3), 57-60.
- Sell, J., Wälchli, O. 1969. Changes in the surface texture of weather exposed wood. *Material und Organismen*, 4(2), 81-87.
- Shams, M.I., Morooka, T., Yano, H. 2006. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin V: Effects of steam pretreatment. *Journal of Wood Science*, 52(5), 389-394.
- Shams, M.I., Yano, H., Endou, K. 2004. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin I: Effects of pressing pressure and pressure holding. *Journal of Wood Science*, 50(4), 337-342.
- Sharrock, R.F. 1990. A European approach to UV protection with a novel pigment. *Journal of Coatings Technology*, 62(789), 125-130.

- Stamm, A.J. 1974. Dimensional stabilization of wood with water soluble fire retardant bulking chemicals compared with polyethylene glycol-1000. *Wood Science and Technology*, 8 (4), 300-306.
- Stamm A.J. 1975. Solid modified wood. In *Principle of Wood Science and Technology II: Wood Based Materials*, Kollmann F.F.P, Kuenzi E.W, Stamm A.J, Eds. Springer-Verlag, Berlin Heidelberg, New York. pp.128-145.
- Stamm, A.J., Baechler R.H. 1960. Decay resistance and dimensional stability of five modified woods. *Forest Products Journal*, 10(1), 22-26.
- Stamm, A.J., Seborg, R.M. 1936. Minimizing wood shrinkage and swelling; treating with synthetic resin-forming materials. *Industrial & Engineering Chemistry*, 28(10), 1164-1169.
- Stamm, A.J., Seborg, R.M. 1939. Resin-treated plywood. *Industrial & Engineering Chemistry*, 31(7), 897-902.
- Stamm, A.J., Seborg, R.M. 1941. Resin treated, laminated, compressed wood. *Transactions of the American Institute of Chemical Engineers*, 37, 385-397.
- Stamm, A.J., Seborg, R.M. 1962. Resin-treated wood (Impreg). PFL1385, USDA, Madison, WI, USA.
- Step, E.N., Turro, N.J., Gande, M.E., Klemchuk, P.P. 1994. Mechanism of polymer stabilization by hindered-amine light stabilizers (HALS), model investigations of the interaction of peroxy radicals with HALS amines and amino ethers. *Macromolecules*, 27(9), 2529-2539.
- Stephens, R.S., Kutscha, N.P. 1987. Effect of resin molecular weight on bonding flakeboard. *Wood and Fiber Science*, 19(4), 353-361.
- Sudiyani, Y., Takahashi, M., Imamura, Y., Minato, K. 1999. Physical and biological properties of chemically modified wood before and after weathering. *Wood Research: Bulletin of the Wood Research Institute Kyoto University*, 86(1), 1-6.
- Sullivan, J.D. 1967. Color characterization of wood: spectrophotometry and wood color. *Forest Products Journal*, 17(7), 43-48.
- Talbott, J.W. 1959. Flapreg flakeboard resin-impregnated, compressed wood flakes. *Forest Products Journal*, 9(2), 103-106.
- Tamez-Guerra, P., McGuire, M.R, Behle, R.W., Hamm, J.J., Sumner, H.R., Shasha, B.S. 2000. Sunlight persistence and rainfastness of spray-dried formulations of baculovirus isolated from *Anagrapha falcifera* (Lepidoptera: Noctuidae). *Journal of Economic Entomology*, 93(2), 210-215.

- Temiz, A., Terziev, N., Eikenes, M., Hafren, J. 2007. Effect of accelerated weathering on surface chemistry of modified wood. *Applied Surface Science*. 253(12), 5355–5362.
- Temiz, A., Terziev, N., Jacobsen, B., Eikenes, M. 2006. Weathering, water absorption, and durability of silicon, acetylated, and heat-treated wood. *Journal of Applied Polymer Science*, 102(5), 4506-4513.
- Theocharopoulos, A., Zou, L., Hill, R., Cattell, M. 2010. Wear quantification of human enamel and dental glass-ceramics using white light profilometry. *Wear*, 269(11-12), 930-936.
- Turkulin, H., Sell, J. 2002. Investigations into the photodegradation of wood using microtensile testing Part IV: Tensile properties and fractography of weathered wood. *Holz als Roh und Werkstoff*, 60(2), 96–105.
- VSN International. 2009. *GENSTAT for Windows*. 12th edition. Hemel Hempstead, HRT, U.K.
- Wan, H., Kim, M.G. 2006. Impregnation of southern pine wood and strands with low molecular weight phenol-formaldehyde resins for stabilization of oriented strandboard. *Wood and Fiber Science*, 38(2), 314-324.
- Wan, H., Kim, M.G. 2008. Distribution of phenol-formaldehyde resin in impregnated southern pine and effects on stabilization. *Wood and Fiber Science*, 40(2), 181-189.
- Weatherwax, R.C., Stamm, A.J. 1956. The electrical resistivity of resin-treated wood (Impreg and Compreg), hydrolyzed-wood sheet (hydroxylin), and laminated resin-treated paper (Papreg). FPL1385, Madison, WI, USA.
- Wengert, E.M. 1966. Effect of atmospheric gases on color changes in wood exposed to ultraviolet light. *Journal of Paint Technology*, 38(493), 71-76.
- Wicks, Z.W., Jones, F.N., Pappas, S.P. 1999. *Organic Coatings: Science and Technology*. 2nd ed., John Wiley & Sons. New York, USA.
- Wilken, L., Hoffmann, V., Wetzig, K. 2003. Erosion rate measurements for GD-OES. *Journal of Analytical Atomic Spectrometry*, 18(9), 1141-1145.
- Williams, R.S. 1983. Effect of grafted UV stabilizers on wood surface erosion and clear coating performance. *Journal of Applied Polymer Science*, 28(6), 2,093-2,103.
- Williams, R.S. 1987. Acid effects on accelerated wood weathering. *Forest Products Journal*. 37 (2), 37-38.
- Williams, R.S. 2005. Weathering of wood. In *Handbook of Wood Chemistry and Wood Composites*, R.M. Rowell, Ed. CRC Press LLC. pp.141-178.

- Williams, R.S., Feist, W.C. 1988. Performance of finishes on wood modified with chromium nitrate versus chromic acid. *Forest Products Journal*, 38(11-12), 32-35.
- Williams, R.S., Knaebe, M.T., Evans, J.W., Feist, W.C. 2001c. Erosion rates of wood during natural weathering. Part III. Effect of exposure angle on erosion rate. *Wood and Fiber Science*, 33(1), 50-57.
- Williams, R.S., Knaebe, M.T., Feist, W.C. 2001b. Erosion rates of wood during natural weathering. Part II. Earlywood and latewood erosion rates. *Wood and Fiber Science*, 33(1), 43-49.
- Williams, R.S., Knaebe, M.T., Sotos, P.G., Feist, W.C. 2001a. Erosion rates of wood during natural weathering. Part I. Effects of grain angle and surface texture. *Wood and Fiber Science*, 33(1), 31-42.
- Williams, R.S., Miller, R., Gangstad, J. 2001d. Characteristics of ten tropical hardwoods from certified forests in Bolivia. Part I. Weathering characteristics and dimensional change. *Wood and Fiber Science*, 33(4), 618-626.
- Xie, Y., Krause, A., Mai, C., Militz, H., Richter, K., Urban, K., Evans, P.D. 2005. Weathering of wood modified with the N-methylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea. *Polymer Degradation and Stability*, 89(2), 189-199.
- Yusuf, S., Sudiyani, Y., Kajita, H., Imamura, Y., Takahashi, M. 1999. Biological and physical properties of phenolic-resin treated wood before and after natural weathering. *International Research Group on Wood Preservation Document*, IRG/WP 99-40133.
- Zahora, A. 2000. Long-term performance of a "wax" type additive for use with water-borne pressure preservative treatments. *The International Research Group on Wood Preservation Document*, IRG/WP 00-40159.
- Zweifel, H. 1997. Stabilization of Polymeric Materials State-of-the-Art, Scope and Limitations. Springer, Heidelberg, Berlin.

APPENDIX I: WESTERN RED CEDAR SPECIMENS EXPOSED TO ARTIFICIAL WEATHERING OR NATURAL WEATHERING

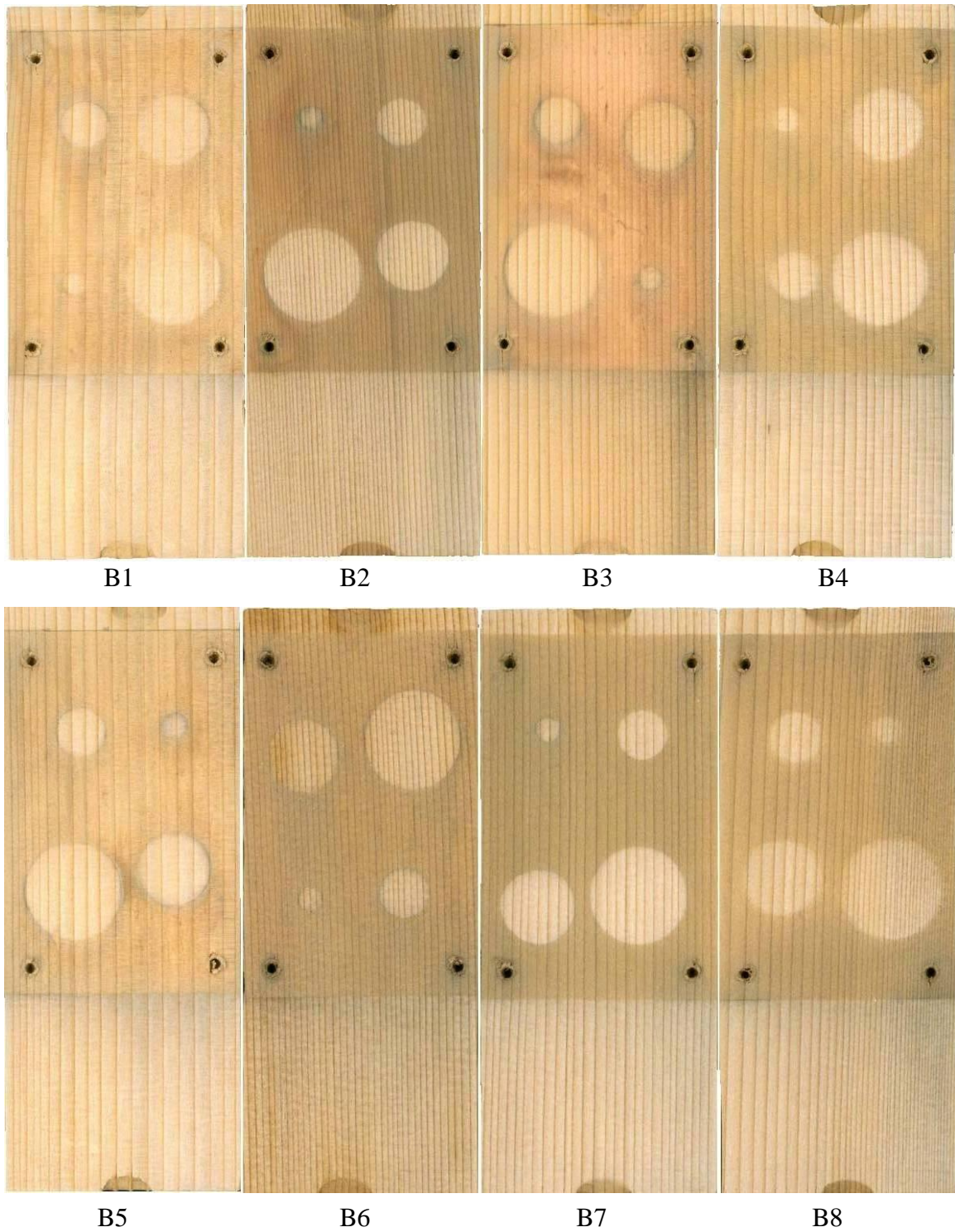
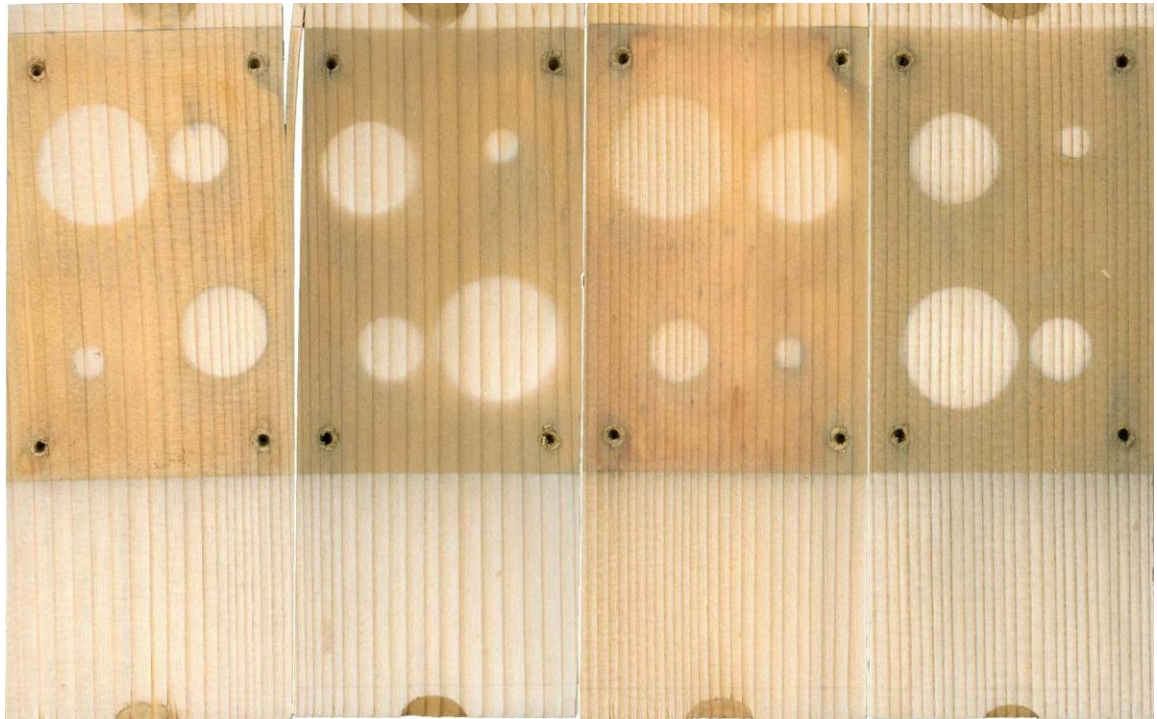


Figure I.1 Western red cedar specimens exposed to natural weathering for 1000 hours

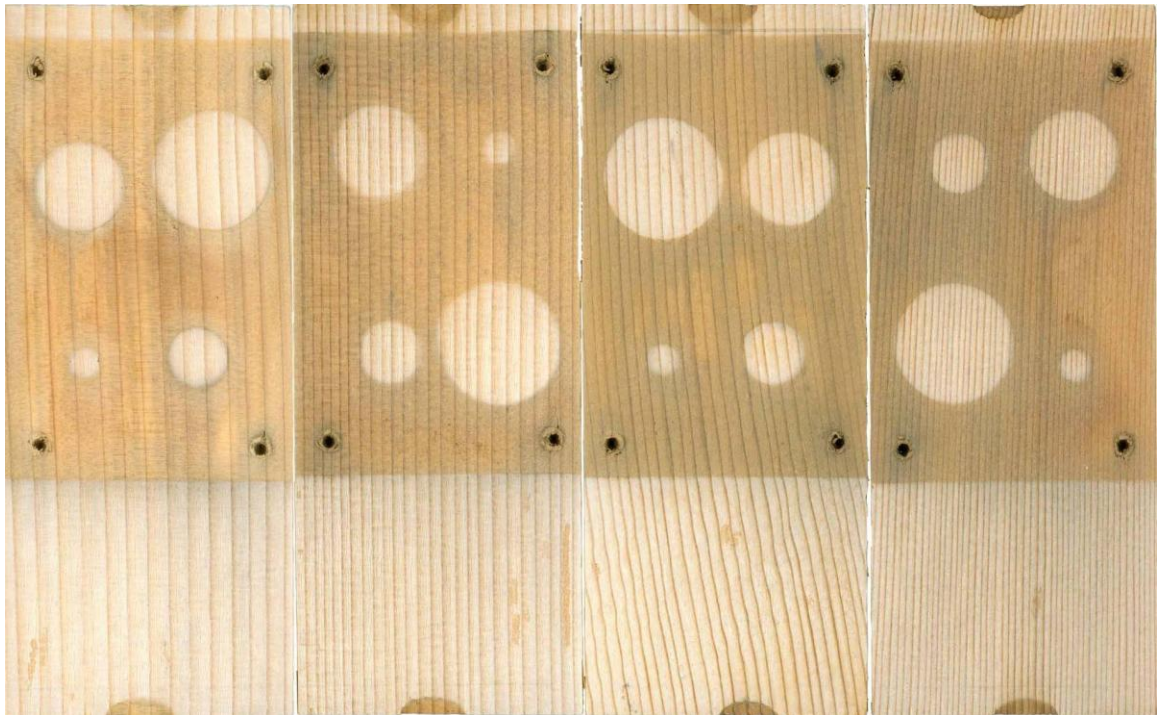


B1

B2

B3

B4



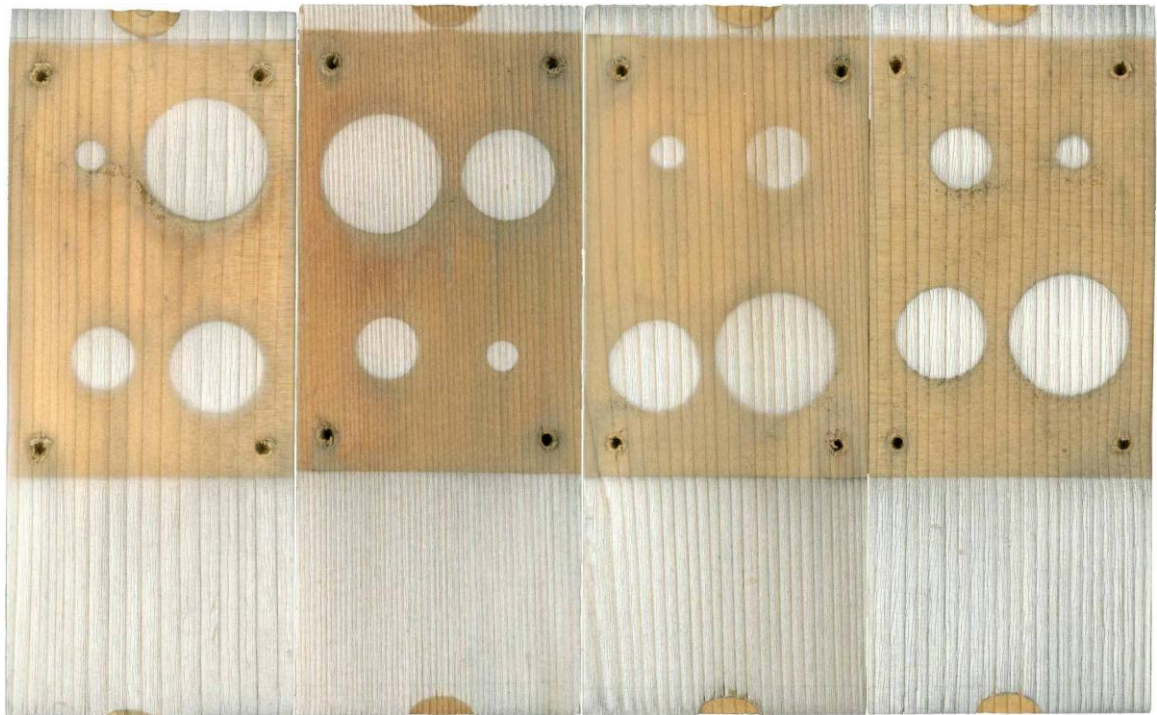
B5

B6

B7

B8

Figure I.2 Western red cedar specimens exposed to natural weathering for 2500 hours

