

AN ABSTRACT OF THE DISSERTATION OF

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Title: Evaluation of Various Chemical Treatments to Prevent the Abiotic Deterioration of Southern Pine Surfaces through Outdoor Screening Trials

Abstract approved:

Jeffery J. Morrell

Rapid discoloration and checking of wooden surfaces when exposed outdoors has caused wood to fall out of favor as an outdoor building material, especially in applications where appearance is important. The surface appearance of wood products exposed outdoors can be improved through the application of film forming coatings or by reducing exposure to solar radiation and moisture. A shift towards environmentally friendly building materials has renewed interest in the outdoor application of wood products, where both biotic and abiotic durability is required, often in the absence of large overhangs or maintenance-intensive film forming coatings. The deterioration processes of wood surfaces have been extensively investigated. It is generally accepted that the loss of lignin and hemicellulose from the surface due to free radical reactions initiated by UV light absorption and moisture leads to discoloration and erosion. In addition, it is thought that these chemical reactions also weaken

the wood surface, resulting in checking. Further, a large body of research has been assembled investigating different treatments, primarily film forming, that prevent the effects of weathering. Yet, only chromic acid treatments have emerged as an economical means for reducing the effects of outdoor exposure without obscuring the natural figure of the wood. However, due to the toxic nature of these compounds, these treatments have never been commercialized.

In this body of work, two outdoor screening weathering studies were conducted to investigate the interactions between the wood surface and four classes of promising surface protection compounds. Representative water repellents, pigments, organic UV inhibitors, and carbon based wood preservatives were selected for the initial study. Samples were pressure impregnated with the candidate systems and subjected to exterior exposure at two sites. Exposure sites were located in the high desert of Oregon and on the leeward side of the island of Hawaii. These locations represent the extremes experienced by most wood based building materials. The Oregon site has low rainfall but high UV exposure while the Hawaiian site has both high rainfall and high UV. Samples were removed from the Oregon site at predetermined radiation intervals over a one year period, while the samples exposed in Hawaii were removed after six months of weathering. Following exposure, the samples were evaluated for discoloration, checking and changes in the chemical composition of the surface. The results from this study indicated that none of the selected treatments completely prevented the effects of weathering on the wood surface; yet some fared better than others in at least some of the categories analyzed. The study also indicated that the mode of deterioration differed significantly between the two exposure locations and that chemical degradation of the surface did not necessarily correlate with checking or discoloration.

Red and yellow iron oxide impregnated loblolly pine (*Pinus taeda*) samples experienced less discoloration and reduced lignin loss during the first study at both exposure locations, suggesting that iron oxides may alter the interaction between UV light and the wood polymers.

In a follow up, study loblolly pine samples were impregnated with iron oxide pigments differing in particle size, shape and loading to determine what characteristics of iron oxide influenced surface protection properties. These samples were only exposed at the eastern Oregon location and removed over a three month period at predetermined radiation intervals. The results from this work suggest that crystal shape, size and pigment concentration influenced polymer losses from the wood surface as well as surface discoloration. However, the results suggested that checking was not affected by any of the variables investigated.

While these studies suggest that the abiotic deterioration of wood surfaces can be controlled through the application of different transparent and semitransparent treatments, no single compound was completely effective. This implies that combinations of partially effective compounds should be investigated. In addition, the data suggest that, lignin and hemicellulose loss do not substantially affect check formation during the first months of outdoor exposure. Instead, the data suggests that wood / water relations dominate. The different exposure locations used in the first study also highlighted differences in weathering characteristics caused by climate. More research must be conducted to understand the effects of different climates on performance and to use these data to tailor surface protection systems to match exposure conditions.

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Evaluation of Various Chemical Treatments to Prevent the Abiotic Deterioration of Southern
Pine Surfaces through Outdoor Screening Trials

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Christoph F. Schauwecker

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Christoph F. Schauwecker, Author

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TABLE OF CONTENTS

	<u>Page</u>
1. Weathering Processes of Wooden Surfaces and Its Prevention, Challenges and Opportunities: An Introduction	1
1.1 Abstract.....	1
1.2 Introduction	1
1.3 Weathering of Wood	3
1.3.1 Material property changes	4
1.3.2 Chemical reactions involved in the weathering process.....	11
1.4 Prevention of Weathering	15
1.4.1 Film forming coatings.....	15
1.4.2 Penetrating finishes	17
1.4.3 Inorganic surface treatments	18
1.4.4 Effects of conventional wood preservatives on weathering.....	20
1.4.5 UV Absorbers and hindered amine light stabilizers.....	22
1.4.6 Cell wall modification and lumen fill treatments.....	23
1.4.7 Influence of wood processing on weathering	25
1.5 Future Directions.....	26
1.6 Literature cited	27
2. A New Look at the Weathering Performance of Solid-Wood Decking Materials.....	36
2.1 Abstract.....	36
2.2 Introduction	36
2.3 Methods	38
2.3.1 Exterior Exposure	40
2.4 Results and Discussion	41
2.5 Conclusion	53
2.6 Literature Cited	53
3. FTIR Analysis of Wood Surfaces Treated with Prospective Surface Protestants and Exposed Outdoors for Various Exposure Periods	56
3.1 Abstract.....	56
3.2 Introduction	56