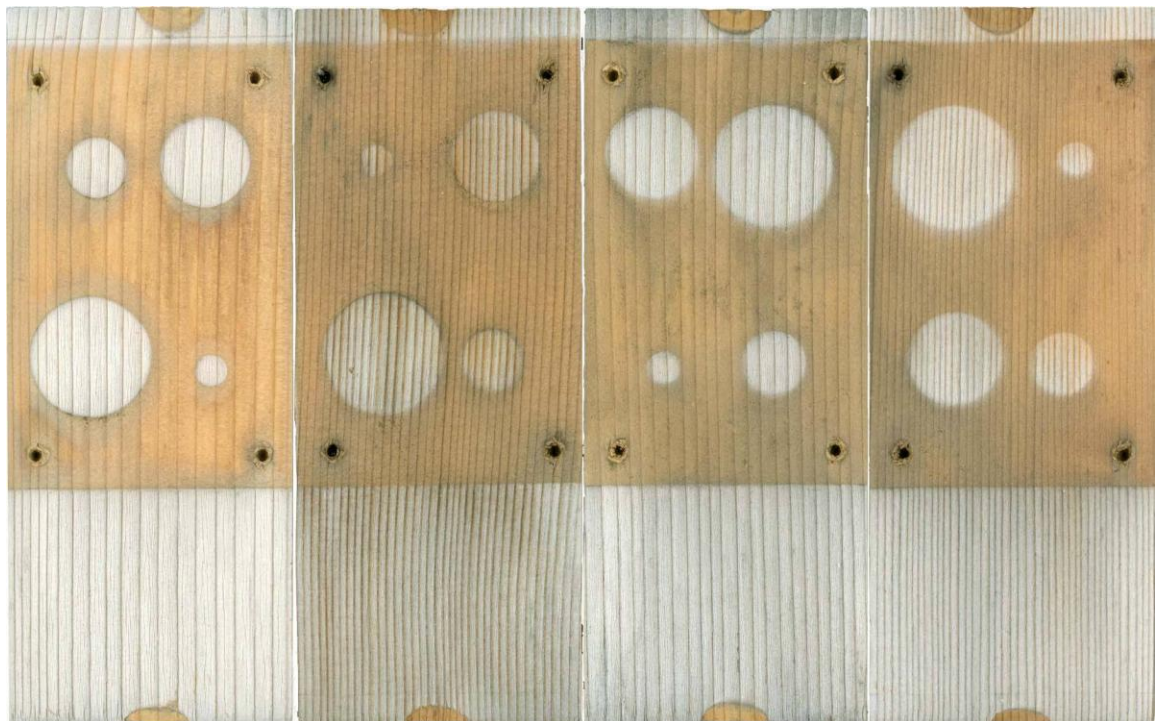


B1

B2

B3

B4



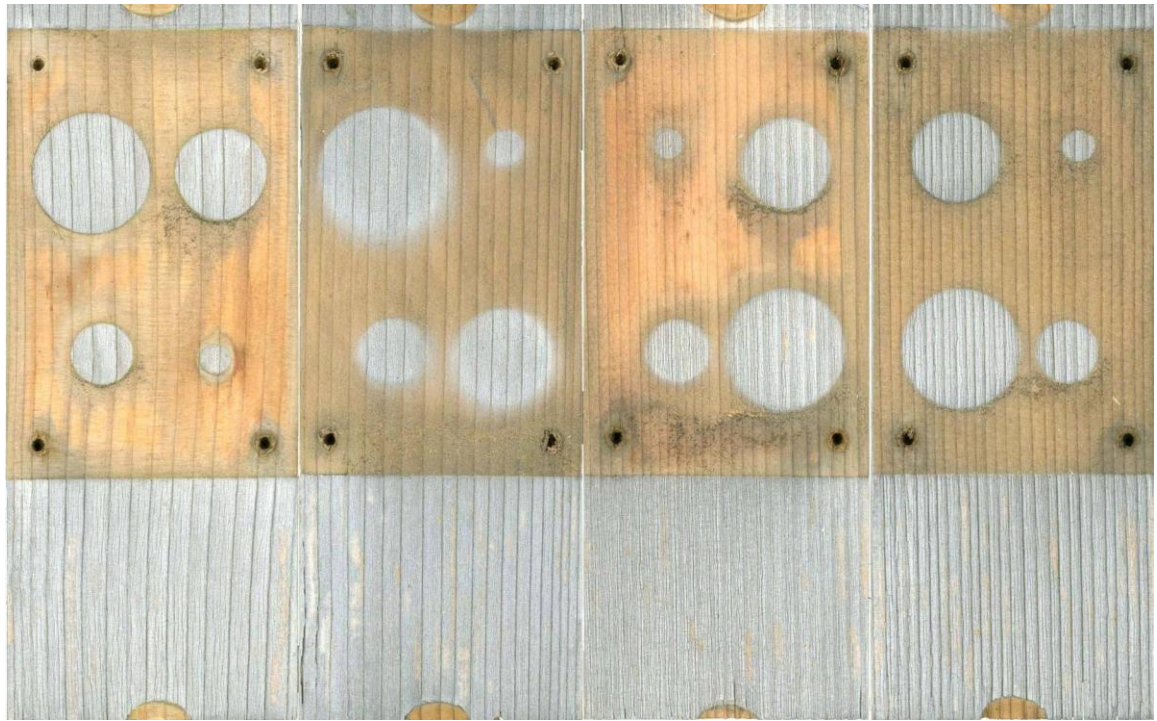
B5

B6

B7

B8

Figure I.3 Western red cedar specimens exposed to natural weathering for 5000 hours

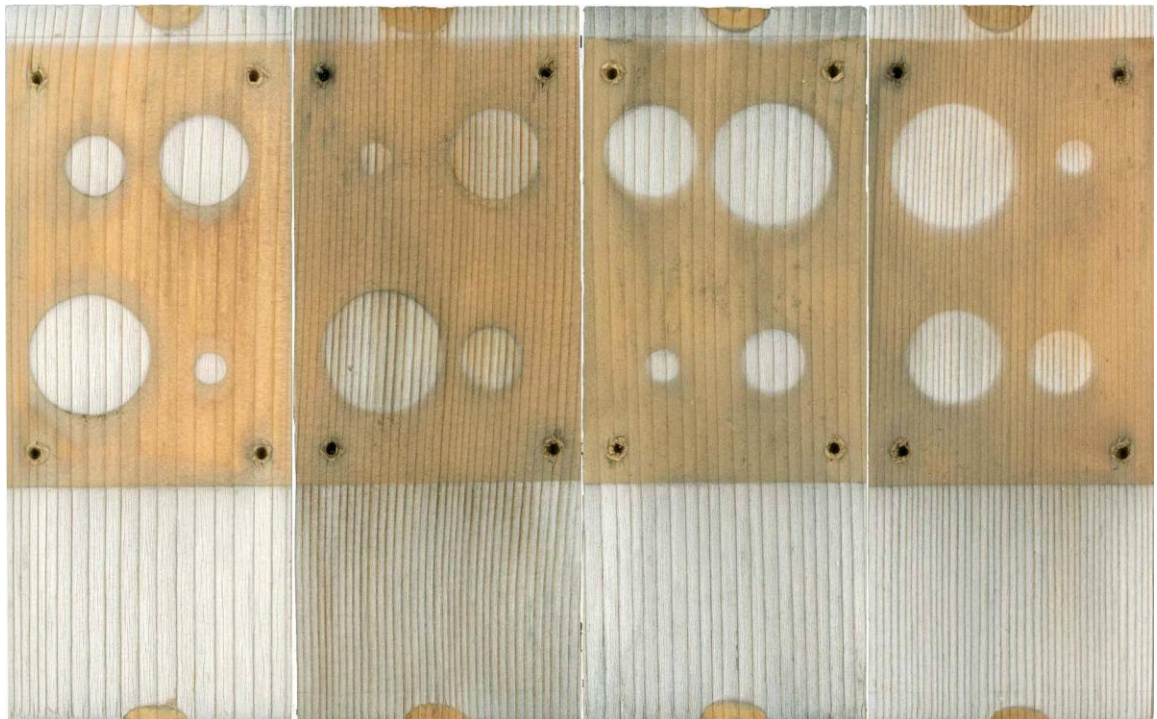


B1

B2

B3

B4



B5

B6

B7

B8

Figure I.4 Western red cedar specimens exposed to natural weathering for 10000 hours



B1

B2

B3

B4



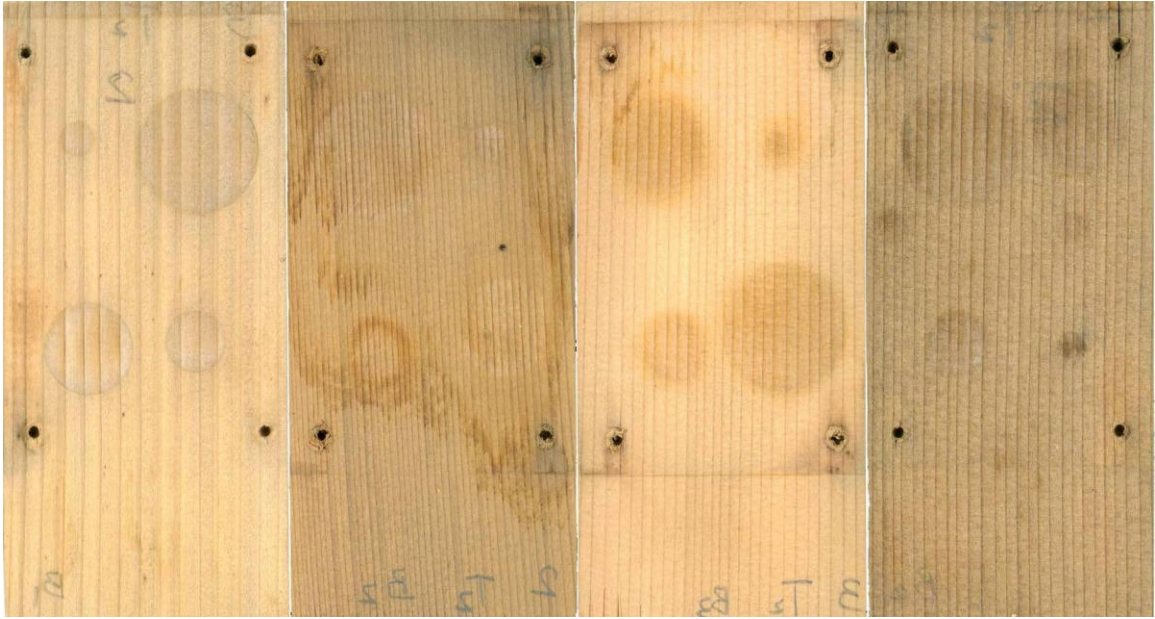
B5

B6

B7

B8

Figure I. 5 Western red cedar specimens exposed in QUV weatherometer for 100 hours



B1

B2

B3

B4



B5

B6

B7

B8

Figure I.6 Western red cedar specimens exposed in QUV weatherometer for 250 hours

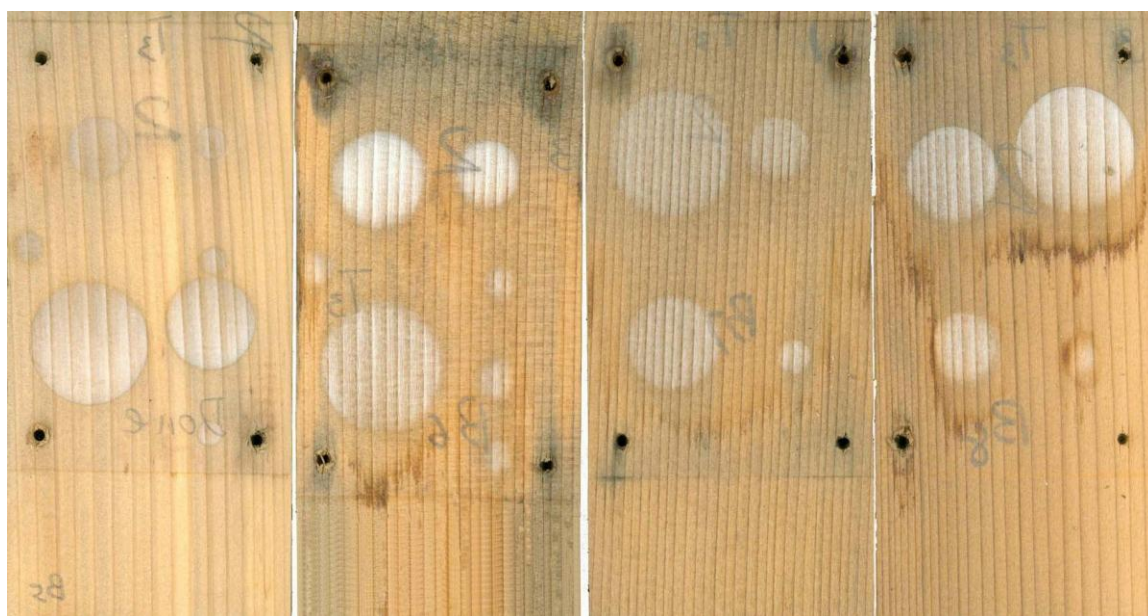


B1

B2

B3

B4



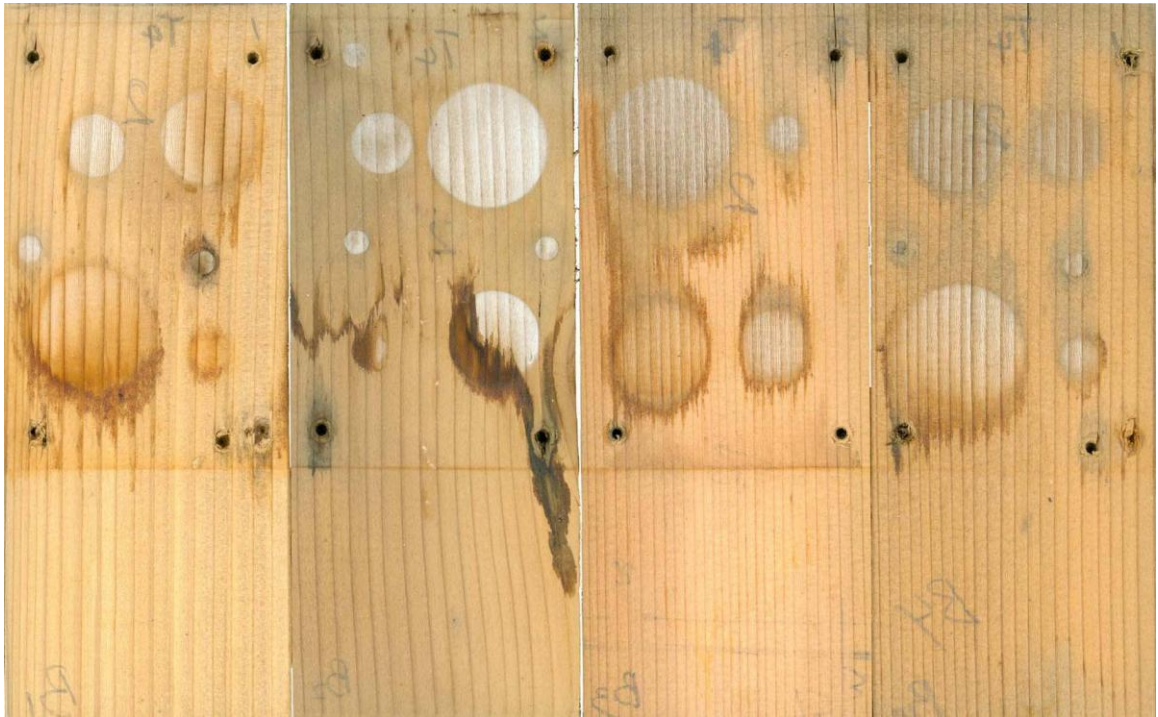
B5

B6

B7

B8

Figure I.7 Western red cedar specimens exposed in QUV weatherometer for 500 hours



B1

B2

B3

B4



B5

B6

B7

B8

Figure I.8 Western red cedar specimens exposed in QUV weatherometer for 1000 hours

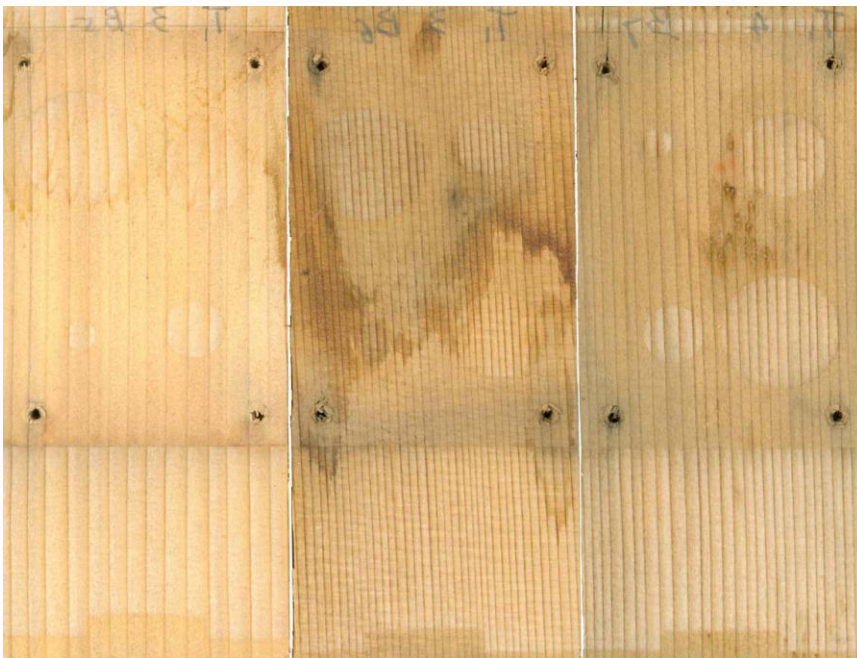


B1

B2

B3

B4



Not available

B5

B6

B7

B8

Figure I.9 Western red cedar specimens exposed in xenon arc weatherometer for 100 hours



B1

B2

B3

B4



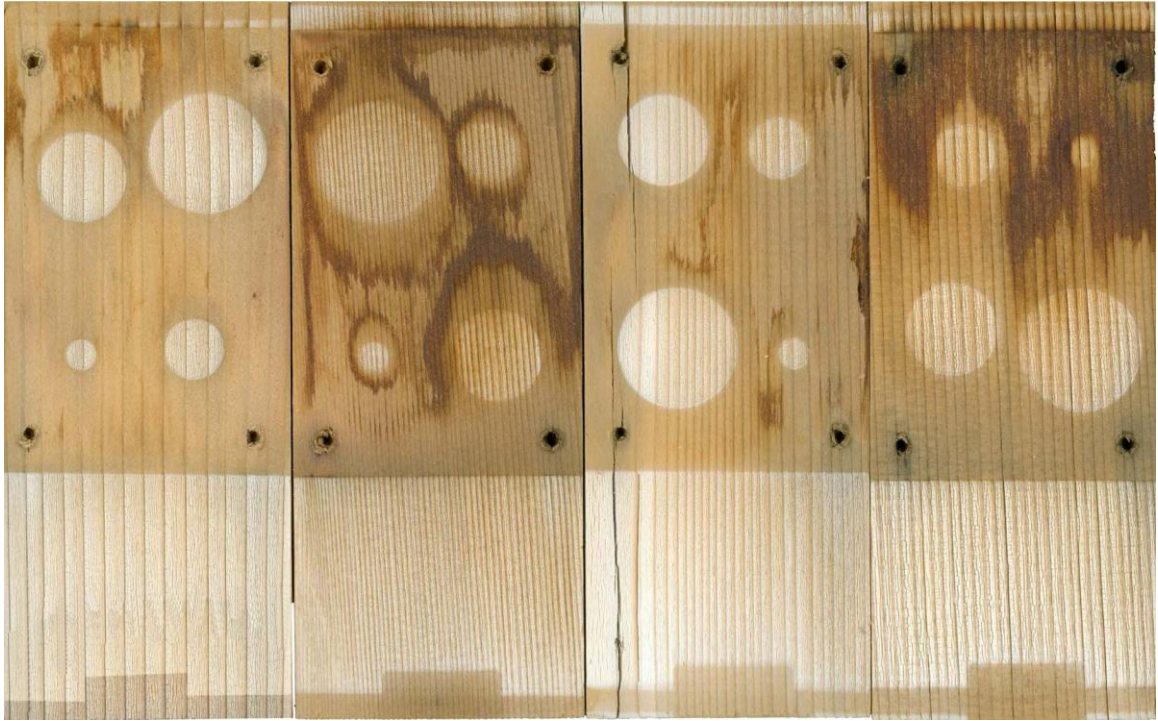
B5

B6

B7

B8

Figure I.10 Western red cedar specimens exposed in xenon arc weatherometer for 250 hours

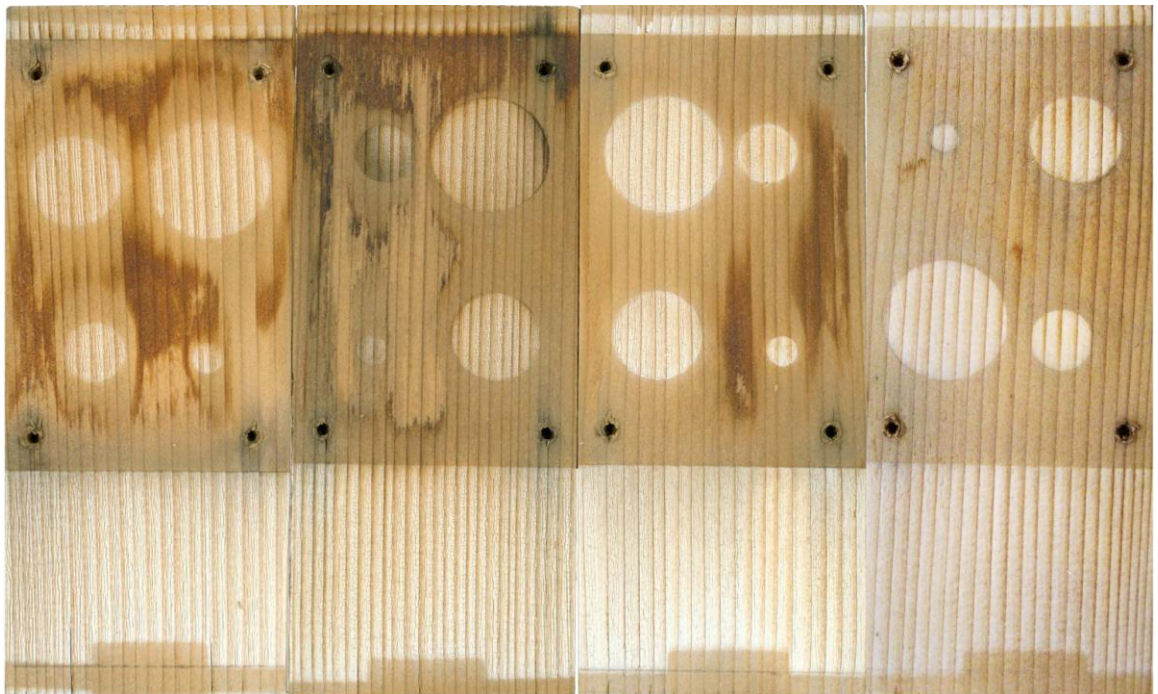


B1

B2

B3

B4



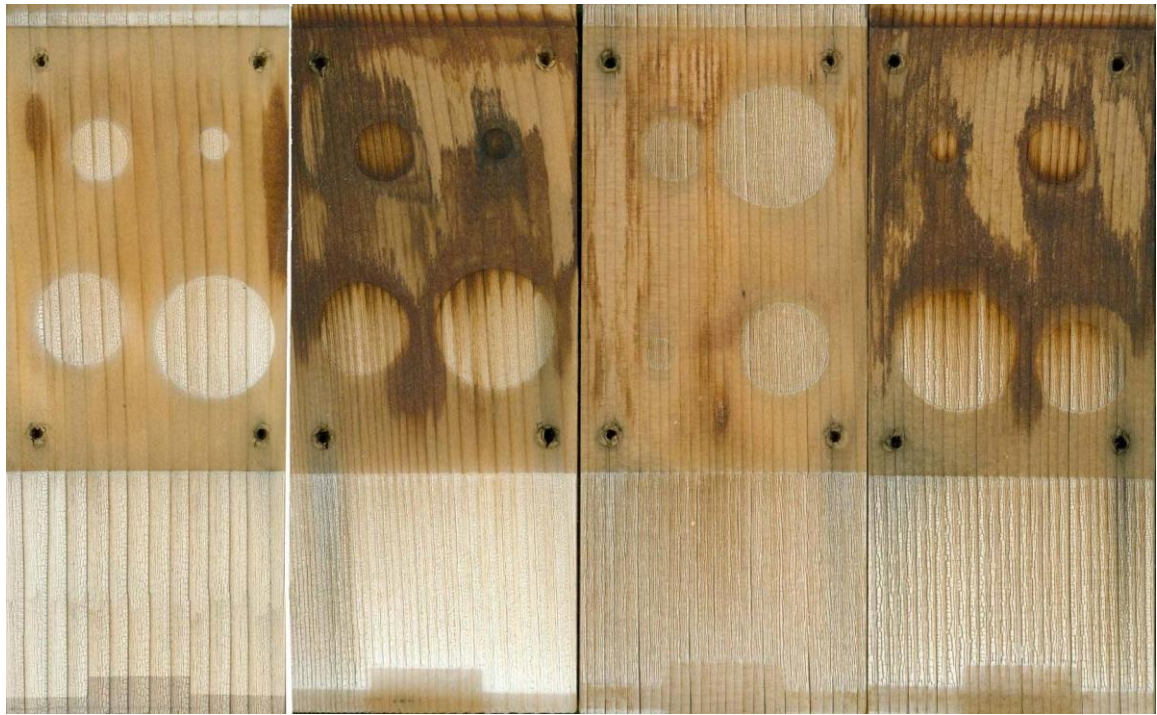
B5

B6

B7

B8

Figure I.11 Western red cedar specimens exposed in xenon arc weatherometer for 500 hours



B1

B2

B3

B4



B5

B6

B7

B8

Figure 1.12 Western red cedar specimens exposed in xenon arc weatherometer for 1000 hours

**APPENDIX II: WOOD VENEERS TREATED WITH PF RESIN OR PF RESIN
CONTAINING DIFFERENT ADDITIVES BEFORE AND AFTER EXPOSED TO
NATURAL WEATHERING**

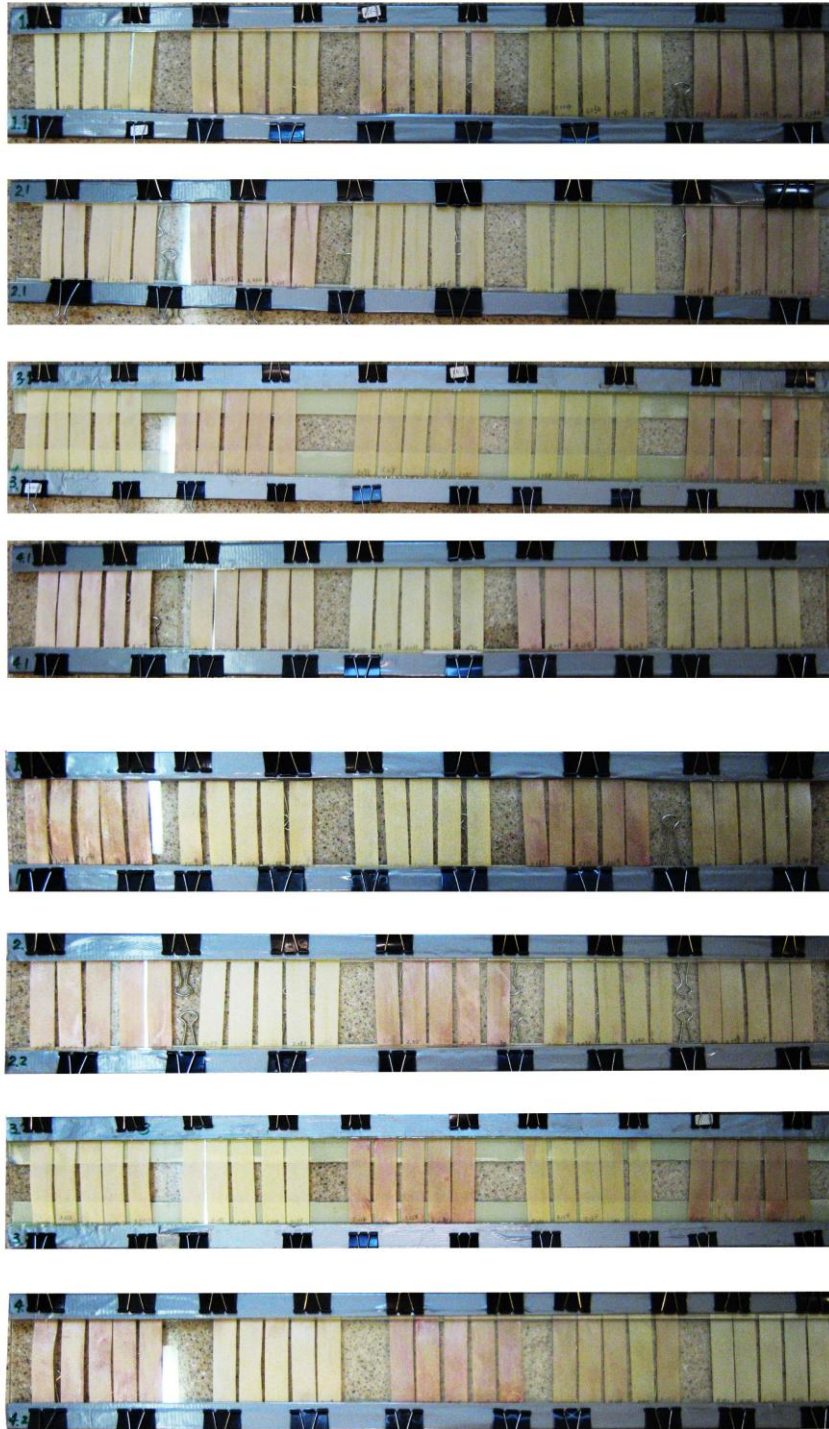


Figure II.1 Veneers treated with different concentration of PF resin (12%, 24%, 36%, 48%) and different concentration of PF resin containing 2.5% wax)

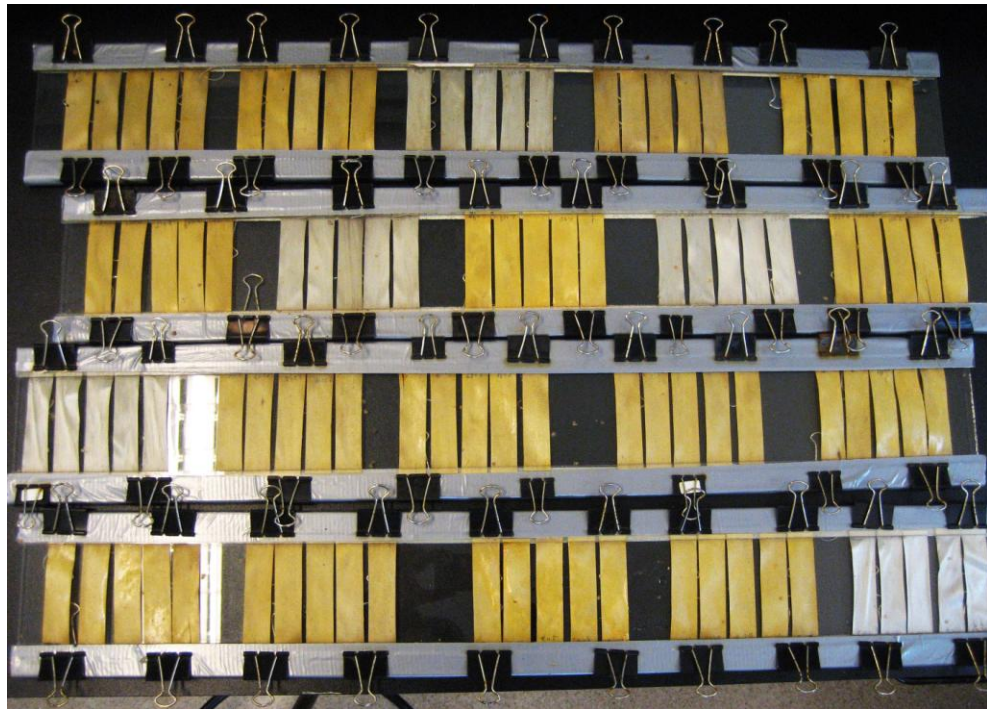
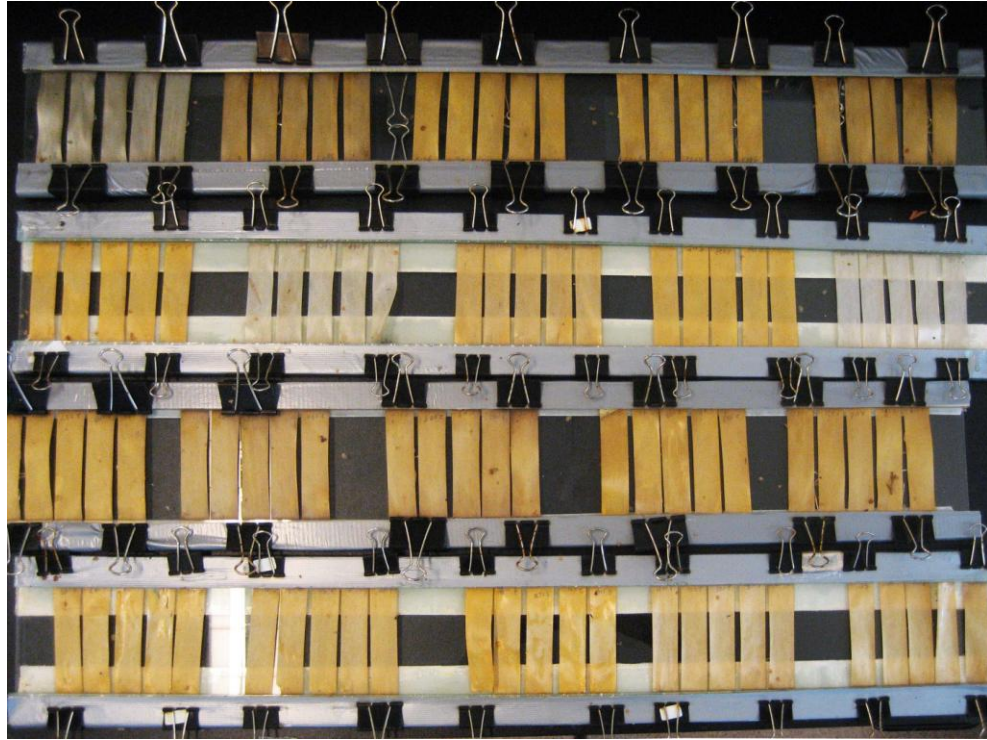


Figure II.2 Veneers treated with different concentration of PF resin (12%, 24%, 36%, 48%) and different concentration of PF resin containing 2.5% wax) after 50 days natural weathering



Figure II.3 Veneers treated with different additives (10% Lignosulphonate, 10% PEG, 1% iron oxide, 2% lignostab 1198)



Figure II.4 Veneers treated with different additives (10% Lignosulphonate, 10% PEG, 1% iron oxide, 2% lignostab 1198) after 50 days natural weathering



Figure II.5 Veneers treated with 12% PF rein, 12% PF resin containing different additives (10% Lignosulphonate, 10% PEG, 1% iron oxide, 2% lignostab 1198)



Figure II.6 Veneers treated with 12% PF rein, 12% PF resin containing different additives (10% Lignosulphonate, 10% PEG, 1% iron oxide, 2% lignostab 1198) after 50 days natural weathering

**APPENDIX III: WOOD COMPOSITE SPECIMENS TREATED WITH PF RESIN OR
PF RESIN CONTAINING DIFFERENT ADDITIVES EXPOSED TO 2000 HOURS
NATURAL WEATHERING**

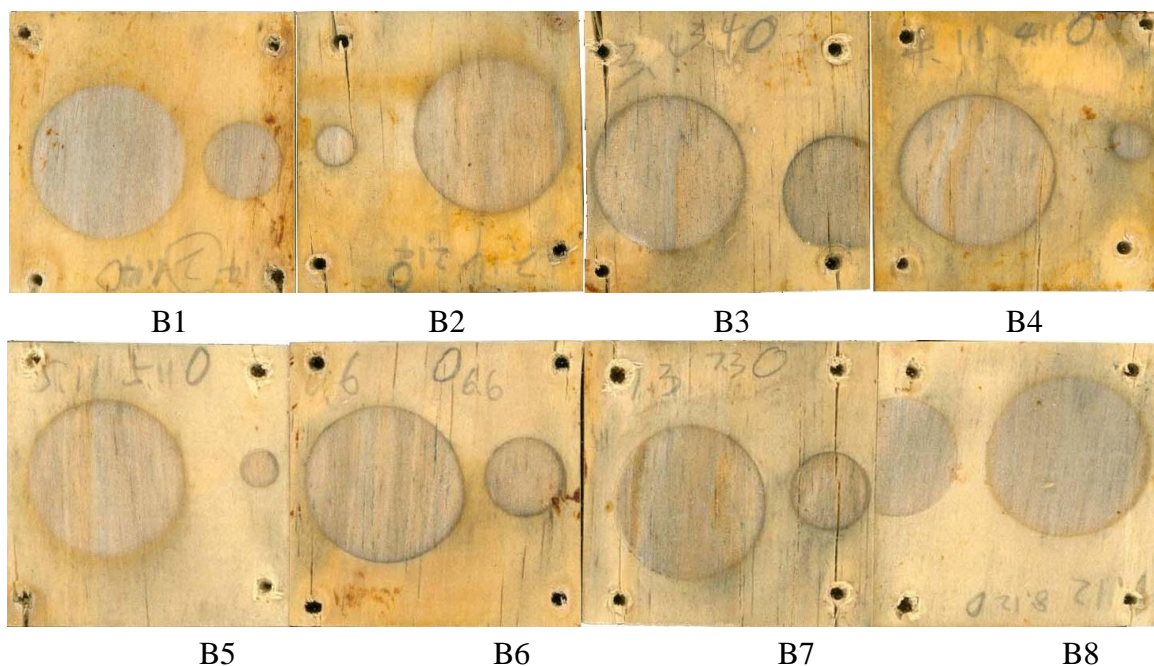


Figure III.1 Veneer-based wood composite specimens (Untreated) after weathering

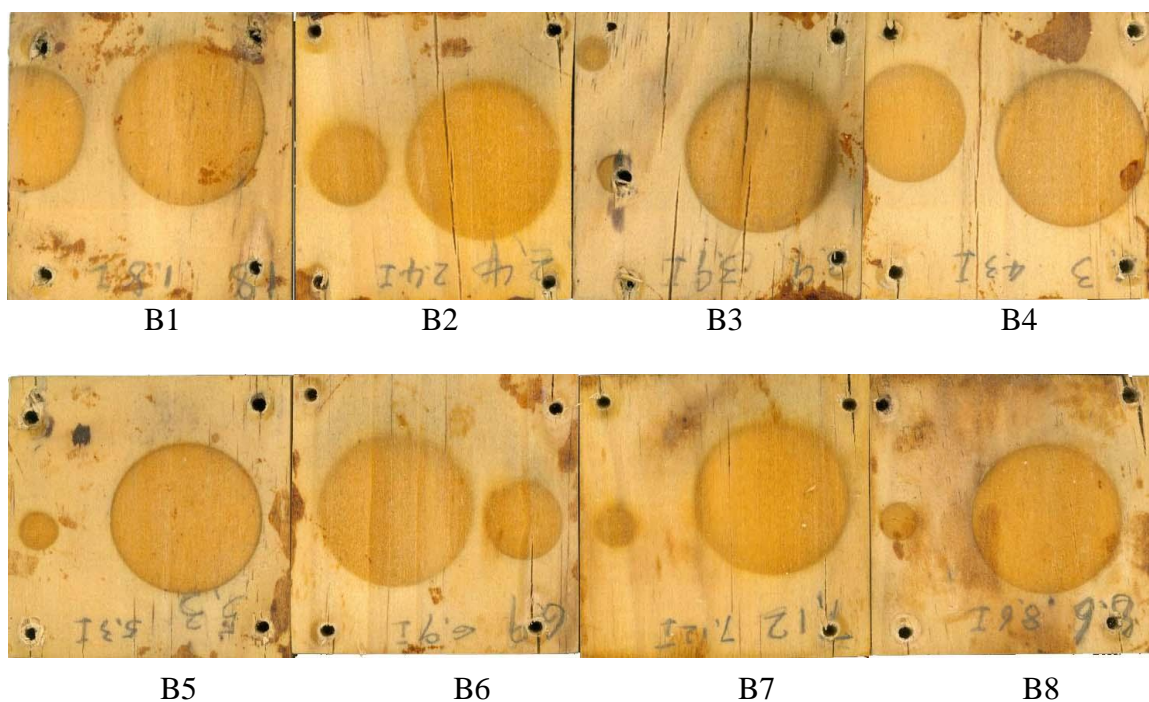


Figure III.2 Veneer-based wood composite specimens (treated with 10%PF) after weathering

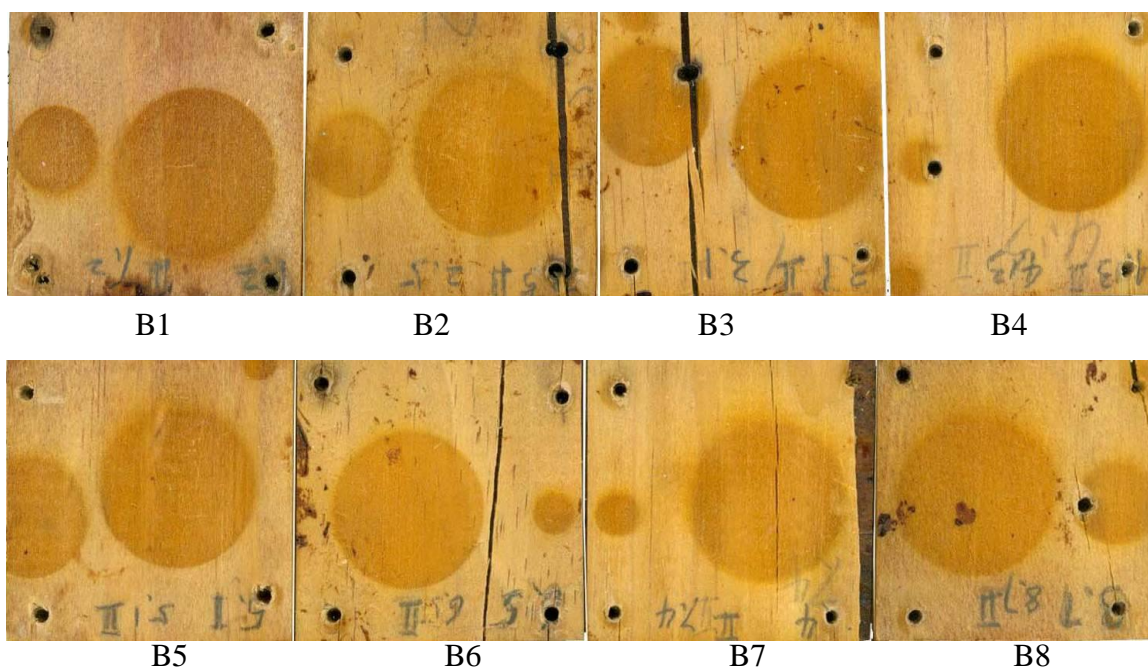


Figure III.3 Veneer-based wood composite specimens (treated with 20%PF) after weathering

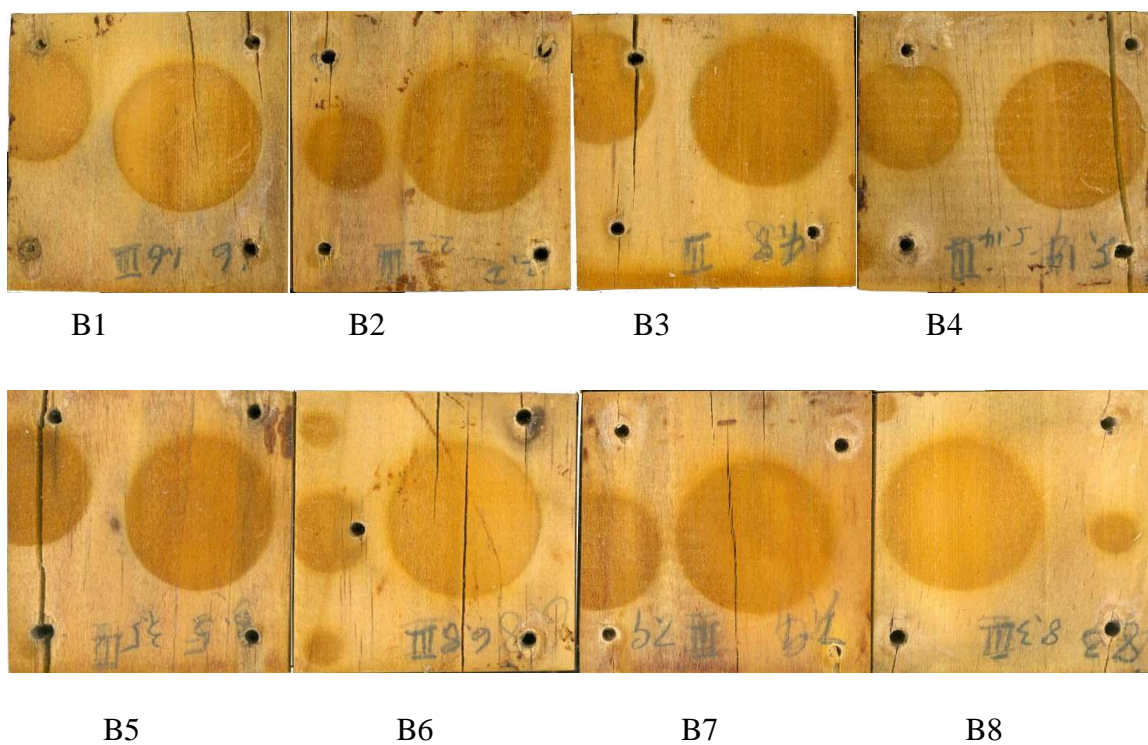


Figure III.4 Veneer-based wood composite specimens (treated with 30%PF) after weathering