TABLE OF CONTENTS (Continued)

	<u>Page</u>
3.3 Methods	58
3.3.1 Outdoor Exposure.....	60
3.3.2 FTIR Spectroscopic Analysis of Wood Surfaces	61
3.4 Results and Discussion	62
3.5 Conclusion	121
3.6 Literature Cited	121
4. Effects of geographical location on weathering of wood surfaces.....	125
4.1 Abstract.....	125
4.2 Introduction	125
4.3 Methods	127
4.4 Results	130
4.4.1 Effects of weathering on positive and negative controls.....	132
4.4.2 Effects of weathering on loblolly pine samples treated with pigments	140
4.4.3 Effects of weathering on loblolly pine samples treated with water repellents	151
4.4.4 Effects of organic UV inhibitors on weathering on loblolly pine samples	162
4.4.5 Effects of weathering on loblolly pine samples treated with the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone	169
4.5 Conclusions	174
4.6 Literature Cited	175
5. Use of Iron oxides to Influence the Weathering Characteristics of Wood Surfaces: a Systematic Survey of Particle Size, Crystal Shape and Concentration.....	177
5.1 Abstract.....	177
5.2 Introduction	177
5.3 Methods	179
5.3.1 Exterior Exposure	180
5.3.2 Physical evaluation	181
5.3.3 Chemical evaluation	182
5.4 Results	183
5.4.1 Development of surface checking.....	185
5.4.2 Discoloration of iron oxide treated samples.....	189

TABLE OF CONTENTS (Continued)

	<u>Page</u>
5.4.3 Changes in chemical composition	192
5.4.4 Effect of iron oxide concentration on chemical composition.....	194
5.4.5 Effects of various iron oxides.....	196
5.5 Conclusions	203
5.6 Literature Cited	204
6. Conclusion	206
6.1 Future directions	207
7. Global Literature Cited.....	210

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1. Time series of infrared spectra of wood after UV irradiation at atmospheric levels	6
1.2. Time series of infrared spectra of wood surfaces after outdoor exposure	7
1.3. Scanning Electron Micrograph (1000x) of the radial face of a southern pine sample after 1000 hours of UV exposure.....	9
1.4. Scanning Electron Micrograph (1000x) of the transverse face of a southern pine sample after 1000 hours of UV exposure	9
1.5. Schematic illustrating the photodegradation of wood.....	14
2.1. Samples mounted on 45° racks and pointed due south in Klamath Falls, Oregon, prior to the installation of the sprinkler heads.	41
2.2. Progression of checking and discoloration within southern pine samples exposed to 0, 486.80, 939.38, 1363.52, 1886.12, 2337.25 or 6096.12 MJ/m ² of irradiation.	45
2.3. Effects of pigments on total color change through time for southern pine samples exposed to sunlight.....	46
2.4. Effect of UV stabilization on total color change through time for southern pine sapwood exposed to sunlight	47
2.5. Effect of water repellent treatment on average number of checks through time on pine sapwood samples in an exterior exposure	49
2.6. Effect of UV stabilization treatment on average number of checks through time on pine sapwood samples in an exterior exposure	49
2.7. Effect of treatment on average check length for pine samples exposed to three levels of UV radiation.....	51
2.8. Effect of treatment on average check width for pine sapwood samples exposed to three levels of UV radiation.....	52
3.1. Samples mounted on 45° racks in Klamath Falls, Oregon, showing sample configuration and orientation, but prior to the installation of the sprinkler heads.	61
3.2. Examples of progressive check and discoloration development on loblolly pine samples exposed to 0, 487, 939, 1363, 1886, 2337 and 6096 MJ/m ² of irradiation.	64