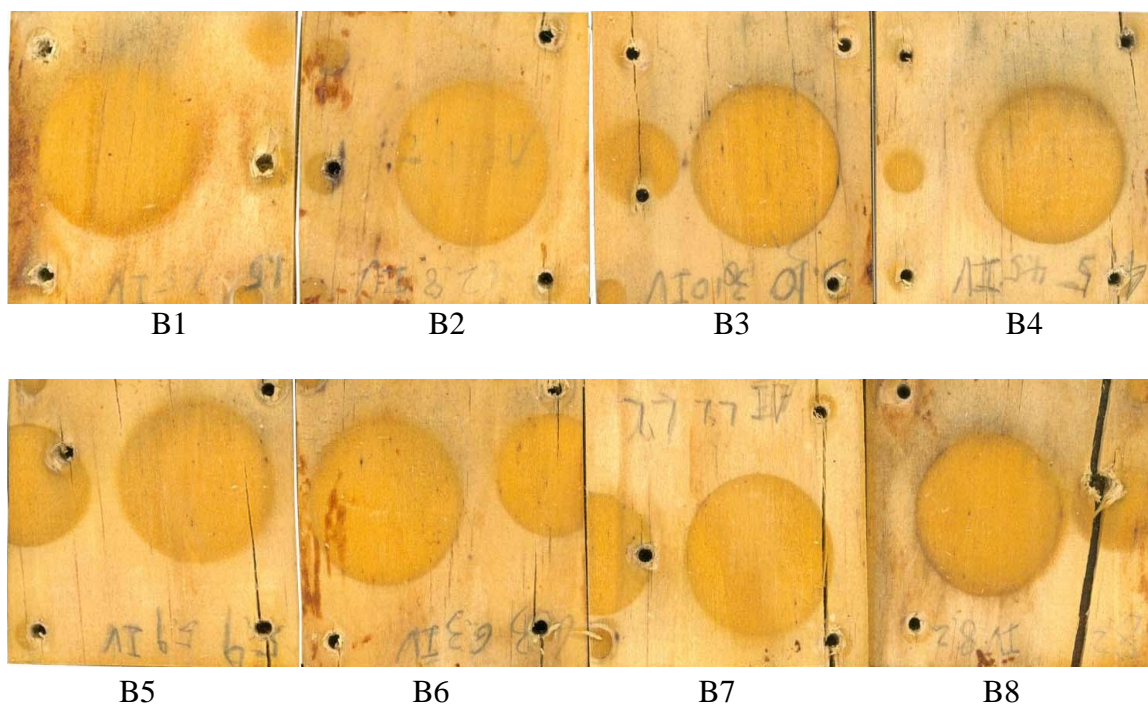


Figure III.5 Veneer-based wood composite specimens (treated with 10%PF containing 10%PEG) after weathering

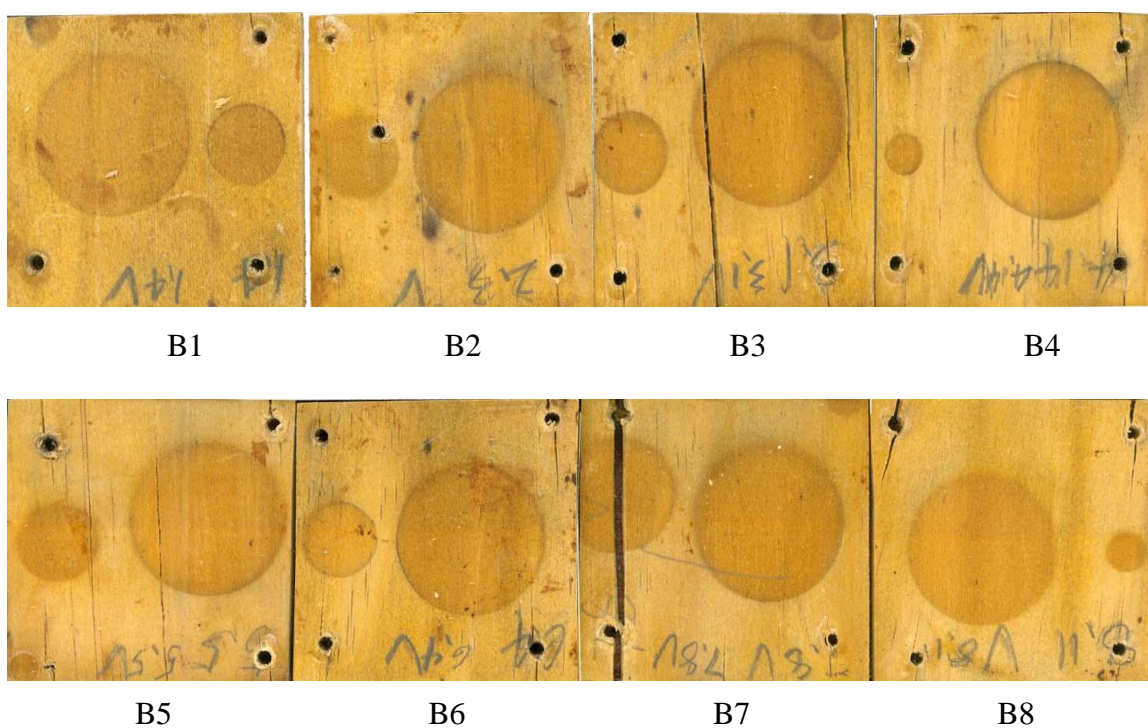


Figure III.6 Veneer-based wood composite specimens (treated with 10%PF containing 1% iron oxide) after weathering



APPENDIX IV: CHARACTERISTICS OF PF RESIN USED TO TREATED WOOD VENEERS AND WOOD COMPOSITES

(Source: Arclin USA Inc. Springfield, Oregon)

IV.1 Resin[#] 368.3B

Table IV.1 Formulation of resin [#] 368.3.B

Phenol (100%)	Adjustment Water	KOH (45%)	Formaldehyde (52%)	Sulfamic Acid	water	Total
27.16	1.25	5.29	61.68	3.62	1	100

MR (F/P) = 3.7 %NV = 52.4%

Table IV.2 Molecular and Structural Characteristic of resin [#] 368.3.B

Sample	Mw	Mn	Mz	Mw/Mn	IV,dL/g	Rg (nm)	M-H "a Value
386.3B	210	200	225	1.07	0.033	0.62	n/a

IV.2 Resin SKG-113-09

Table IV.2 Formulation of Resin SKG-113-09

Phenol (100%)	KOH (50%)	Formaldehyde (50%)	water	Total
36.29	3.8	39.37	20.54	100

MR (F/P) = 1.7 %NV = 50%

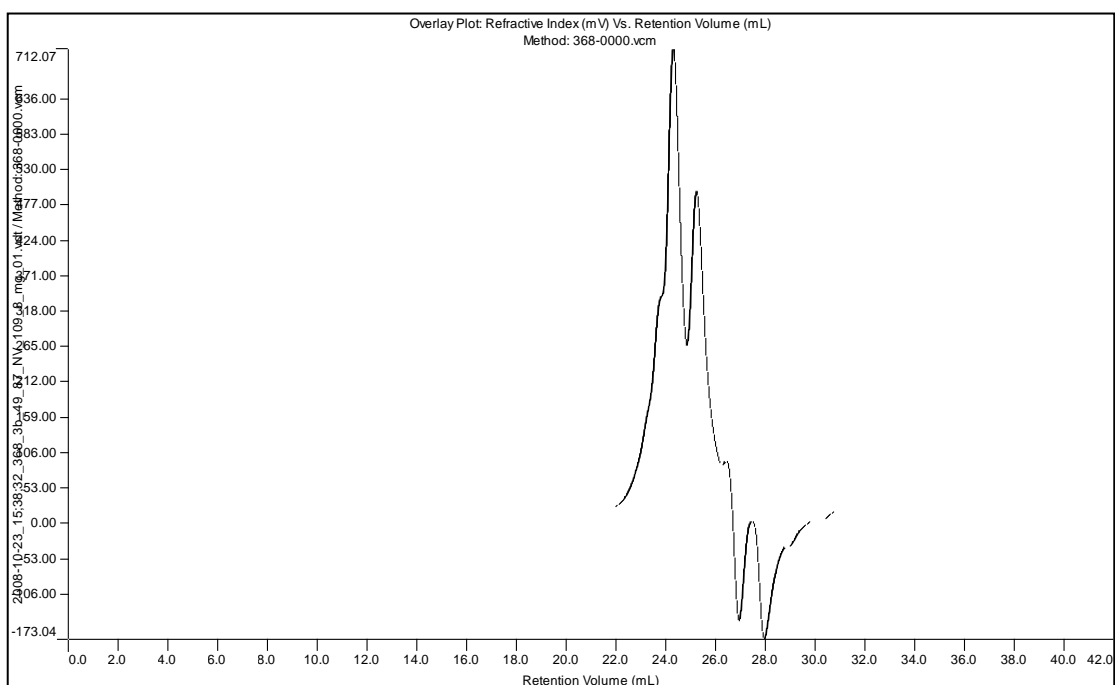


Figure IV.1 RI Chromatogram of 368.3B

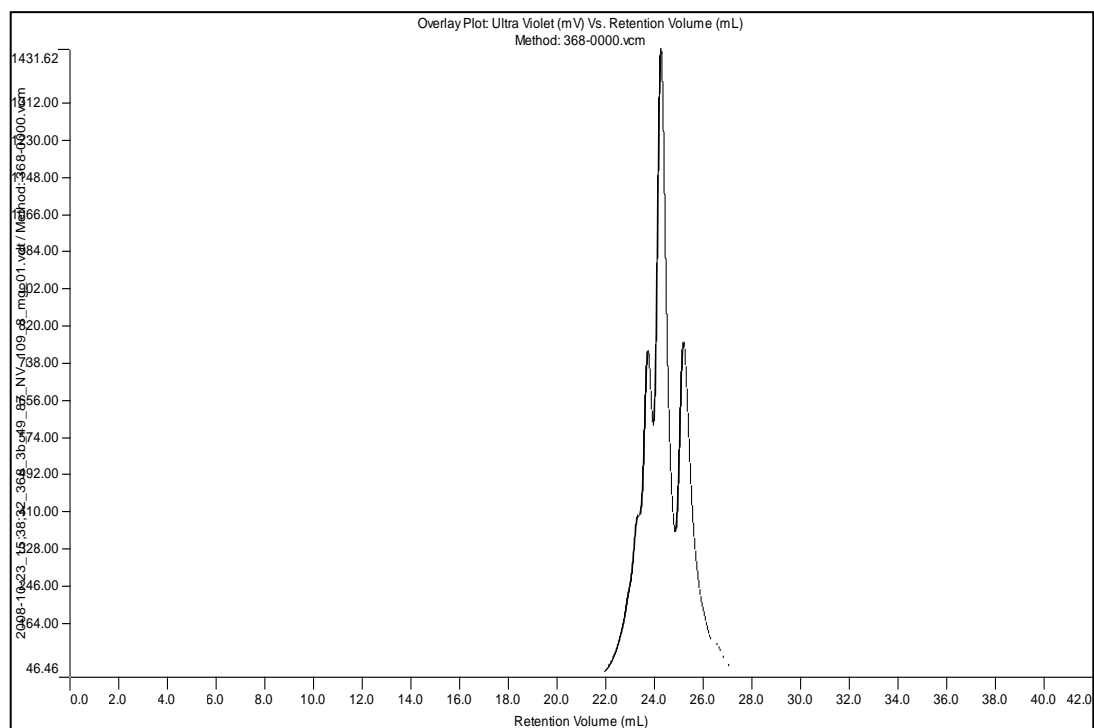


Figure IV.2 UV Chromatogram of 368.3B

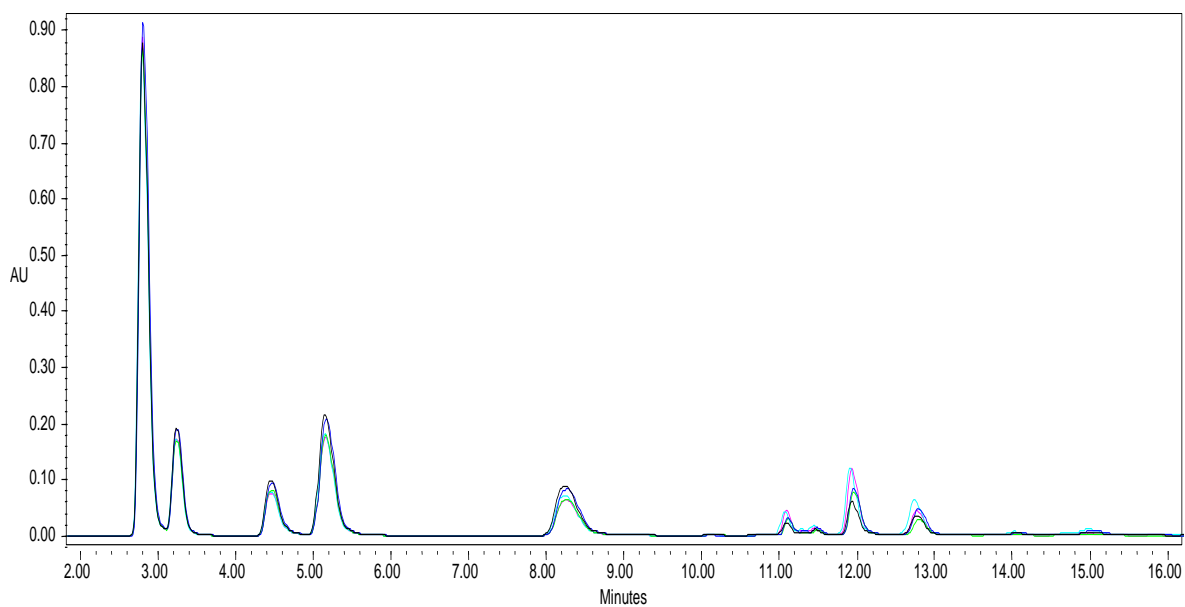


Figure IV.3 HPLC Speciation for 1.7MR 60degC series Chromatograph (Resin SKG-113-09)

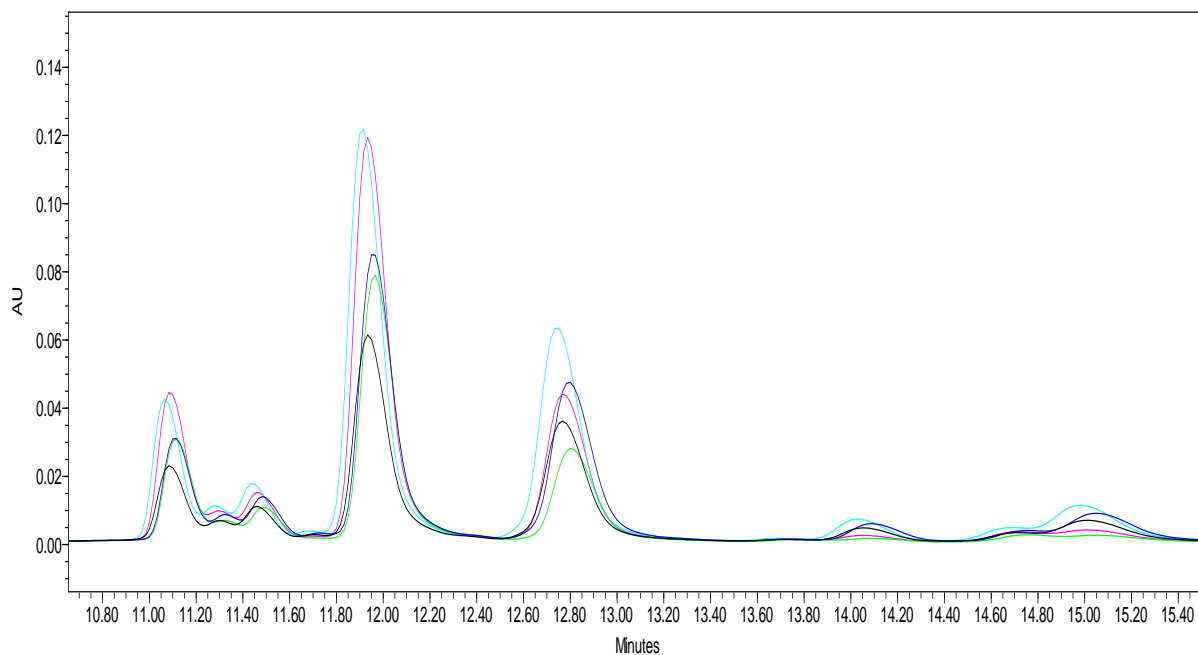


Figure IV.4 Expanded Dimers Region for 1.7MR 60deg C series Chromatograph (Resin SKG-113-09)

APPENDIX V: STATISTICAL ANALYSIS: CHAPTER 3

V.1 Erosion of western red cedar exposed to artificial weathering in QUV or Xenon-arc weatherometers for 100, 250, 500 and 1000 hours

GenStat Release 12.1 (PC/Windows XP) 19 July 2010 12:10:52
Copyright 2009, VSN International Ltd.

Registered to: Philip Evans

GenStat Twelfth Edition
GenStat Procedure Library Release PL20.1

```
1 %CD 'C:/Documents and Settings/phevens/My Documents'
2 "Data taken from File: \
-3 C:/Documents and Settings/phevens/Desktop/data_of_artificial_weathering.xls"
4 DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
5 READ [PRINT=*; SETNVALUES=yes] _stitle_
9 PRINT [IPRINT=*_stitle_]; JUST=left
```

Data imported from Excel file: C:\Documents and Settings\phevens\Desktop\data_of_artificial_weathering.xls
on: 19-Jul-2010 12:11:09
taken from sheet ""Sheet1"", cells Q2:AB257

```
10 DELETE [REDEFINE=yes] Block,Sample,Specimen,Area,Time,Weathermeter,Hole_size\
11 ,Volume_taken_mm3,Maximum_depth_mm,Mean_depth_mm,Volume_taken_mm3_mm2,\
12 Mass_loss_mg_mm2
13 UNITS [NVALUES=*]
14 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=8; REFERENCE=1] Block
15 READ Block; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Block	256	0	8

```
23 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=4; REFERENCE=1] Sample
24 READ Sample; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Sample	256	0	4

```
32 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=2; REFERENCE=1] Specimen
33 READ Specimen; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Specimen	256	0	2

```
41 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=4; REFERENCE=1] Area
42 READ Area; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Area	256	0	4

50 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=4; LABELS=!t('1000hr','100hr',\
51 '250hr','500hr'); REFERENCE=1] Time
52 READ Time; FREPRESENTATION=ordinal

Identifier	Values	Missing	Levels
Time	256	0	4

60 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=2; LABELS=!t('QUV','XA')\
61 ; REFERENCE=1] Weathermeter
62 READ Weathermeter; FREPRESENTATION=ordinal

Identifier	Values	Missing	Levels
Weathermeter	256	0	2

70 FACTOR [MODIFY=yes; NVALUES=256; LEVELS=4; LABELS=!t('1 (S)','2 (M)',\
71 '3 (L)','4 (V.L)'); REFERENCE=1] Hole_size
72 READ Hole_size; FREPRESENTATION=ordinal

Identifier	Values	Missing	Levels
Hole_size	256	0	4

80 VARIATE [NVALUES=256] Volume_taken_mm³
81 READ Volume_taken_mm³

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Volume_taken_mm ³	0.4175	24.99	213.0	256	0	

101 VARIATE [NVALUES=256] Maximum_depth_mm
102 READ Maximum_depth_mm

Identifier	Minimum	Mean	Maximum	Values	Missing
Maximum_depth_mm	0.1100	0.9423	2.800	256	0

123 VARIATE [NVALUES=256] Mean_depth_mm
124 READ Mean_depth_mm

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Mean_depth_mm	0.009800	0.09588	0.4190	256	0	

149 VARIATE [NVALUES=256] Volume_taken_mm³_mm²
150 READ Volume_taken_mm³_mm²

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Volume_taken_mm3_mm2	0.01313	0.09435	0.4201	256	0	

215 VARIATE [NVALUES=256] Mass_loss_mg_mm²
216 READ Mass_loss_mg_mm²

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Mass_loss_mg_mm ²	0.004621	0.02830	0.1359	256	0	


```

287
288 %PostMessage 1129; 0; 26004576 "Sheet Update Completed"
289 "Split-Split-Plot Design."
290 BLOCK Block/Sample/Specimen/Area
291 TREATMENTS Time*Weathermeter*Hole_size
292 COVARIATE "No Covariate"
293 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
294 PSE=diff,lsd; LSDLEVEL=5] Volume_taken_mm3

```

Analysis of variance

Variate: Volume_taken_mm³

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	2155.66	307.95	4.37	
Block.Sample stratum					
Time	3	71052.78	23684.26	335.86	<.001
Residual	21	1480.88	70.52	0.48	
Block.Sample.Specimen stratum					
Weathermeter	1	47287.52	47287.52	324.07	<.001
Time.Weathermeter	3	33805.22	11268.41	77.22	<.001
Residual	28	4085.68	145.92	2.60	
Block.Sample.Specimen.Area stratum					
Hole_size	3	112730.51	37576.84	669.43	<.001
Time.Hole_size	9	48555.32	5395.04	96.11	<.001
Weathermeter.Hole_size	3	31369.07	10456.36	186.28	<.001
Time.Weathermeter.Hole_size	9	22951.06	2550.12	45.43	<.001
Residual	168	9430.30	56.13		
Total	255	384904.01			

Message: the following units have large residuals.

Block 6 Sample 4	-5.53	s.e. 2.41
Block 2 Sample 4 Specimen 1	8.66	s.e. 3.99
Block 2 Sample 4 Specimen 2	-8.66	s.e. 3.99
Block 6 Sample 4 Specimen 1	10.47	s.e. 3.99
Block 6 Sample 4 Specimen 2	-10.47	s.e. 3.99
Block 2 Sample 4 Specimen 1 Area 4	20.39	s.e. 6.07
Block 3 Sample 3 Specimen 2 Area 4	19.65	s.e. 6.07
Block 6 Sample 3 Specimen 2 Area 4	-18.10	s.e. 6.07
Block 6 Sample 4 Specimen 2 Area 1	18.36	s.e. 6.07
Block 6 Sample 4 Specimen 2 Area 4	-28.70	s.e. 6.07
Block 7 Sample 3 Specimen 2 Area 4	17.21	s.e. 6.07
Block 8 Sample 1 Specimen 2 Area 4	21.86	s.e. 6.07
Block 8 Sample 2 Specimen 2 Area 4	23.61	s.e. 6.07

Tables of means

Variate: Volume_taken_mm³

Grand mean 24.99

Time	1000hr	100hr	250hr	500hr
	50.95	7.76	13.51	27.74

Weathermeter	QUV	XA
	11.40	38.58

Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
	2.28	11.18	29.31	57.19

Time	Weathermeter	QUV	XA
1000hr		19.90	82.01
100hr		5.73	9.80
250hr		8.88	18.14
500hr		11.10	44.39

Time	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr		4.64	23.55	60.14	115.47
100hr		0.73	3.26	8.76	18.29
250hr		1.27	5.93	16.32	30.52
500hr		2.49	12.00	32.03	64.47

Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
QUV		0.91	4.80	13.09	26.80
XA		3.65	17.57	45.53	87.57

Time	Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr	QUV		1.37	8.19	24.34	45.68
	XA		7.92	38.91	95.94	185.25
100hr	QUV		0.64	2.73	6.44	13.09
	XA		0.82	3.78	11.08	23.50
250hr	QUV		0.72	3.43	9.03	22.35
	XA		1.82	8.44	23.60	38.69
500hr	QUV		0.92	4.85	12.53	26.09
	XA		4.05	19.15	51.52	102.84

Standard errors of differences of means

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
s.e.d.	1.484	1.510	1.324	2.601
d.f.	21	28	168	46.97
Except when comparing means with the same level(s) of				
Time				3.020
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
s.e.d.	2.732	2.216	4.158
d.f.	140.73	106.32	183.01
Except when comparing means with the same level(s) of			
Time	2.649		4.432
d.f.	168		106.32
Weathermeter		1.873	
d.f.		168	
Time.Weathermeter			3.746
d.f.			168
Time.Hole_size			4.432
d.f.			106.32

Least significant differences of means (5% level)

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
l.s.d.	3.087	3.093	2.615	5.232
d.f.	21	28	168	46.97
Except when comparing means with the same level(s) of				
Time				6.186
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
l.s.d.	5.402	4.394	8.204
d.f.	140.73	106.32	183.01
Except when comparing means with the same level(s) of			
Time	5.229		8.787
d.f.	168		106.32
Weathermeter		3.698	
d.f.		168	
Time.Weathermeter			7.395
d.f.			168
Time.Hole_size			8.787
d.f.			106.32

295 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

296 UNITS [NVALUES=*]

297 READ Volume_taken_mm³[\$[192]

Identifier	Minimum	Mean	Maximum	Values	Missing
Volume_taken_mm ³ [\$[192]	*	*	*	1	1

299

300 %PostMessage 1129; 0; 26004576 "Sheet Update Completed"

301 "Split-Split-Plot Design."

```

302 BLOCK Block/Sample/Specimen/Area
303 TREATMENTS Time*Weathermeter*Hole_size
304 COVARIATE "No Covariate"
305 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
306 PSE=diff,lsd; LSDLEVEL=5] Volume_taken_mm3

```

Analysis of variance

Variate: Volume_taken_mm³

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		1722.50	246.07	4.48	
Block.Sample stratum						
Time	3		73346.14	24448.71	444.81	<.001
Residual	21		1154.25	54.96	0.46	
Block.Sample.Specimen stratum						
Weathermeter	1		48483.95	48483.95	401.74	<.001
Time.Weathermeter	3		35355.41	11785.14	97.65	<.001
Residual	28		3379.18	120.69	2.47	
Block.Sample.Specimen.Area stratum						
Hole_size	3		115569.35	38523.12	786.98	<.001
Time.Hole_size	9		51450.04	5716.67	116.78	<.001
Weathermeter.Hole_size	3		32860.47	10953.49	223.77	<.001
Time.Weathermeter.Hole_size	9		24937.41	2770.82	56.60	<.001
Residual	167	(1)	8174.75	48.95		
Total	254	(1)	372754.56			

Message: the following units have large residuals.

Block 8 Sample 2	4.38	s.e. 2.12
Block 8 Sample 4	-5.20	s.e. 2.12
Block 2 Sample 4 Specimen 1	9.35	s.e. 3.63
Block 2 Sample 4 Specimen 2	-9.35	s.e. 3.63
Block 2 Sample 3 Specimen 2 Area 4	-16.56	s.e. 5.65
Block 2 Sample 4 Specimen 1 Area 4	20.39	s.e. 5.65
Block 2 Sample 4 Specimen 2 Area 4	-17.66	s.e. 5.65
Block 3 Sample 3 Specimen 2 Area 4	19.65	s.e. 5.65
Block 6 Sample 3 Specimen 2 Area 4	-18.10	s.e. 5.65
Block 7 Sample 3 Specimen 2 Area 4	17.21	s.e. 5.65
Block 8 Sample 1 Specimen 2 Area 4	21.86	s.e. 5.65
Block 8 Sample 2 Specimen 2 Area 4	23.61	s.e. 5.65

Tables of means

Variate: Volume_taken_mm³

Grand mean 25.16

Time	1000hr	100hr	250hr	500hr
	51.63	7.76	13.51	27.74
Weathermeter	QUV	XA		
	11.40	38.92		
Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
	2.28	11.18	29.31	57.87

Time	Weathermeter	QUV	XA
1000hr		19.90	83.37
100hr		5.73	9.80
250hr		8.88	18.14
500hr		11.10	44.39

Time	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr		4.64	23.55	60.14	118.20
100hr		0.73	3.26	8.76	18.29
250hr		1.27	5.93	16.32	30.52
500hr		2.49	12.00	32.03	64.47

Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
QUV		0.91	4.80	13.09	26.80
XA		3.65	17.57	45.53	88.94

Time	Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr	QUV		1.37	8.19	24.34	45.68
	XA		7.92	38.91	95.94	190.72
100hr	QUV		0.64	2.73	6.44	13.09
	XA		0.82	3.78	11.08	23.50
250hr	QUV		0.72	3.43	9.03	22.35
	XA		1.82	8.44	23.60	38.69
500hr	QUV		0.92	4.85	12.53	26.09
	XA		4.05	19.15	51.52	102.84

Standard errors of differences of means

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
s.e.d.	1.311	1.373	1.237	2.343
d.f.	21	28	167	46.46
Except when comparing means with the same level(s) of				
Time				2.746
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
s.e.d.	2.511	2.045	3.830
d.f.	149.20	110.23	186.60
Except when comparing means with the same level(s) of			
Time	2.474		4.089
d.f.	167		110.23
Weathermeter		1.749	
d.f.		167	
Time.Weathermeter			
			3.498
d.f.			167
Time.Hole_size			4.089
d.f.			110.23

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
l.s.d.	2.726	2.813	2.442	4.715
d.f.	21	28	167	46.46
Except when comparing means with the same level(s) of				
Time				5.626
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
l.s.d.	4.962	4.052	7.555
d.f.	149.20	110.23	186.60
Except when comparing means with the same level(s) of			
Time	4.884		8.104
d.f.	167		110.23
Weathermeter		3.453	
d.f.		167	
Time.Weathermeter			
			6.906
d.f.			167
Time.Hole_size			8.104
d.f.			110.23

(Not adjusted for missing values)

```

307 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
308 "Split-Split-Plot Design."
309 BLOCK Block/Sample/Specimen/Area
310 TREATMENTS Time*Weathermeter*Hole_size
311 COVARIATE "No Covariate"

```

312 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
 FPROB=yes;\n
 313 PSE=diff,lsd; LSDLEVEL=5] Maximum_depth_mm

Analysis of variance

Variate: Maximum_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	3.8936	0.5562	2.47	
Block.Sample stratum					
Time	3	6.4898	2.1633	9.60	<.001
Residual	21	4.7321	0.2253	0.65	
Block.Sample.Specimen stratum					
Weathermeter	1	19.5903	19.5903	56.41	<.001
Time.Weathermeter	3	5.3344	1.7781	5.12	0.006
Residual	28	9.7244	0.3473	1.71	
Block.Sample.Specimen.Area stratum					
Hole_size	3	11.0276	3.6759	18.06	<.001
Time.Hole_size	9	1.5127	0.1681	0.83	0.593
Weathermeter.Hole_size	3	0.5221	0.1740	0.85	0.466
Time.Weathermeter.Hole_size	9	2.3232	0.2581	1.27	0.258
Residual	168	34.1989	0.2036		
Total	255	99.3490			

Message: the following units have large residuals.

Block 4	0.275	s.e. 0.123
Block 3 Sample 1	0.349	s.e. 0.136
Block 3 Sample 2	-0.359	s.e. 0.136
Block 2 Sample 2 Specimen 1	-0.449	s.e. 0.195
Block 2 Sample 2 Specimen 2	0.449	s.e. 0.195
Block 4 Sample 4 Specimen 1	0.468	s.e. 0.195
Block 4 Sample 4 Specimen 2	-0.468	s.e. 0.195
Block 2 Sample 1 Specimen 2 Area 2	1.190	s.e. 0.365
Block 7 Sample 1 Specimen 2 Area 1	1.193	s.e. 0.365

Tables of means

Variate: Maximum_depth_mm

Grand mean 0.942

Time	1000hr	100hr	250hr	500hr		
	1.199	0.798	0.822	0.951		
Weathermeter	QUV	XA				
	0.666	1.219				
Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)		
	0.723	0.763	1.061	1.222		
Time	Weathermeter	QUV	XA			
1000hr		0.799	1.599			
100hr		0.747	0.848			
250hr		0.570	1.073			
500hr		0.546	1.355			
Time	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)	
1000hr		0.943	1.167	1.297	1.391	
100hr		0.518	0.562	0.918	1.193	
250hr		0.566	0.673	0.912	1.136	
500hr		0.866	0.651	1.118	1.168	
Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)	
QUV		0.387	0.482	0.852	0.942	
XA		1.060	1.044	1.270	1.502	
Time	Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr	QUV		0.494	0.612	0.995	1.097
	XA		1.391	1.721	1.599	1.684
100hr	QUV		0.433	0.606	0.967	0.984
	XA		0.603	0.519	0.870	1.401
250hr	QUV		0.218	0.471	0.821	0.769
	XA		0.914	0.874	1.002	1.503
500hr	QUV		0.404	0.238	0.626	0.917
	XA		1.329	1.064	1.610	1.419

Standard errors of differences of means

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
s.e.d.	0.0839	0.0737	0.0798	0.1338
d.f.	21	28	168	48.76
Except when comparing means with the same level(s) of				
Time				0.1473
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
s.e.d.	0.1616	0.1223	0.2368
d.f.	150.70	140.59	206.24
Except when comparing means with the same level(s) of			
Time	0.1595		0.2447
d.f.	168		140.59
Weathermeter		0.1128	
d.f.		168	
Time.Weathermeter			0.2256
d.f.			168
Time.Hole_size			0.2447
d.f.			140.59

Least significant differences of means (5% level)

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
l.s.d.	0.1745	0.1509	0.1575	0.2689
d.f.	21	28	168	48.76
Except when comparing means with the same level(s) of				
Time				0.3018
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
l.s.d.	0.3194	0.2419	0.4668
d.f.	150.70	140.59	206.24
Except when comparing means with the same level(s) of			
Time	0.3149		0.4838
d.f.	168		140.59
Weathermeter		0.2227	
d.f.		168	
Time.Weathermeter			0.4454
d.f.			168
Time.Hole_size			0.4838
d.f.			140.59

314 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

315 "Split-Split-Plot Design."

316 BLOCK Block/Sample/Specimen/Area

317 TREATMENTS Time*Weathermeter*Hole_size

318 COVARIATE "No Covariate"

319 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7; FPROB=yes;\

320 PSE=diff,lsd; LSDLEVEL=5] Mean_depth_mm

Analysis of variance

Variate: Mean_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.0355335	0.0050762	4.27	
Block.Sample stratum					
Time	3	0.9819778	0.3273259	275.12	<.001
Residual	21	0.0249847	0.0011897	0.52	
Block.Sample.Specimen stratum					
Weathermeter	1	0.6945092	0.6945092	301.64	<.001
Time.Weathermeter	3	0.5224498	0.1741499	75.64	<.001
Residual	28	0.0644680	0.0023024	4.14	
Block.Sample.Specimen.Area stratum					
Hole_size	3	0.0554702	0.0184901	33.27	<.001
Time.Hole_size	9	0.0275132	0.0030570	5.50	<.001
Weathermeter.Hole_size	3	0.0136733	0.0045578	8.20	<.001
Time.Weathermeter.Hole_size	9	0.0100711	0.0011190	2.01	0.041
Residual	168	0.0933721	0.0005558		
Total	255	2.5240230			

Message: the following units have large residuals.

Block 4 Sample 4	0.0201	s.e.	0.0099
Block 5 Sample 4	0.0202	s.e.	0.0099
Block 6 Sample 4	-0.0261	s.e.	0.0099
Block 2 Sample 4 Specimen 1	0.0365	s.e.	0.0159
Block 2 Sample 4 Specimen 2	-0.0365	s.e.	0.0159
Block 6 Sample 4 Specimen 1	0.0443	s.e.	0.0159
Block 6 Sample 4 Specimen 2	-0.0443	s.e.	0.0159
Block 1 Sample 1 Specimen 2 Area 2	0.1034	s.e.	0.0191
Block 1 Sample 3 Specimen 1 Area 1	0.0804	s.e.	0.0191
Block 5 Sample 2 Specimen 1 Area 2	0.1080	s.e.	0.0191

Tables of means

Variate: Mean_depth_mm

Grand mean 0.0959

Time	1000hr	100hr	250hr	500hr
	0.1928	0.0319	0.0537	0.1052
Weathermeter	QUV	XA		
	0.0438	0.1480		
Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
	0.0734	0.0935	0.1036	0.1130

Time	Weathermeter	QUV	XA			
1000hr		0.0703	0.3152			
100hr		0.0235	0.0404			
250hr		0.0367	0.0706			
500hr		0.0447	0.1656			
Time	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)	
1000hr		0.1461	0.1863	0.2125	0.2262	
100hr		0.0231	0.0359	0.0313	0.0374	
250hr		0.0384	0.0569	0.0579	0.0614	
500hr		0.0859	0.0950	0.1127	0.1271	
Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)	
	QUV	0.0324	0.0430	0.0470	0.0528	
	XA	0.1143	0.1440	0.1602	0.1733	
Time	Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr	QUV		0.0425	0.0647	0.0869	0.0870
	XA		0.2498	0.3079	0.3380	0.3654
100hr	QUV		0.0204	0.0217	0.0237	0.0281
	XA		0.0259	0.0500	0.0389	0.0468
250hr	QUV		0.0225	0.0470	0.0329	0.0444
	XA		0.0542	0.0668	0.0829	0.0785
500hr	QUV		0.0442	0.0386	0.0445	0.0516
	XA		0.1275	0.1514	0.1809	0.2026

Standard errors of differences of means

Table	Time	Weathermeter	Hole_size	Time
rep.	64	128	64	Weathermeter
s.e.d.	0.00610	0.00600	0.00417	32
d.f.	21	28	168	0.01045
Except when comparing means with the same level(s) of				47.50
Time				0.01200
d.f.				28

Table	Time	Weathermeter	Time
	Hole_size	Hole_size	Weathermeter
rep.	16	32	Hole_size
s.e.d.	0.00945	0.00788	8
d.f.	97.23	76.55	0.01461
Except when comparing means with the same level(s) of			
Time	0.00834		144.33
d.f.	168		0.01575
Weathermeter		0.00589	76.55
d.f.		168	
Time.Weathermeter			
			0.01179
d.f.			168
Time.Hole_size			0.01575
d.f.			76.55

\

Least significant differences of means (5% level)

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
l.s.d.	0.01268	0.01229	0.00823	0.02101
d.f.	21	28	168	47.50
Except when comparing means with the same level(s) of				
Time				0.02457
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
l.s.d.	0.01875	0.01568	0.02887
d.f.	97.23	76.55	144.33
Except when comparing means with the same level(s) of			
Time	0.01645		0.03137
d.f.	168		76.55
Weathermeter		0.01164	
d.f.		168	
Time.Weathermeter			
			0.02327
d.f.			168
Time.Hole_size			
			0.03137
d.f.			76.55

```

321 A PLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
322 "Split-Split-Plot Design."
323 BLOCK Block/Sample/Specimen/Area
324 TREATMENTS Time*Weathermeter*Hole_size
325 COVARIATE "No Covariate"
326 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
327 PSE=diff,lsd; LSDLEVEL=5] Mean_depth_mm

```

Analysis of variance

Variate: Mean_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.0355335	0.0050762	4.27	
Block.Sample stratum					
Time	3	0.9819778	0.3273259	275.12	<.001
Residual	21	0.0249847	0.0011897	0.52	
Block.Sample.Specimen stratum					
Weathermeter	1	0.6945092	0.6945092	301.64	<.001
Time.Weathermeter	3	0.5224498	0.1741499	75.64	<.001
Residual	28	0.0644680	0.0023024	4.14	
Block.Sample.Specimen.Area stratum					
Hole_size	3	0.0554702	0.0184901	33.27	<.001
Time.Hole_size	9	0.0275132	0.0030570	5.50	<.001
Weathermeter.Hole_size	3	0.0136733	0.0045578	8.20	<.001
Time.Weathermeter.Hole_size	9	0.0100711	0.0011190	2.01	0.041
Residual	168	0.0933721	0.0005558		
Total	255	2.5240230			

Message: the following units have large residuals.

Block 4 Sample 4	0.0201	s.e.	0.0099
Block 5 Sample 4	0.0202	s.e.	0.0099
Block 6 Sample 4	-0.0261	s.e.	0.0099
Block 2 Sample 4 Specimen 1	0.0365	s.e.	0.0159
Block 2 Sample 4 Specimen 2	-0.0365	s.e.	0.0159
Block 6 Sample 4 Specimen 1	0.0443	s.e.	0.0159
Block 6 Sample 4 Specimen 2	-0.0443	s.e.	0.0159
Block 1 Sample 1 Specimen 2 Area 2	0.1034	s.e.	0.0191
Block 1 Sample 3 Specimen 1 Area 1	0.0804	s.e.	0.0191
Block 5 Sample 2 Specimen 1 Area 2	0.1080	s.e.	0.0191

Tables of means

Variate: Mean_depth_mm

Grand mean 0.0959

Time	1000hr 0.1928	100hr 0.0319	250hr 0.0537	500hr 0.1052
Weathermeter	QUV 0.0438	XA 0.1480		
Hole_size	1 (S) 0.0734	2 (M) 0.0935	3 (L) 0.1036	4 (V.L) 0.1130

Time	Weathermeter	QUV	XA
1000hr		0.0703	0.3152
100hr		0.0235	0.0404
250hr		0.0367	0.0706
500hr		0.0447	0.1656

Time	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr		0.1461	0.1863	0.2125	0.2262
100hr		0.0231	0.0359	0.0313	0.0374
250hr		0.0384	0.0569	0.0579	0.0614
500hr		0.0859	0.0950	0.1127	0.1271

Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
QUV		0.0324	0.0430	0.0470	0.0528
XA		0.1143	0.1440	0.1602	0.1733

Time	Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr	QUV		0.0425	0.0647	0.0869	0.0870
	XA		0.2498	0.3079	0.3380	0.3654
100hr	QUV		0.0204	0.0217	0.0237	0.0281
	XA		0.0259	0.0500	0.0389	0.0468
250hr	QUV		0.0225	0.0470	0.0329	0.0444
	XA		0.0542	0.0668	0.0829	0.0785
500hr	QUV		0.0442	0.0386	0.0445	0.0516
	XA		0.1275	0.1514	0.1809	0.2026

Standard errors of differences of means

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
s.e.d.	0.00610	0.00600	0.00417	0.01045
d.f.	21	28	168	47.50
Except when comparing means with the same level(s) of				
Time				0.01200
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
s.e.d.	0.00945	0.00788	0.01461
d.f.	97.23	76.55	144.33
Except when comparing means with the same level(s) of			
Time	0.00834		0.01575
d.f.	168		76.55
Weathermeter		0.00589	
d.f.		168	
Time.Weathermeter			
			0.01179
d.f.			168
Time.Hole_size			0.01575
d.f.			76.55

Least significant differences of means (5% level)

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
l.s.d.	0.01268	0.01229	0.00823	0.02101
d.f.	21	28	168	47.50
Except when comparing means with the same level(s) of Time				0.02457
d.f.				28

Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size
rep.	16	32	8
l.s.d.	0.01875	0.01568	0.02887
d.f.	97.23	76.55	144.33
Except when comparing means with the same level(s) of Time			0.03137
d.f.	168		76.55
Weathermeter		0.01164	
d.f.		168	
Time.Weathermeter			0.02327
d.f.			168
Time.Hole_size			0.03137
d.f.			76.55

328 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
 329 "Split-Split-Plot Design."
 330 BLOCK Block/Sample/Specimen/Area
 331 TREATMENTS Time*Weathermeter*Hole_size
 332 COVARIATE "No Covariate"
 333 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7; FPROB=yes;\n
 334 PSE=diff,lsd; LSDLEVEL=5] Mass_loss_mg_mm²

Analysis of variance

Variate: Mass_loss_mg_mm²

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.00291320	0.00041617	3.30	
Block.Sample stratum					
Time	3	0.09126879	0.03042293	240.87	<.001
Residual	21	0.00265237	0.00012630	0.67	
Block.Sample.Specimen stratum					
Weathermeter	1	0.06423518	0.06423518	340.40	<.001
Time.Weathermeter	3	0.04702416	0.01567472	83.06	<.001
Residual	28	0.00528374	0.00018870	7.32	
Block.Sample.Specimen.Area stratum					
Hole_size	3	0.00572205	0.00190735	73.99	<.001
Time.Hole_size	9	0.00236004	0.00026223	10.17	<.001
Weathermeter.Hole_size	3	0.00099334	0.00033111	12.85	<.001
Time.Weathermeter.Hole_size					
	9	0.00067618	0.00007513	2.91	0.003
Residual	168	0.00433056	0.00002578		
Total	255	0.22745959			

Message: the following units have large residuals.