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.3. Comparisons between FTIR spectra of the untreated unexposed southern pine samples collected using Perkin Elmer and Thermo-Scientific instruments.	65
3.4. FTIR spectra collected from untreated southern pine samples after being exposed outdoors to irradiation dosage increments of 454 Mj/m ²	68
3.5. Reduction in peak intensity in FTIR spectra from untreated southern pine samples after being exposed outdoors to irradiation dosage increments of 454 Mj/m ²	69
3.6. Changes in the carbonyl region of FTIR spectra collected from southern pine after being exposed outdoors to irradiation dosage increments of 454 Mj/m ²	70
3.7. FTIR spectra collected from 1% chromic acid treated southern pine samples after outdoor exposure to irradiation dosage increments of 454 Mj/m ²	72
3.8. Reduction in FTIR peak intensity for chromic acid (3%) brushed southern pine samples after being exposed outdoors to irradiation dosage increments of 454 Mj/m ²	73
3.9. Changes in the carbonyl region of FTIR spectra collected from southern pine samples brushed with chromic acid (3%) and after exposure outdoors to irradiation dosage increments of 454 Mj/m ²	74
3.10. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 190 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m ²	77
3.11. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 190 nm red iron oxide particles after being exposed outdoors to irradiation dosage increments of 454 Mj/m ²	78
3.12. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 1000 ppm solution of 190 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m ²	79
3.13. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 190 nm yellow iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m ²	80
3.14. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 190 nm yellow iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m ²	81

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.15. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 190 nm yellow iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	82
3.16. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 700 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	83
3.17. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 700 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	84
3.18. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 700nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	85
3.19. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 130 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	87
3.20. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 130 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	88
3.21. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 1000 ppm solution of 130nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	89
3.22. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 195 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	90
3.23. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 195 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	91
3.24. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 195nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	92
3.25. FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C.....	95

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.26. Reduction in FTIR peak intensity from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	96
3.27. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	97
3.28. FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C.	98
3.29. Reduction in FTIR peak intensity from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	99
3.30. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	100
3.31. FTIR spectra collected from southern pine samples treated with a 20000ppm wax in water emulsion with a melt point of 65.5-75°C.....	101
3.32. Reduction in FTIR peak intensity from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 65.5-75 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	102
3.33. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 65.5-75 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	103
3.34. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 8-20 nm silicate particles and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m ²	105
3.35. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 100-220 nm silicate particles and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m ²	106
3.36. FTIR spectra collected from southern pine samples treated with a 4000 ppm solution of acrylic polymer and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m ²	107

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.37. Reduction in peak intensity from southern pine samples treated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	108
3.38. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	109
3.39. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	111
3.40. Reduction in peak intensity from southern pine samples treated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	112
3.41. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	113
3.42. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of an organic free radical scavenger of the hindered amine light stabilizer class and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m ²	114
3.43. Reduction in FTIR peak intensity from southern pine samples treated with 1000 ppm of an organic free radical scavenger of the hindered amine light stabilizer class and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	115
3.44. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 1000 ppm solution of organic free radical scavenger of the hindered amine light stabilizer class and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	116
3.45. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	118
3.46. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed outdoors to irradiation dosage increments of 454 MJ/m ²	119

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.47. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed outdoors to irradiation dosage increments of 454 Mj/m^2	120
4.1. Degree of color change (discoloration) on the surfaces of untreated and chromic acid treated samples exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	132
4.2. Surface appearance of untreated samples exposed to A) 2337 Mj/m^2 of solar radiation in Eastern Oregon or (B) six months on the leeward side of Hawaii.	133
4.3. Number of surface checks on untreated and chromic acid treated samples after exposure to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	134
4.4. Reduction in FTIR peak height on untreated loblolly pine samples exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	136
4.5. FTIR peak heights for the carbonyl region on unexposed loblolly pine samples exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	137
4.6. FTIR peak heights for the carbonyl region on loblolly pine samples brushed with a 3% chromic acid solution and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	138
4.7. Reduction in FTIR peak height on loblolly pine samples brushed with a 3% solution of chromic acid and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	139
4.8. Effects of pigments on color change of loblolly pine samples exposed to 1886 to 6096 Mj/m^2 of irradiation in Eastern Oregon or for six months in Hawaii.	140
4.9. Number of surface checks present on samples treated with different inorganic pigment formulations and then exposed to 1886 to 6096 Mj/m^2 of solar radiation in Eastern Oregon or for six months in Hawaii.	141
4.10. Reduction in FTIR peak height on loblolly pine samples impregnated with a 1000 ppm suspension of 190 nm red iron oxide particles and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	143

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
4.11. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm suspension of 700 nm red iron oxide and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	144
4.12. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm suspension of yellow iron oxide and exposed outdoors to irradiation dosages ranging from 1886 to 2337 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	145
4.13. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm suspension of titanium dioxide and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	146
4.14. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of red iron oxide particles and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or to six months in Hawaii.	147
4.15. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of 700 nm red iron oxide and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or to six months in Hawaii.	148
4.16. Peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of yellow iron oxide particles and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or to six months on Hawaii.....	149
4.17. Peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of titanium dioxide particles and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	150
4.18. Effects of water repellents on color fastness of loblolly pine samples exposed to 1886 to 6096 Mj/m^2 of irradiation in Eastern Oregon or for six months in Hawaii.	151
4.19. Number of surface checks on samples treated with different water repellents and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.	152
4.20. Reduction in FTIR peak height for loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	154