Block 5 Sample 4	0.00867	s.e.	0.00322
Block 6 Sample 4	-0.00812	s.e.	0.00322
Block 2 Sample 4 Specimen 1	0.01208	s.e.	0.00454
Block 2 Sample 4 Specimen 2	-0.01208	s.e.	0.00454
Block 6 Sample 4 Specimen 1	0.01250	s.e.	0.00454
Block 6 Sample 4 Specimen 2	-0.01250	s.e.	0.00454
Block 1 Sample 4 Specimen 2 Area 2	0.01179	s.e.	0.00411
Block 2 Sample 4 Specimen 1 Area 4	0.01275	s.e.	0.00411
Block 2 Sample 4 Specimen 2 Area 1	-0.01394	s.e.	0.00411
Block 2 Sample 4 Specimen 2 Area 3	0.01481	s.e.	0.00411
Block 3 Sample 3 Specimen 2 Area 4	0.01520	s.e.	0.00411
Block 4 Sample 4 Specimen 2 Area 1	0.01181	s.e.	0.00411
Block 5 Sample 4 Specimen 2 Area 1	0.01179	s.e.	0.00411
Block 8 Sample 1 Specimen 2 Area 4	0.01144	s.e.	0.00411

Tables of means

Variate: Mass_loss_mg_mm²

Grand mean 0.02830

Time	1000hr	100hr	250hr	500hr
	0.05788	0.00882	0.01549	0.03100

Weathermeter	QUV	XA
	0.01246	0.04414

Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
	0.02160	0.02648	0.03101	0.03411

Time	Weathermeter	QUV	XA
1000hr		0.02125	0.09452
100hr		0.00699	0.01065
250hr		0.00948	0.02150
500hr		0.01212	0.04989

Time	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr		0.04384	0.05578	0.06352	0.06840
100hr		0.00692	0.00774	0.00942	0.01121
250hr		0.01208	0.01404	0.01733	0.01851
500hr		0.02354	0.02836	0.03379	0.03833

Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
QUV		0.00858	0.01137	0.01398	0.01591
XA		0.03461	0.04159	0.04805	0.05231

Time	Weathermeter	Hole_size	1 (S)	2 (M)	3 (L)	4 (V.L)
1000hr	QUV		0.01284	0.01947	0.02585	0.02683
	XA		0.07484	0.09209	0.10119	0.10997
100hr	QUV		0.00605	0.00650	0.00712	0.00830
	XA		0.00780	0.00897	0.01172	0.01412
250hr	QUV		0.00676	0.00807	0.00979	0.01330
	XA		0.01740	0.02001	0.02486	0.02372
500hr	QUV		0.00868	0.01144	0.01315	0.01522
	XA		0.03840	0.04527	0.05444	0.06144

Standard errors of differences of means

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
s.e.d.	0.001987	0.001717	0.000898	0.003138
d.f.	21	28	168	48.85
Except when comparing means with the same level(s) of				
Time				0.003434
d.f.				28
Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size	
rep.	16	32	8	
s.e.d.	0.002523	0.002039	0.003831	
d.f.	52.14	54.14	101.48	
Except when comparing means with the same level(s) of				
Time	0.001795		0.004078	
d.f.	168		54.14	
Weathermeter		0.001269		
d.f.		168		
Time.Weathermeter			0.002539	
d.f.			168	
Time.Hole_size			0.004078	
d.f.			54.14	

Least significant differences of means (5% level)

Table	Time	Weathermeter	Hole_size	Time Weathermeter
rep.	64	128	64	32
l.s.d.	0.004132	0.003517	0.001772	0.006306
d.f.	21	28	168	48.85
Except when comparing means with the same level(s) of				
Time				0.007035
d.f.				28
Table	Time Hole_size	Weathermeter Hole_size	Time Weathermeter Hole_size	
rep.	16	32	8	
l.s.d.	0.005062	0.004087	0.007599	
d.f.	52.14	54.14	101.48	
Except when comparing means with the same level(s) of				
Time	0.003544		0.008175	
d.f.	168		54.14	
Weathermeter		0.002506		
d.f.		168		
Time.Weathermeter			0.005012	
d.f.			168	
Time.Hole_size			0.008175	
d.f.			54.14	

PLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

V.2 Erosion of western red cedar exposed to natural weathering for 1000, 2500, 5000 and 10,000 hours

GenStat Release 12.1 (PC/Windows XP) 30 June 2010 15:36:25
Copyright 2009, VSN International Ltd.

Registered to: Philip Evans

GenStat Twelfth Edition
GenStat Procedure Library Release PL20.1

```
1 %CD 'C:/Documents and Settings/phevens/My Documents'
2 "Data taken from File: \
-3 C:/Documents and Settings/phevens/Desktop/Natural_weathering_data.xls"
4 DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
5 READ [PRINT=*; SETNVALUES=yes] _stitle_
9 PRINT [IPRINT=*_stitle_; JUST=left
```

Data imported from Excel file: C:\Documents and Settings\phevens\Desktop\Natural_weathering_data.xls
on: 30-Jun-2010 15:36:54
taken from sheet ""Sheet1"", cells A2:J129

```
10 DELETE [REDEFINE=yes] Block,Sample,Area,Time,Hole_size,Volume_taken_mm3,\
11 Maximum_depth_mm,Mean_depth_mm,Volume_taken_mm3_mm2,Mass_loss_mg_mm2
12 UNITS [NVALUES=*]
13 FACTOR [MODIFY=yes; NVALUES=128; LEVELS=8; REFERENCE=1] Block
14 READ Block; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Block	128	0	8

```
19 FACTOR [MODIFY=yes; NVALUES=128; LEVELS=4; REFERENCE=1] Sample
20 READ Sample; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Sample	128	0	4

```
25 FACTOR [MODIFY=yes; NVALUES=128; LEVELS=4; REFERENCE=1] Area
26 READ Area; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Area	128	0	4

```
31 FACTOR [MODIFY=yes; NVALUES=128; LEVELS=4; LABELS=!t('10000hr','1000hr',\
32 '2500hr','5000hr'); REFERENCE=1] Time
33 READ Time; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Time	128	0	4

```

38 FACTOR [MODIFY=yes; NVALUES=128; LEVELS=4; LABELS=!t('aSmall','bMedium',\
39 'cLarge','dVery large'); REFERENCE=1] Hole_size
40 READ Hole_size; FREPRESENTATION=ordinal

```

Identifier	Values	Missing	Levels
Hole_size	128	0	4

```

45 VARIATE [NVALUES=128] Volume_taken_mm3
46 READ Volume_taken_mm3

```

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Volume_taken_mm ³	0.5070	27.25	120.0	128	0	

```

56 VARIATE [NVALUES=128] Maximum_depth_mm
57 READ Maximum_depth_mm

```

Identifier	Minimum	Mean	Maximum	Values	Missing
Maximum_depth_mm	0.09990	0.9818	2.410	128	0

```

68 VARIATE [NVALUES=128] Mean_depth_mm
69 READ Mean_depth_mm

```

Identifier	Minimum	Mean	Maximum	Values	Missing
Mean_depth_mm	0.01590	0.1031	0.2360	128	0

```

81 VARIATE [NVALUES=128] Volume_taken_mm3_mm2
82 READ Volume_taken_mm3_mm2

```

Identifier	Minimum	Mean	Maximum	Values	Missing
Volume_taken_mm ³ _mm ²	0.01594	0.1025	0.2358	128	0

```

114 VARIATE [NVALUES=128] Mass_loss_mg_mm2
115 READ Mass_loss_mg_mm2

```

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Mass_loss_mg_mm ²	0.1415	8.143	34.68	128	0	

```

130
131 %PostMessage 1129; 0; 26004576 "Sheet Update Completed"
132 "Split-Plot Design."
133 BLOCK Block/Sample/Area
134 TREATMENTS Time*Hole_size
135 COVARIATE "No Covariate"
136 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
137 PSE=diff] Mean_depth_mm

```

Analysis of variance

Variate: Mean_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.0245206	0.0035029	4.65	
Block.Sample stratum					
Time	3	0.3820387	0.1273462	169.17	<.001
Residual	21	0.0158081	0.0007528	2.61	
Block.Sample.Area stratum					
Hole_size	3	0.0360299	0.0120100	41.65	<.001
Time.Hole_size	9	0.0062420	0.0006936	2.40	0.018
Residual	84	0.0242242	0.0002884		
Total	127	0.4888635			

Message: the following units have large residuals.

Block 8 Sample 4	-0.0223	s.e.	0.0111
Block 4 Sample 1 Area 4	0.0456	s.e.	0.0138
Block 5 Sample 3 Area 1	-0.0359	s.e.	0.0138
Block 7 Sample 3 Area 2	0.0407	s.e.	0.0138
Block 8 Sample 3 Area 3	0.0403	s.e.	0.0138

Tables of means

Variate: Mean_depth_mm

Grand mean 0.1031

Time	10000hr	1000hr	2500hr	5000hr	
	0.1648	0.0365	0.0626	0.1484	
Hole_size	aSmall	bMedium	cLarge	dVery large	
	0.0769	0.1034	0.1089	0.1232	
Time	Hole_size	aSmall	bMedium	cLarge	dVery large
10000hr		0.1276	0.1656	0.1785	0.1876
1000hr		0.0214	0.0329	0.0335	0.0582
2500hr		0.0476	0.0588	0.0665	0.0777
5000hr		0.1108	0.1562	0.1574	0.1692

Standard errors of differences of means

Table	Time	Hole_size	Time Hole_size
rep.	32	32	8
s.e.d.	0.00686	0.00425	0.01006
d.f.	21	84	72.93
Except when comparing means with the same level(s) of			
Time			0.00849
d.f.			84

```

138 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
139 "Split-Plot Design."
140 BLOCK Block/Sample/Area
141 TREATMENTS Time*Hole_size
142 COVARIATE "No Covariate"
143 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
144 PSE=diff] Maximum_depth_mm

```

Analysis of variance

Variate: Maximum_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	5.2664	0.7523	1.30	
Block.Sample stratum					
Time	3	8.6909	2.8970	5.01	0.009
Residual	21	12.1368	0.5779	4.13	
Block.Sample.Area stratum					
Hole_size	3	1.4725	0.4908	3.51	0.019
Time.Hole_size	9	0.5750	0.0639	0.46	0.900
Residual	84	11.7624	0.1400		
Total	127	39.9040			

Message: the following units have large residuals.

Block 6 Sample 2	-0.780	s.e. 0.308
Block 1 Sample 1 Area 2	0.942	s.e. 0.303
Block 2 Sample 1 Area 2	-0.904	s.e. 0.303
Block 3 Sample 2 Area 3	-0.853	s.e. 0.303
Block 7 Sample 1 Area 1	-0.923	s.e. 0.303
Block 8 Sample 1 Area 3	-1.044	s.e. 0.303

Tables of means

Variate: Maximum_depth_mm

Grand mean 0.982

Time	10000hr 0.556	1000hr 1.263	2500hr 1.042	5000hr 1.067	
Hole_size	aSmall 0.802	bMedium 1.009	cLarge 1.035	dVery large 1.082	
Time	Hole_size	aSmall	bMedium	cLarge	dVery large
10000hr		0.454	0.578	0.568	0.622
1000hr		1.200	1.263	1.258	1.330
2500hr		0.774	1.089	1.072	1.232
5000hr		0.778	1.106	1.241	1.143

Standard errors of differences of means

Table	Time	Hole_size	Time Hole_size
rep.	32	32	8
s.e.d.	0.1901	0.0936	0.2498
d.f.	21	84	55.32
Except when comparing means with the same level(s) of			
Time			0.1871
d.f.			84

```

145 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
146 "Split-Plot Design."
147 BLOCK Block/Sample/Area
148 TREATMENTS Time*Hole_size
149 COVARIATE "No Covariate"
150 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
151 PSE=diff] Mass_loss_mg_mm2

```

Analysis of variance

Variate: Mass_loss_μg_mm²

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	123.663	17.666	2.59	
Block.Sample stratum					
Time	3	2161.049	720.350	105.66	<.001
Residual	21	143.171	6.818	2.07	
Block.Sample.Area stratum					
Hole_size	3	5909.995	1969.998	598.40	<.001
Time.Hole_size	9	1248.459	138.718	42.14	<.001
Residual	84	276.536	3.292		
Total	127	9862.872			

Message: the following units have large residuals.

Block 1 Sample 4 Area 4	4.14	s.e. 1.47
Block 4 Sample 1 Area 4	5.36	s.e. 1.47

Tables of means

Variate: Mass_loss_μg_mm²

Grand mean 8.14

Time	10000hr	1000hr	2500hr	5000hr
	12.88	3.23	4.99	11.47
Hole_size	aSmall	bMedium	cLarge	dVery large
	0.76	3.88	9.26	18.67

Time	Hole_size	aSmall	bMedium	cLarge	dVery large
10000hr		1.28	6.40	15.28	28.54
1000hr		0.20	1.25	2.84	8.64
2500hr		0.45	2.25	5.63	11.63
5000hr		1.10	5.63	13.29	25.88

Standard errors of differences of means

Table	Time	Hole_size	Time Hole_size
rep.	32	32	8
s.e.d.	0.653	0.454	1.021
d.f.	21	84	82.58
Except when comparing means with the same level(s) of			
Time			0.907
d.f.			84

152 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
 153 "Split-Plot Design."
 154 BLOCK Block/Sample/Area
 155 TREATMENTS Time*Hole_size
 156 COVARIATE "No Covariate"
 157 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
 FPROB=yes;\n
 158 PSE=diff] Volume_taken_mm3

Analysis of variance

Variate: Volume_taken_mm³

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	1972.54	281.79	4.05	
Block.Sample stratum					
Time	3	23999.12	7999.71	115.03	<.001
Residual	21	1460.46	69.55	1.62	
Block.Sample.Area stratum					
Hole_size	3	66350.68	22116.89	516.10	<.001
Time.Hole_size	9	13799.91	1533.32	35.78	<.001
Residual	84	3599.70	42.85		
Total	127	111182.41			

Message: the following units have large residuals.

Block 1 Sample 4	7.19	s.e. 3.38
Block 1 Sample 4 Area 4	16.13	s.e. 5.30
Block 3 Sample 2 Area 4	-13.93	s.e. 5.30
Block 4 Sample 1 Area 4	21.86	s.e. 5.30
Block 4 Sample 2 Area 4	13.86	s.e. 5.30

Tables of means

Variate: Volume_taken_mm³

Grand mean 27.25

Time	10000hr	1000hr	2500hr	5000hr	
	43.05	10.85	16.79	38.30	
Hole_size	aSmall	bMedium	cLarge	dVery large	
	2.53	13.00	30.91	62.55	
Time	Hole_size	aSmall	bMedium	cLarge	dVery large
10000hr		4.27	21.50	51.00	95.43
1000hr		0.68	4.19	9.53	29.00
2500hr		1.51	7.48	18.89	39.30
5000hr		3.68	18.83	44.21	86.48

Standard errors of differences of means

Table	Time	Hole_size	Time Hole_size
rep.	32	32	8
s.e.d.	2.085	1.637	3.519
d.f.	21	84	91.90
Except when comparing means with the same level(s) of			
Time			3.273
d.f.			84

159 A PLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
 160 "Split-Plot Design."
 161 BLOCK Block/Sample/Area
 162 TREATMENTS Time*Hole_size
 163 COVARIATE "No Covariate"
 164 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
 FPROB=yes;\n
 165 PSE=diff] Volume_taken_mm³_mm²

Analysis of variance

Variate: Volume_taken_mm³_mm²

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.0250597	0.0035800	4.70	
Block.Sample stratum					
Time	3	0.3752633	0.1250878	164.38	<.001
Residual	21	0.0159805	0.0007610	2.93	
Block.Sample.Area stratum					
Hole_size	3	0.0363057	0.0121019	46.64	<.001
Time.Hole_size	9	0.0055399	0.0006155	2.37	0.019
Residual	84	0.0217942	0.0002595		
Total	127	0.4799433			

Message: the following units have large residuals.

Block 8 Sample 3	0.0232	s.e. 0.0112
Block 8 Sample 4	-0.0229	s.e. 0.0112
Block 4 Sample 1 Area 4	0.0458	s.e. 0.0130
Block 5 Sample 3 Area 1	-0.0380	s.e. 0.0130
Block 8 Sample 3 Area 3	0.0377	s.e. 0.0130

Tables of means

Variate: Volume_taken_mm³_mm²

Grand mean 0.1025

Time	10000hr	1000hr	2500hr	5000hr	
	0.1649	0.0365	0.0627	0.1461	
Hole_size	aSmall	bMedium	cLarge	dVery large	
	0.0768	0.1010	0.1090	0.1232	
Time	Hole_size	aSmall	bMedium	cLarge	dVery large
10000hr		0.1276	0.1657	0.1786	0.1876
1000hr		0.0215	0.0328	0.0335	0.0583
2500hr		0.0476	0.0588	0.0665	0.0778
5000hr		0.1107	0.1468	0.1576	0.1694

Standard errors of differences of means

Table	Time	Hole_size	Time Hole_size
rep.	32	32	8
s.e.d.	0.00690	0.00403	0.00981
d.f.	21	84	68.11
Except when comparing means with the same level(s) of			
Time			0.00805
d.f.			84

166 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

APPENDIX VI: STATISTICAL ANALYSIS: CHAPTER 4

VI.1 Effects of different concentration of PF resin (12%, 24%, 36%, 48%) and wax (2.5%) treatment on weight losses and tensile strength of wood veneers exposed to 50 days natural weathering

GenStat Release 12.1 (PC/Windows XP) 17 November 2010 16:00:31
Copyright 2009, VSN International Ltd.

Registered to: Philip Evans

GenStat Twelfth Edition
GenStat Procedure Library Release PL20.1

```
1 %CD 'C:/Documents and Settings/phevans/My Documents'
2 "Data taken from File: \
-3 C:/Documents and Settings/phevans/Desktop/PFWax08(2)new(2).xls"
4 DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
5 READ [PRINT=*; SETNVALUES=yes] _stitle_
9 PRINT [IPRINT=*] _stitle_; JUST=left
```

Data imported from Excel file: C:\Documents and Settings\phevans\Desktop\PFWax08(2)new(2).xls
on: 17-Nov-2010 16:00:59
taken from sheet ""Sheet1"", cells A2:J41

```
10 DELETE [REDEFINE=yes] Block,Treatment,Thickness,W_bef_Treat,W_aft_Treat,\
11 W_aft_Wea,WL_%,P,TS_kg_mm2,Wt_ratio
12 UNITS [NVALUES=*]
13 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=4; REFERENCE=1] Block
14 READ Block; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Block	40	0	4

```
17 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=10; LABELS=!t('0%P','0%PW','12%P',\
18 '12%PW','24%P','24%PW','36%P','36%PW','48%P','48%PW')\
19 ; REFERENCE=1] Treatment
20 READ Treatment; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Treatment	40	0	10

```
23 VARIATE [NVALUES=40] Thickness
24 READ Thickness
```

Identifier	Minimum	Mean	Maximum	Values	Missing
Thickness	81.60	85.92	91.00	40	0

28 VARIATE [NVALUES=40] W_bef_Treat

29 READ W_bef_Treat

Identifier	Minimum	Mean	Maximum	Values	Missing
W_bef_Treat	0.05554	0.06235	0.06946	40	0

35 VARIATE [NVALUES=40] W_aft_Treat

36 READ W_aft_Treat

Identifier	Minimum	Mean	Maximum	Values	Missing
W_aft_Treat	0.05668	0.1094	0.1812	40	0

42 VARIATE [NVALUES=40] W_aft_Wea

43 READ W_aft_Wea

Identifier	Minimum	Mean	Maximum	Values	Missing
W_aft_Wea	0.04242	0.09785	0.1655	40	0

49 VARIATE [NVALUES=40] WL_%

50 READ WL_%

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
WL_%	7.398	11.38	25.14	40	0	

61 VARIATE [NVALUES=40] P

62 READ P

Identifier	Minimum	Mean	Maximum	Values	Missing
P	19.80	30.52	45.36	40	0

67 VARIATE [NVALUES=40] TS_kg_mm²

68 READ TS_kg_mm²

Identifier	Minimum	Mean	Maximum	Values	Missing
TS_kg_mm ²	5.319	8.298	12.76	40	0

79 VARIATE [NVALUES=40] Wt_ratio

80 READ Wt_ratio

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Wt_ratio	0.7486	0.8862	0.9260	40	0	

91

92 %PostMessage 1129; 0; 26128520 "Sheet Update Completed"

93 "One-way design in randomized blocks"

94 DELETE [REDEFINE=yes] _ibalance

95 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\

96 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Wt_ratio; SAVE=_a2save

Analysis of variance

Variate: Wt_ratio

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.0020685	0.0006895	2.83	
Block.*Units* stratum					
Treatment	9	0.0617501	0.0068611	28.16	<.001
Residual	27	0.0065782	0.0002436		
Total	39	0.0703967			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 3 *units* 1	-0.0400	s.e. 0.0128
Block 3 *units* 2	-0.0283	s.e. 0.0128

Tables of means

Variate: Wt_ratio

Grand mean 0.8862

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	0.7963	0.8231	0.9116	0.9013	0.8937	0.8976	0.9104
Treatment	36%PW	48%P	48%PW				
	0.9188	0.9055	0.9036				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.01104

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	0.02265

97 SET [IN=*

103 "One-way design in randomized blocks"

104 DELETE [REDEFINE=yes] _ibalance

105 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\

106 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] TS_kg_mm2; SAVE=_a2save

Analysis of variance

Variate: TS_kg_mm²

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	25.496	8.499	5.44	
Block.*Units* stratum					
Treatment	9	47.664	5.296	3.39	0.007
Residual	27	42.173	1.562		
Total	39	115.333			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 1 *units* 9	-2.15	s.e.	1.03
Block 3 *units* 8	-2.88	s.e.	1.03

Tables of means

Variate: TS_kg_mm²

Grand mean 8.30

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	6.31	7.09	8.22	7.41	9.46	8.24	9.55
Treatment	36%PW	48%P	48%PW				
	9.42	7.85	9.44				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.884

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	1.813

107 SET [IN=*

113 "One-way design in randomized blocks"

114 DELETE [REDEFINE=yes] _ibalance

115 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\

116 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] WL_%; SAVE=_a2save

Analysis of variance

Variate: WL_%

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	20.685	6.895	2.83	
Block.*Units* stratum					
Treatment	9	617.501	68.611	28.16	<.001
Residual	27	65.782	2.436		
Total	39	703.967			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 3 *units* 1	4.00	s.e. 1.28
Block 3 *units* 2	2.83	s.e. 1.28

Tables of means

Variate: WL_%

Grand mean 11.38

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	20.37	17.69	8.84	9.87	10.63	10.24	8.96
Treatment	36%PW	48%P	48%PW				
	8.12	9.45	9.64				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	1.104

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	2.265
117	ET [IN=*]

VI.2 Effects of PF resin (12%, 24%, 36%, 48%) and wax (2.5%) treatment on color changes (L*, a*, b*) of wood veneers exposed to 50 days natural weathering.

GenStat Release 12.1 (PC/Windows XP) 17 November 2010 16:08:51
Copyright 2009, VSN International Ltd.

Registered to: Philip Evans

GenStat Twelfth Edition
GenStat Procedure Library Release PL20.1

```
1 %CD 'C:/Documents and Settings/phevens/My Documents'
2 "Data taken from File: \
-3 C:/Documents and Settings/phevens/Desktop/PFWax08(2)new(2).xls"
4 DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
5 READ [PRINT=*; SETNVALUES=yes] _stitle_
9 PRINT [IPRINT=*_stitle_; JUST=left
```

Data imported from Excel file: C:\Documents and Settings\phevens\Desktop\PFWax08(2)new(2).xls
on: 17-Nov-2010 16:09:10
taken from sheet ""Sheet2"", cells A2:N41

```
10 DELETE [REDEFINE=yes] Block,Treatment,L,a,b,L_1,a_1,b_1,%L,%a,%b,Lrat,a_rat,\
11 b_rat
12 UNITS [NVALUES=*]
13 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=4; REFERENCE=1] Block
14 READ Block; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Block	40	0	4

```
17 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=10; LABELS=!t('0%P','0%PW','12%P',\
18 '12%PW','24%P','24%PW','36%P','36%PW','48%P','48%PW')\
19 ; REFERENCE=1] Treatment
20 READ Treatment; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Treatment	40	0	10

```
23 VARIATE [NVALUES=40] L
24 READ L
```

Identifier	Minimum	Mean	Maximum	Values	Missing
L	58.28	68.31	79.12	40	0

```
29 VARIATE [NVALUES=40] a
30 READ a
```

Identifier	Minimum	Mean	Maximum	Values	Missing
a	4.470	15.28	25.80	40	0

35 VARIATE [NVALUES=40] b
36 READ b

Identifier	Minimum	Mean	Maximum	Values	Missing
b	23.45	43.63	53.74	40	0

41 VARIATE [NVALUES=40] L_1; EXTRA=' L'
42 READ L_1

Identifier	Minimum	Mean	Maximum	Values	Missing
L_1	67.38	80.43	90.26	40	0

47 VARIATE [NVALUES=40] a_1; EXTRA=' a'
48 READ a_1

Identifier	Minimum	Mean	Maximum	Values	Missing
a_1	0.9440	6.610	12.77	40	0

53 VARIATE [NVALUES=40] b_1; EXTRA=' b'
54 READ b_1

Identifier	Minimum	Mean	Maximum	Values	Missing
b_1	29.47	37.92	44.40	40	0

59 VARIATE [NVALUES=40] %L
60 READ %L

Identifier	Minimum	Mean	Maximum	Values	Missing
%L	0.7306	0.8567	1.180	40	0

71 VARIATE [NVALUES=40] %a
72 READ %a

Identifier	Minimum	Mean	Maximum	Values	Missing	
%a	1.468	2.856	7.985	40	0	Skew

83 VARIATE [NVALUES=40] %b
84 READ %b

Identifier	Minimum	Mean	Maximum	Values	Missing
%b	0.6841	1.146	1.441	40	0

95 VARIATE [NVALUES=40] Lrat
96 READ Lrat

Identifier	Minimum	Mean	Maximum	Values	Missing
Lrat	0.9903	1.180	1.368	40	0

107 VARIATE [NVALUES=40] a_rat
108 READ a_rat

Identifier	Minimum	Mean	Maximum	Values	Missing
a_rat	0.1569	0.4265	0.6850	40	0


```
119 VARIATE [NVALUES=40] b_rat
120 READ b_rat
```

Identifier	Minimum	Mean	Maximum	Values	Missing
b_rat	0.6979	0.9072	1.462	40	0

```
131
132 %PostMessage 1129; 0; 21227144 "Sheet Update Completed"
133 "One-way design in randomized blocks"
134 DELETE [REDEFINE=yes] _ibalance
135 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\
136 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %L; SAVE=_a2save
```

Analysis of variance

Variate: %L

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.043805	0.014602	5.39	
Block.*Units* stratum					
Treatment	9	0.108197	0.012022	4.44	0.001
Residual	27	0.073157	0.002710		
Total	39	0.225159			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 3 *units* 8	0.1331	s.e. 0.0428
-------------------	--------	-------------

Tables of means

Variate: %L

Grand mean 0.8567

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	0.8521	0.8258	0.8173	0.8007	0.8778	0.8097	0.8660

Treatment	36%PW	48%P	48%PW
	0.9919	0.8753	0.8508

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.03681

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	0.07552

```

137 SET [IN=]
143 "One-way design in randomized blocks"
144 DELETE [REDEFINE=yes] _ibalance
145 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\
146 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %a; SAVE=_a2save

```

Analysis of variance

Variate: %a

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	9.864	3.288	2.13	
Block.*Units* stratum					
Treatment	9	31.260	3.473	2.25	0.050
Residual	27	41.714	1.545		
Total	39	82.838			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 2 *units* 1	3.41	s.e.	1.02
Block 4 *units* 2	2.53	s.e.	1.02

Tables of means

Variate: %a

Grand mean 2.86

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	4.18	3.95	2.94	4.02	1.83	3.22	2.08
Treatment	36%PW	48%P	48%PW				
	2.00	2.00	2.33				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.879

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	1.803

```

147 SET [IN=]
153 "One-way design in randomized blocks"

```

```

154 DELETE [REDEFINE=yes] _ibalance
155 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\
156 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %b; SAVE=_a2save

```

Analysis of variance

Variate: %b

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.026597	0.008866	1.61	
Block.*Units* stratum					
Treatment	9	1.367914	0.151990	27.57	<.001
Residual	27	0.148857	0.005513		
Total	39	1.543368			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 1 *units* 7	-0.179	s.e. 0.061
Block 3 *units* 7	0.135	s.e. 0.061

Tables of means

Variate: %b

Grand mean 1.146

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	0.847	0.770	1.089	1.206	1.162	1.224	1.326
Treatment	36%PW	48%P	48%PW				
	1.364	1.193	1.275				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.0525

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	0.1077

```

157 SET [IN=]
163 "One-way design in randomized blocks"
164 DELETE [REDEFINE=yes] _ibalance
165 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\
166 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %b; SAVE=_a2save

```

Analysis of variance

Variate: %b

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.026597	0.008866	1.61	
Block.*Units* stratum					
Treatment	9	1.367914	0.151990	27.57	<.001
Residual	27	0.148857	0.005513		
Total	39	1.543368			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 1 *units* 7	-0.179	s.e. 0.061
Block 3 *units* 7	0.135	s.e. 0.061

Tables of means

Variate: %b

Grand mean 1.146

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	0.847	0.770	1.089	1.206	1.162	1.224	1.326
Treatment	36%PW	48%P	48%PW				
	1.364	1.193	1.275				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.0525

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	0.1077


```

177 SET [IN=]
183 "One-way design in randomized blocks"
184 DELETE [REDEFINE=yes] _ibalance
185 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\
186 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] a_rat; SAVE=_a2save

```

Analysis of variance

Variate: a_rat

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.07026	0.02342	1.88	
Block.*Units* stratum					
Treatment	9	0.32128	0.03570	2.86	0.016
Residual	27	0.33647	0.01246		
Total	39	0.72801			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 3 *units* 1 0.229 s.e. 0.092

Tables of means

Variate: a_rat

Grand mean 0.427

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	0.388	0.366	0.360	0.275	0.560	0.336	0.499
Treatment	36%PW	48%P	48%PW				
	0.512	0.519	0.451				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.0789

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	0.1620

```

187 SET [IN=]
193 "One-way design in randomized blocks"
194 DELETE [REDEFINE=yes] _ibalance
195 A2WAY [PRINT=aovtable,information,means; TREATMENTS=Treatment; BLOCKS=Block; FPROB=yes;\
196 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] b_rat; SAVE=_a2save

```

Analysis of variance

Variate: b_rat

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.034471	0.011490	1.90	
Block.*Units* stratum					
Treatment	9	1.324474	0.147164	24.37	<.001
Residual	27	0.163070	0.006040		
Total	39	1.522016			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

Block 2 *units* 1	-0.155	s.e.	0.064
Block 3 *units* 1	0.184	s.e.	0.064

Tables of means

Variate: b_rat

Grand mean 0.907

Treatment	0%P	0%PW	12%P	12%PW	24%P	24%PW	36%P
	1.200	1.309	0.919	0.831	0.866	0.818	0.763
Treatment	36%PW	48%P	48%PW				
	0.735	0.842	0.791				

Standard errors of differences of means

Table	Treatment
rep.	4
d.f.	27
s.e.d.	0.0550

Least significant differences of means (5% level)

Table	Treatment
rep.	4
d.f.	27
l.s.d.	0.1128

197 ET [IN=]

VI.3 Effects of additives (2% Lignostab 1198, 1% Iron oxide, 10% PEG, 10% Lignosulphonate) treatment on weight losses, tensile strength and color changes of wood veneers exposed to 35 days natural weathering

Analysis of variance

Variate: W_loss_%						
Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	3		880.194	293.398	15.89	
Block.Batch stratum						
Treatment	4		6041.205	1510.301	81.78	<.001
Residual	12		221.626	18.469	2.79	
Block.Batch.Veneer stratum						
	79	(1)	522.541	6.614		
Total	98	(1)	7664.464			

Message: the following units have large residuals.

Block 4 Batch 2	-3.51	s.e.	1.49
Block 1 Batch 1 Veneer 1	-5.74	s.e.	2.29
Block 4 Batch 3 Veneer 5	10.72	s.e.	2.29

Tables of means

Variate: W_loss_%						
Grand mean	28.23					
Treatment	IROX	LGST	LIG	None	PEG	
	18.27	25.63	37.37	22.63	37.24	

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	12
s.e.d.	1.359

Analysis of variance

Variate: Tensile_Strength						
Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.	
Block stratum	3	194.7928	64.9309	160.52		
Block.Batch stratum						
Treatment	4	24.3864	6.0966	15.07	<.001	
Residual	12	4.8540	0.4045	2.60		
Block.Batch.Veneer stratum						
	80	12.4667	0.1558			
Total	99	236.4998				

Message: the following units have large residuals.

Block 4 Batch 4	-0.543	s.e.	0.220
Block 1 Batch 5 Veneer 4	-0.984	s.e.	0.353
Block 2 Batch 3 Veneer 5	-0.910	s.e.	0.353

Tables of means

Variate: Tensile_Strength

Grand mean 5.575

Treatment	IROX	LGST	LIG	None	PEG
	6.550	5.465	5.330	5.219	5.310

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	12
s.e.d.	0.2011

185 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

Analysis of variance

Variate: Lrat (RATIO OF L AFTER WEATHERING TO L BEFORE)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.0954757	0.0318252	7.81	
Block.Batch stratum					
Treatment	4	2.4938642	0.6234660	153.06	<.001
Residual	12	0.0488794	0.0040733	4.17	
Block.Batch.Veneer stratum					
	80	0.0781924	0.0009774		
Total	99	2.7164116			

Message: the following units have large residuals.

Block 1 Batch 3	0.0485	s.e. 0.0221
Block 3 Batch 3	-0.0454	s.e. 0.0221
Block 1 Batch 3 Veneer 3	-0.0722	s.e. 0.0280
Block 2 Batch 3 Veneer 5	0.0797	s.e. 0.0280
Block 4 Batch 3 Veneer 1	0.0934	s.e. 0.0280

Tables of means

Variate: Lrat

Grand mean 0.9977

Treatment	IROX	LGST	LIG	None	PEG
	0.8503	0.9712	1.3035	0.9360	0.9275

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	12
s.e.d.	0.02018

Analysis of variance

Variate: brat (RATIO OF B AFTER WEATHERING TO B BEFORE)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.425173	0.141724	5.72	
Block.Batch stratum					
Treatment	4	1.580404	0.395101	15.95	<.001
Residual	12	0.297273	0.024773	7.09	
Block.Batch.Veneer stratum					
	80	0.279526	0.003494		
Total	99	2.582377			

Message: the following units have large residuals.

Block 2 Batch 2 Veneer 4	-0.2080	s.e.	0.0529
Block 2 Batch 2 Veneer 5	0.1571	s.e.	0.0529
Block 4 Batch 1 Veneer 2	0.1649	s.e.	0.0529

Tables of means

Variate: brat

Grand mean 0.9322

Treatment	IROX	LGST	LIG	None	PEG
	0.7483	0.9326	1.1405	0.9473	0.8923

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	12
s.e.d.	0.04977

209 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

VI.4 Effects of PF resin (12%) and additives (2% Lignostab 1198, 1% Iron oxide, 10% PEG, 10% Lignosulphonate) treatment on weight losses and tensile strength of wood veneers exposed to 50 days natural weathering

Analysis of variance

Variate: wtloss

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	3		226.477	75.492	1.29	
Block.Batch stratum						
Treatment	5		5228.410	1045.682	17.88	<.001
Residual	15		877.484	58.499	16.93	
Block.Batch.Veneer stratum						
	94	(2)	324.831	3.456		
Total	117	(2)	6620.168			

Message: the following units have large residuals.

Block 3 Batch 4	7.28	s.e. 2.70
Block 4 Batch 4	-6.36	s.e. 2.70
Block 3 Batch 1 Veneer 3	4.80	s.e. 1.65
Block 3 Batch 1 Veneer 4	-4.25	s.e. 1.65
Block 3 Batch 4 Veneer 4	-4.88	s.e. 1.65

Tables of means

Variate: wtloss

Grand mean 15.59

Treatment	non	PF	PFIO	PFlig	PFPEG	Pfstab
	20.84	8.48	9.09	22.36	23.24	9.52

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	15
s.e.d.	2.419

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Treatment
rep.	20
d.f.	15
l.s.d.	5.155

(Not adjusted for missing values)

Analysis of variance

Variate: ten

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	227.9361	75.9787	70.24	
Block.Batch stratum					
Treatment	5	125.5569	25.1114	23.21	<.001
Residual	15	16.2265	1.0818	5.17	
Block.Batch.Veneer stratum					
	96	20.0813	0.2092		
Total	119	389.8008			

Message: the following units have large residuals.

Block 3 Batch 1	0.916	s.e. 0.368
Block 3 Batch 4	-0.778	s.e. 0.368
Block 4 Batch 2 Veneer 5	1.180	s.e. 0.409
Block 4 Batch 6 Veneer 1	1.307	s.e. 0.409

Tables of means

Variate: ten

Grand mean 6.674

Treatment	non	PF	PFIO	PFlig	PFPEG	Pfstab
	4.637	6.414	7.305	7.107	6.689	7.889

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	15
s.e.d.	0.3289

Least significant differences of means (5% level)

Table	Treatment
rep.	20
d.f.	15
l.s.d.	0.7010

VI.5 Effects of PF resin (12%) and additives (2% Lignostab 1198, 1% Iron oxide, 10% PEG, 10% Lignosulphonate) treatment on color changes (L*, a*, b*) of wood veneers exposed to 50 days natural weathering

Analysis of variance

Variate: Lrat

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	0.264000	0.088000	26.45	
Block.Batch stratum					
Treatment	5	1.285516	0.257103	77.29	<.001
Residual	15	0.049900	0.003327	1.91	
Block.Batch.Veneer stratum					
	96	0.167073	0.001740		
Total	119	1.766489			

Message: the following units have large residuals.

Block 2 Batch 6	0.0435	s.e.	0.0204
Block 4 Batch 6	-0.0449	s.e.	0.0204
Block 1 Batch 4 Veneer 2	-0.1026	s.e.	0.0373
Block 3 Batch 1 Veneer 2	-0.1140	s.e.	0.0373
Block 4 Batch 3 Veneer 4	-0.0976	s.e.	0.0373
Block 4 Batch 4 Veneer 3	0.1146	s.e.	0.0373
Block 4 Batch 4 Veneer 4	-0.0987	s.e.	0.0373

Tables of means

Variate: Lrat

Grand mean 0.8491

Treatment	con	PF	PFIO	PFLig	PFPEG	PFSTAB
	0.7943	0.7829	0.7470	1.0434	0.7989	0.9279

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	15
s.e.d.	0.01824

```

183 AGRAPH [METHOD=means; PSE=differences] X=
184 "General Analysis of Variance."
185 BLOCK Block/Batch/Veneer
186 TREATMENTS Treatment
187 COVARIATE "No Covariate"
188 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
189 PSE=diff] Arat

```

Analysis of variance

Variate: Brat

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	3	1.002217	0.334072	15.20	
Block.Batch stratum					
Treatment	5	7.242079	1.448416	65.88	<.001
Residual	15	0.329767	0.021984	6.11	
Block.Batch.Veneer stratum					
	96	0.345473	0.003599		
Total	119	8.919537			

Message: the following units have large residuals.

Block 2 Batch 3	-0.1174	s.e.	0.0524
Block 3 Batch 4 Veneer 4	0.1481	s.e.	0.0537
Block 3 Batch 4 Veneer 5	-0.1389	s.e.	0.0537
Block 4 Batch 4 Veneer 3	0.1447	s.e.	0.0537
Block 4 Batch 4 Veneer 4	-0.1715	s.e.	0.0537

Tables of means

Variate: Brat

Grand mean 1.1888

Treatment	con	PF	PFIO	PFLig	PFPEG	PFSTAB
	0.9801	1.3026	0.8815	1.5151	1.0013	1.4524

Standard errors of differences of means

Table	Treatment
rep.	20
d.f.	15
s.e.d.	0.04689

234 AGRAPH [METHOD=means; PSE=differences] X=

VI.6 Effects of different concentration of PF resin (10%, 20%, 30%) and additives (2% Lignostab 1198, 1% Iron oxide, 10% PEG) treatment on color changes (L*, a*, b*) of veneer-based wood composites exposed to 2000 hours natural weathering

GenStat Release 12.1 (PC/Windows XP) 17 August 2010 13:01:31
Copyright 2009, VSN International Ltd.

Registered to: Philip Evans

GenStat Twelfth Edition
GenStat Procedure Library Release PL20.1

```
1 %CD 'C:/Documents and Settings/phevans/My Documents'
2 "Data taken from File: \
-3 C:/Documents and Settings/phevans/Desktop/Color__PF+additive(1).xls"
4 DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
5 READ [PRINT=*; SETNVALUES=yes] _stitle_
9 PRINT [IPRINT=*; JUST=left
```

Data imported from Excel file: C:\Documents and Settings\phevans\Desktop\Color__PF+additive(1).xls
on: 17-Aug-2010 13:01:48
taken from sheet ""Sheet1"", cells A2:N57

```
10 DELETE [REDEFINE=yes] BLOCK,SAMPLE,TREATMENT,Lbefore,Abefore,Bbefore,Lafter,\
11 Aafter,Bafter,%L%,%A%,%B%
12 UNITS [NVALUES=*]
13 FACTOR [MODIFY=yes; NVALUES=56; LEVELS=8; REFERENCE=1] BLOCK
14 READ BLOCK; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
BLOCK	56	0	8

```
17 FACTOR [MODIFY=yes; NVALUES=56; LEVELS=7; REFERENCE=1] SAMPLE
18 READ SAMPLE; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
SAMPLE	56	0	7

```
21 FACTOR [MODIFY=yes; NVALUES=56; LEVELS=7; LABELS=!t('10PF','20PF','30PF',\
22 'Con','PFHALS','PFIO','PFPEG'); REFERENCE=1] TREATMENT
23 READ TREATMENT; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
TREATMENT	56	0	7

```
26 VARIATE [NVALUES=56] Lbefore
27 READ Lbefore
```

Identifier	Minimum	Mean	Maximum	Values	Missing
Lbefore	53.75	70.33	85.64	56	0

33 VARIATE [NVALUES=56] Abefore
34 READ Abefore

Identifier	Minimum	Mean	Maximum	Values	Missing
Abefore	3.050	6.343	12.00	56	0

39 VARIATE [NVALUES=56] Bbefore
40 READ Bbefore

Identifier	Minimum	Mean	Maximum	Values	Missing
Bbefore	19.61	26.61	34.00	56	0

46 VARIATE [NVALUES=56] Lafter
47 READ Lafter

Identifier	Minimum	Mean	Maximum	Values	Missing
Lafter	45.75	57.67	66.66	56	0

53 VARIATE [NVALUES=56] Aafter
54 READ Aafter

Identifier	Minimum	Mean	Maximum	Values	Missing
Aafter	3.540	12.50	17.18	56	0

60 VARIATE [NVALUES=56] Bafter
61 READ Bafter

Identifier	Minimum	Mean	Maximum	Values	Missing
Bafter	12.48	32.67	39.71	56	0

67 VARIATE [NVALUES=56] %L%
68 READ %L%

Identifier	Minimum	Mean	Maximum	Values	Missing
%L%	-9.284	17.57	29.01	56	0

83 VARIATE [NVALUES=56] %A%
84 READ %A%

Identifier	Minimum	Mean	Maximum	Values	Missing
%A%	-341.0	-116.9	39.82	56	0

99 VARIATE [NVALUES=56] %B%
100 READ %B%

Identifier	Minimum	Mean	Maximum	Values	Missing
%B%	-90.21	-24.16	46.35	56	0

115

116 %PostMessage 1129; 0; 26182600 "Sheet Update Completed"

117 DELETE [REDEFINE=yes] Lrat

118 CALCULATE Lrat=Lafter/Lbefore

119 FSPREADSHEET [SHEET=26182600; METHOD=replace] Lrat

120 DELETE [REDEFINE=yes] Arat

121 CALCULATE Arat=Aafter/Abefore


```

122 FSPREADSHEET [SHEET=26182600; METHOD=replace] Arat
123 DELETE [REDEFINE=yes] Brat
124 CALCULATE Brat=Bafter/Bbefore
125 FSPREADSHEET [SHEET=26182600; METHOD=replace] Brat
126 "One-way design in randomized blocks"
127 DELETE [REDEFINE=yes] _ibalance
128 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
129 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Lrat; SAVE=_a2save

```

Analysis of variance

Variate: Lrat					
Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	0.009464	0.001352	0.78	
BLOCK.*Units* stratum					
TREATMENT	6	0.259204	0.043201	24.82	<.001
Residual	42	0.073108	0.001741		
Total	55	0.341776			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1 *units* 7	0.1182	s.e. 0.0361
BLOCK 2 *units* 7	-0.1135	s.e. 0.0361

Tables of means

Variate: Lrat
Grand mean 0.8243

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	0.8406	0.7722	0.7515	0.7711	0.9697	0.8297	0.8351

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	0.02086

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	0.04210

```

130 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
131 SET [IN=]
137 "One-way design in randomized blocks"
138 DELETE [REDEFINE=yes] _ibalance

```

```

139 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
140 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Arat; SAVE=_a2save

```

Analysis of variance

Variate: Arat

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	2.8193	0.4028	1.69	
BLOCK.*Units* stratum					
TREATMENT	6	40.2510	6.7085	28.12	<.001
Residual	42	10.0186	0.2385		
Total	55	53.0889			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1 *units* 5	1.314	s.e. 0.423
BLOCK 3 *units* 4	-0.982	s.e. 0.423

Tables of means

Variate: Arat

Grand mean 2.169

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	2.472	3.018	3.323	0.779	1.623	1.440	2.524

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	0.2442

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	0.4928

```

141 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT

```

```

142 SET [IN=]

```

```

148 "One-way design in randomized blocks"

```

```

149 DELETE [REDEFINE=yes] _ibalance

```

```

150 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\

```

```

151 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Brat; SAVE=_a2save

```


Analysis of variance

Variate: Lbefore

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	138.07	19.72	1.47	
BLOCK.*Units* stratum					
TREATMENT	6	2094.47	349.08	25.99	<.001
Residual	42	564.19	13.43		
Total	55	2796.73			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1 *units* 7	-7.90	s.e. 3.17
BLOCK 2 *units* 7	8.65	s.e. 3.17

Tables of means

Variate: Lbefore

Grand mean 70.33

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	74.36	68.55	67.94	82.04	62.22	64.87	72.33

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	1.833

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	3.698

```
163 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
164 SET [IN=*]
170 "One-way design in randomized blocks"
171 DELETE [REDEFINE=yes] _ibalance
172 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
173 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Lafter; SAVE=_a2save
```

Analysis of variance

Variate: Lafter

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	36.086	5.155	0.81	
BLOCK.*Units* stratum					
TREATMENT	6	1185.576	197.596	31.19	<.001
Residual	42	266.105	6.336		
Total	55	1487.767			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 4	1.77	s.e. 0.80
BLOCK 1 *units* 3	-5.17	s.e. 2.18

Tables of means

Variate: Lafter

Grand mean 57.67

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	62.43	52.92	51.03	63.25	59.99	53.75	60.32

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	1.259

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	2.540

```
174 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
175 SET [IN=*]
181 "One-way design in randomized blocks"
182 DELETE [REDEFINE=yes] _ibalance
183 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
184 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Abefore; SAVE=_a2save
```

Analysis of variance

Variate: Abefore

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	17.567	2.510	2.21	
BLOCK.*Units* stratum					
TREATMENT	6	153.866	25.644	22.54	<.001
Residual	42	47.790	1.138		
Total	55	219.223			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1 *units* 7 3.30 s.e. 0.92

Tables of means

Variate: Abefore

Grand mean 6.34

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	5.36	5.26	5.01	6.07	7.80	9.76	5.14

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	0.533

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	1.076

```
185 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
186 SET [IN=*]
192 "One-way design in randomized blocks"
193 DELETE [REDEFINE=yes] _ibalance
194 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
195 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Aafter; SAVE=_a2save
```

Analysis of variance

Variate: Aafter

Source of variation	d.f.	s.s.	m.s.	v.r.	F	pr.
BLOCK stratum		7	15.1038		2.1577	2.77
BLOCK.*Units* stratum						
TREATMENT	6	678.0159	113.0026	145.02	<.001	
Residual	42	32.7265	0.7792			
Total	55	725.8462				

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 4	-1.11	s.e. 0.52
BLOCK 3 *units* 2	-1.82	s.e. 0.76
BLOCK 8 *units* 1	-1.85	s.e. 0.76

Tables of means

Variate: Aafter

Grand mean 12.50

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	12.69	15.72	15.75	4.65	12.44	13.96	12.26

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	0.441

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	0.891

```

196 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
197 SET [IN=]
203 "One-way design in randomized blocks"
204 DELETE [REDEFINE=yes] _ibalance
205 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
206 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Bbefore; SAVE=_a2save

```

Analysis of variance

Variate: Bbefore

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	112.262	16.037	3.18	
BLOCK.*Units* stratum					
TREATMENT	6	378.137	63.023	12.49	<.001
Residual	42	211.973	5.047		
Total	55	702.372			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1	-2.87	s.e. 1.42
BLOCK 7 *units* 4	5.48	s.e. 1.95

Tables of means

Variate: Bbefore

Grand mean 26.61

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	26.25	26.07	26.03	24.19	23.65	32.07	28.06

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	1.123

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	2.267

```

207 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
208 SET [IN=*]
214 "One-way design in randomized blocks"
215 DELETE [REDEFINE=yes] _ibalance
216 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
217 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] Bafter; SAVE=_a2save

```


Analysis of variance

Variate: Bafter

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	61.894	8.842	1.59	
BLOCK.*Units* stratum					
TREATMENT	6	2577.245	429.541	77.43	<.001
Residual	42	233.008	5.548		
Total	55	2872.148			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 4 *units* 6 4.64 s.e. 2.04

Tables of means

Variate: Bafter

Grand mean 32.67

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	34.88	36.00	35.85	16.34	35.95	32.65	37.01

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	1.178

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	2.377

```
218 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
219 SET [IN=]
225 "One-way design in randomized blocks"
226 DELETE [REDEFINE=yes] _ibalance
227 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
228 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %L%; SAVE=_a2save
```

Analysis of variance

Variate: %L%

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	94.64	13.52	0.78	
BLOCK.*Units* stratum					
TREATMENT	6	2592.04	432.01	24.82	<.001
Residual	42	731.08	17.41		
Total	55	3417.76			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1 *units* 7	-11.82	s.e. 3.61
BLOCK 2 *units* 7	11.35	s.e. 3.61

Tables of means

Variate: %L%

Grand mean 17.57

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	15.94	22.78	24.85	22.89	3.03	17.03	16.49

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	2.086

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	4.210

```

229 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
230 SET [IN=]
236 "One-way design in randomized blocks"
237 DELETE [REDEFINE=yes] _ibalance
238 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
239 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %A%; SAVE=_a2save

```

Analysis of variance

Variate: %A%

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	28193.	4028.	1.69	
BLOCK.*Units* stratum					
TREATMENT	6	402510.	67085.	28.12	<.001
Residual	42	100186.	2385.		
Total	55	530889.			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 1 *units* 5	-131.4	s.e. 42.3
BLOCK 3 *units* 4	98.2	s.e. 42.3

Tables of means

Variate: %A%

Grand mean -116.9

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	-147.2	-201.8	-232.3	22.1	-62.3	-44.0	-152.4

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	24.42

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	49.28

```
240 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
241 SET [IN=*]
247 "One-way design in randomized blocks"
248 DELETE [REDEFINE=yes] _ibalance
249 A2WAY [PRINT=aovtable,information,means; TREATMENTS=TREATMENT; BLOCKS=BLOCK;
FPROB=yes;\
250 PSE=diff,lsd; LSDLEVEL=5; PLOT=fitt,norm,half,hist; EXIT=_ibalance] %B%; SAVE=_a2save
```

Analysis of variance

Variate: %B%

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
BLOCK stratum	7	2753.4	393.3	1.82	
BLOCK.*Units* stratum					
TREATMENT	6	42022.5	7003.7	32.44	<.001
Residual	42	9068.8	215.9		
Total	55	53844.8			

Information summary

All terms orthogonal, none aliased.

Message: the following units have large residuals.

BLOCK 7 *units* 4 33.4 s.e. 12.7

Tables of means

Variate: %B%

Grand mean -24.2

TREATMENT	10PF	20PF	30PF	Con	PFHALS	PFIO	PFPEG
	-33.0	-39.1	-39.9	32.3	-54.8	-1.7	-32.9

Standard errors of differences of means

Table	TREATMENT
rep.	8
d.f.	42
s.e.d.	7.35

Least significant differences of means (5% level)

Table	TREATMENT
rep.	8
d.f.	42
l.s.d.	14.83

```
251 AGRAPH [SAVE=_a2save[2]; METHOD=means; PSE=differences] X=TREATMENT
252 SET [IN=*
```

VI.7 Effects of different concentration of PF resin (10%, 20%, 30%) and additives (2% Lignostab 1198, 1% Iron oxide, 10% PEG) treatment on erosion of veneer-based wood composites exposed to 2000 hours natural weathering

GenStat Release 12.1 (PC/Windows XP) 15 December 2010 16:29:39
Copyright 2009, VSN International Ltd.

Registered to: Philip Evans

GenStat Twelfth Edition
GenStat Procedure Library Release PL20.1

```
1 %CD 'C:/Documents and Settings/phevens/My Documents'
2 "Data taken from File: \
-3 C:/Documents and Settings/phevens/Desktop/pf+_additives_wood_erosion2.xls"
4 DELETE [REDEFINE=yes] _stitle_: TEXT _stitle_
5 READ [PRINT=*; SETNVALUES=yes] _stitle_
9 PRINT [IPRINT=*; _stitle_; JUST=left
```

Data imported from Excel file: C:\Documents and Settings\phevens\Desktop\pf+_additives_wood_erosion2.xls
on: 15-Dec-2010 16:30:23
taken from sheet ""Sheet2"", cells A2:I41

```
10 DELETE [REDEFINE=yes] Block,Sample,Treatment,Surface_mm2,Volume_taken_mm3,\
11 Maximum_depth_mm,Mean_depth_mm,Volume_taken_mm3_mm2,Mass_loss_mg_mm2
12 UNITS [NVALUES=*]
13 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=8; REFERENCE=1] Block
14 READ Block; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Block	40	0	8

```
17 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=5; REFERENCE=1] Sample
18 READ Sample; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Sample	40	0	5

```
21 FACTOR [MODIFY=yes; NVALUES=40; LEVELS=5; LABELS=!t('10PF','Con','PFHALS',\
22 'PFIO','PFPEG'); REFERENCE=1] Treatment
23 READ Treatment; FREPRESENTATION=ordinal
```

Identifier	Values	Missing	Levels
Treatment	40	0	5

```
26 VARIATE [NVALUES=40] Surface_mm2
27 READ Surface_mm2
```

Identifier	Minimum	Mean	Maximum	Values	Missing
Surface_mm ²	68.50	276.9	509.0	40	0

31 VARIATE [NVALUES=40] Volume_taken_mm³
 32 READ Volume_taken_mm³

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Volume_taken_mm ³	1.350	7.919	29.00	40	0	

36 VARIATE [NVALUES=40] Maximum_depth_mm
 37 READ Maximum_depth_mm

Identifier	Minimum	Mean	Maximum	Values	Missing	Skew
Maximum_depth_mm	0.1560	0.5505	1.820	40	0	

42 VARIATE [NVALUES=40] Mean_depth_mm
 43 READ Mean_depth_mm

Identifier	Minimum	Mean	Maximum	Values	Missing
Mean_depth_mm	0.01350	0.02537	0.05880	40	0

49 VARIATE [NVALUES=40] Volume_taken_mm³_mm²
 50 READ Volume_taken_mm³_mm²

Identifier	Minimum	Mean	Maximum	Values	Missing
Volume_taken_mm ³ _mm ²	0.01359	0.02638	0.05870	40	0

61 VARIATE [NVALUES=40] Mass_loss_mg_mm²
 62 READ Mass_loss_mg_mm²

Identifier	Minimum	Mean	Maximum	Values	Missing
Mass_loss_mg_mm ²	0.004907	0.01034	0.02483	40	0

74
 75 %PostMessage 1129; 0; 26127736 "Sheet Update Completed"
 76 "General Analysis of Variance."
 77 BLOCK Block
 78 TREATMENTS Treatment
 79 COVARIATE "No Covariate"
 80 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
 FPROB=yes;\n
 81 PSE=diff] Mass_loss_mg_mm²

Analysis of variance

Variate: Mass_loss_mg_mm²

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.00011265	0.00001609	1.23	
Block.*Units* stratum					
Treatment	4	0.00008552	0.00002138	1.64	0.193
Residual	28	0.00036575	0.00001306		
Total	39	0.00056393			

Message: the following units have large residuals.

Block 4 *units* 1	0.00951	s.e.	0.00302
Block 7 *units* 3	0.00746	s.e.	0.00302

Tables of means

Variate: Mass_loss_mg_mm²
Grand mean 0.01034

Treatment	10PF	Con	PFHALS	PFIO	PFPEG
	0.00960	0.01319	0.00927	0.00940	0.01022

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	28
s.e.d.	0.001807

82 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
83 UNITS [NVALUES=*]
84 READ Mass_loss_mg_mm²\$(16,33)]

Identifier	Minimum	Mean	Maximum	Values	Missing
Mass_loss_mg_mm ² \$(16,33)] *	*	*	*	2	2

86
87 %PostMessage 1129; 0; 26127736 "Sheet Update Completed"
88 "General Analysis of Variance."
89 BLOCK Block
90 TREATMENTS Treatment
91 COVARIATE "No Covariate"
92 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\n
93 PSE=diff] Mass_loss_mg_mm2

Analysis of variance

Variate: Mass_loss_mg_mm²

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		8.367E-05	1.195E-05	1.90	
Block.*Units* stratum						
Treatment	4		3.358E-05	8.396E-06	1.33	0.284
Residual	26	(2)	1.638E-04	6.301E-06		
Total	37	(2)	2.753E-04			

Message: the following units have large residuals.

Block 2	0.00362	s.e.	0.00145
Block 1 *units* 4	-0.00444	s.e.	0.00202
Block 5 *units* 4	0.00523	s.e.	0.00202

Tables of means

Variate: Mass_loss_mg_mm²

Grand mean 0.00975

Treatment	10PF	Con	PFHALS	PFIO	PFPEG
	0.00960	0.01153	0.00927	0.00940	0.00895

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	26
s.e.d.	0.001255

(Not adjusted for missing values)

```
94 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
95 "General Analysis of Variance."
96 BLOCK Block
97 TREATMENTS Treatment
98 COVARIATE "No Covariate"
99 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
100 PSE=diff] Maximum_depth_mm
```

Analysis of variance

Variate: Maximum_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	1.3602	0.1943	1.53	
Block.*Units* stratum					
Treatment	4	1.6092	0.4023	3.18	0.029
Residual	28	3.5474	0.1267		
Total	39	6.5168			

Tables of means

Variate: Maximum_depth_mm

Grand mean 0.550

Treatment	10PF	Con	PFHALS	PFIO	PFPEG
	0.337	0.511	0.527	0.448	0.929

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	28
s.e.d.	0.1780


```

101 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
102 "General Analysis of Variance."
103 BLOCK Block
104 TREATMENTS Treatment
105 COVARIATE "No Covariate"
106 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
107 PSE=diff] Mean_depth_mm

```

Analysis of variance

Variate: Mean_depth_mm

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.00062855	0.00008979	1.31	
Block.*Units* stratum					
Treatment	4	0.00075302	0.00018826	2.76	0.047
Residual	28	0.00191221	0.00006829		
Total	39	0.00329378			

Message: the following units have large residuals.

Block 4 *units* 1	0.0219	s.e.	0.0069
Block 7 *units* 3	0.0179	s.e.	0.0069

Tables of means

Variate: Mean_depth_mm

Grand mean 0.0254

Treatment	10PF	Con	PFHALS	PFIO	PFPEG
	0.0247	0.0337	0.0219	0.0219	0.0248

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	28
s.e.d.	0.00413

```

108 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
109 "General Analysis of Variance."
110 BLOCK Block
111 TREATMENTS Treatment
112 COVARIATE "No Covariate"
113 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
114 PSE=diff] Volume_taken_mm3_mm2

```

Analysis of variance

Variate: Volume_taken_mm ³ _mm ²					
Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Block stratum	7	0.00060338	0.00008620	1.05	
Block.*Units* stratum					
Treatment	4	0.00056298	0.00014074	1.72	0.173
Residual	28	0.00228814	0.00008172		
Total	39	0.00345450			

Message: the following units have large residuals.

Block 4 *units* 1	0.0219	s.e.	0.0076
Block 7 *units* 3	0.0176	s.e.	0.0076

Tables of means

Variate: Volume_taken_mm³_mm²
Grand mean 0.0264

Treatment	10PF	Con	PFHALS	PFIO	PFPEG
	0.0247	0.0337	0.0236	0.0239	0.0260

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	28
s.e.d.	0.00452

```

115 APLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram
116 UNITS [NVALUES=*]
117 READ Volume_taken_mm3_mm2$[!(16,33)]

Identifier Minimum Mean Maximum Values Missing
Volume_taken_mm3_mm2$[!(16,33)] * * * 2 2
119
120 %PostMessage 1129; 0; 26127736 "Sheet Update Completed"
121 "General Analysis of Variance."
122 BLOCK Block
123 TREATMENTS Treatment
124 COVARIATE "No Covariate"
125 ANOVA [PRINT=aovtable,information,means; FACT=32; CONTRASTS=7; PCONTRASTS=7;
FPROB=yes;\
126 PSE=diff] Volume_taken_mm3_mm2

```

Analysis of variance

Variate: Volume_taken_mm³_mm²

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		0.00066794	0.00009542	2.07	
Block.*Units* stratum						
Treatment	4		0.00025120	0.00006280	1.36	0.274
Residual	26	(2)	0.00119831	0.00004609		
Total	37	(2)	0.00206988			

Message: the following units have large residuals.

Block 1 *units* 4	-0.0147	s.e. 0.0055
Block 5 *units* 4	0.0141	s.e. 0.0055

Tables of means

Variate: Volume_taken_mm³_mm²

Grand mean 0.0250

Treatment	10PF	Con	PFHALS	PFIO	PFPEG
	0.0247	0.0299	0.0236	0.0239	0.0229

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	26
s.e.d.	0.00339

(Not adjusted for missing values)

127 A PLOT [RMETHOD=simple] fitted,normal,halfnormal,histogram

Comparison of PF's v. Control

Analysis of variance (mass loss per area)

Variate: Mass_loss_mg_mm²

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		2.832E-05	4.045E-06	0.89	
Block.*Units* stratum						
Treatment	3		4.457E-05	1.486E-05	3.26	0.044
Residual	19	(2)	8.662E-05	4.559E-06		
Total	29	(2)	1.571E-04			

Tables of means

Variate: Mass_loss_mg_mm²

Grand mean 0.00946

Treatment	10PF	20PF	30PF	Con
	0.00960	0.00877	0.00816	0.01130

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	19
s.e.d.	0.001068

Analysis of variance (mean depth)

Variate: Mean_depth_mm

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		0.00108910	0.00015559	2.59	
Block.*Units* stratum						
Treatment	3		0.00097832	0.00032611	5.44	0.007
Residual	19	(2)	0.00113926	0.00005996		
Total	29	(2)	0.00282722			

Tables of means

Variate: Mean_depth_mm

Grand mean 0.0268

Treatment	10PF	20PF	30PF	Con
	0.0247	0.0238	0.0226	0.0363

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	19
s.e.d.	0.00387

Analysis of variance (volume taken)

Variate: Volume_taken_mm³_mm²

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		0.00061336	0.00008762	2.88	
Block.*Units* stratum						
Treatment	3		0.00032205	0.00010735	3.53	0.035
Residual	19	(2)	0.00057823	0.00003043		
Total	29	(2)	0.00146599			

Tables of means

Variate: Volume_taken_mm³_mm²

Grand mean 0.02442

Treatment	10PF	20PF	30PF	Con
	0.02470	0.02293	0.02072	0.02934

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	19
s.e.d.	0.002758

(Not adjusted for missing values)

Analysis of Additives

Analysis of variance (max depth)

Variate: Maximum_depth_mm

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Block stratum	7		2.3509	0.3358	3.11	
Block.*Units* stratum						
Treatment	5		2.0718	0.4144	3.84	0.007
Residual	33	(2)	3.5597	0.1079		
Total	45	(2)	7.7615			

Tables of means

Variate: Maximum_depth_mm

Grand mean 0.493

Treatment	10PF	20PF	30PF	PFHALS	PFIO	PFPEG
	0.337	0.411	0.306	0.527	0.448	0.929

Standard errors of differences of means

Table	Treatment
rep.	8
d.f.	33
s.e.d.	0.1642