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
4.21. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.....	155
4.22. Reductions in FTIR peak height for loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.....	156
4.23. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to solar radiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.....	157
4.24. Reductions in FTIR peak height for loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 65-75 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.....	158
4.25. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 20,000ppm wax in water emulsion with a melt point of 65-75°C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.....	159
4.26. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.....	160
4.27. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or for six months in Hawaii.	161
4.28. Effects of organic UV stabilizers on color fastness for loblolly pine samples exposed to outdoor conditions in Eastern Oregon or Hawaii.	162
4.29. Number of surface checks present in samples treated with different organic UV stabilizers and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m ² in Eastern Oregon or in for six months in Hawaii.	163

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
4.30. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	165
4.31. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	166
4.32. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 1000 ppm solution of an organic free radical scavenger and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	167
4.33. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm solution of an organic free radical scavenger and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	168
4.34. Effect of the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) on color fastness for loblolly pine samples exposed to 1886 to 6096 Mj/m^2 of irradiation in Eastern Oregon or for six months in Hawaii.....	170
4.35. Number of surface checks developed in samples treated with the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) when exposed to 1886 to 6096 Mj/m^2 of solar radiation in Eastern Oregon or for six months in Hawaii.....	170
4.36. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 1000 ppm emulsion of 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	172
4.37. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm emulsion of 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.....	173
5.1. Actual retentions for samples treated with 1000 ppm solutions of various iron oxides.....	183

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
5.2. Actual retentions for samples treated with 500, 5000, or 10,000 ppm solutions of 122 nm red iron oxide dispersions.....	184
5.3. Mean number of checks that developed on the surface of samples treated with different loadings of 122 nm red iron oxide and exposed in the Eastern Oregon high desert.	186
5.4. Mean check area on the surface of samples treated with different loadings of 122 nm red iron oxide and exposed in the Eastern Oregon high desert.	186
5.5. Mean number of checks that developed on the surface of samples treated with various iron oxide dispersions (1000 ppm) and exposed in the Eastern Oregon high desert.	187
5.6. Mean check area on the surface of samples treated with various iron oxide dispersions (1000 ppm) and exposed in the Eastern Oregon high desert.	187
5.7. Mean number of checks on the surface of samples treated with different levels of 122nm red iron oxide, with and without 1% resin brushed onto the surface, and exposed to 1848 Mj/m ² of radiation in the high desert of Eastern Oregon.....	188
5.8. Mean number of checks on the surface of samples treated with different iron oxide dispersions (1000 ppm), with and without a resin topcoat and exposed to 1848 Mj/m ² of radiation in the high desert of Eastern Oregon.....	189
5.9. Mean discoloration of samples treated with different loadings of 122nm red iron oxide and exposed in the Eastern Oregon high desert	190
5.10. Mean discoloration of samples treated with various iron oxides dispersions (1000 ppm) and exposed in the Eastern Oregon high desert.	191
5.11. Mean discoloration of samples treated with different levels of 122nm red iron oxide, with and without 1% resin brushed onto the surface, and exposed to 1848 Mj/m ² of irradiation in the high desert of Eastern Oregon.....	191
5.12. Mean discoloration of samples treated with different dispersions of iron oxide (1000 ppm), with and without a resin topcoat, and exposed to 1848 Mj/m ² of irradiation in the high desert of Eastern Oregon.....	192
5.13. FTIR spectra of dehydrated iron oxide suspension compared to untreated unexposed loblolly pine with the area of interest highlighted.	193

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
5.14. Reduction in the primary lignin peak (at 1518 cm^{-1}) in FTIR spectra for samples treated with various loadings of 122 nm red iron oxide or brushed with 3% chromic acid and exposed to irradiation dosages ranging from 515 and 1848 MJ/m^2 in Eastern Oregon.	195
5.15. Reduction in the lignin ether peak (1466 cm^{-1}) in FTIR spectra for samples treated with various loadings of 122 nm red iron oxide or brushed with 3% chromic acid and then exposed to irradiation dosages ranging from 515 and 1848 MJ/m^2 in Eastern Oregon.	195
5.16. Reduction in the aliphatic peak (2950 cm^{-1}) in FTIR spectra for samples treated with various loadings of 122 nm red iron oxide or brushed with 3% chromic acid and exposed to irradiation dosages ranging from 515 and 1848 MJ/m^2 in Eastern Oregon.	196
5.17. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 124 nm yellow iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	197
5.18. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 417 nm yellow iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	198
5.19. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 1480 nm yellow iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	198
5.20. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 122 nm red iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	199
5.21. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 1850 nm red iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	199
5.22. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 1074 nm black iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	200
5.23. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 4173 nm black iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m^2 in Eastern Oregon.	201

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
5.24. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 162 nm carbon black particles and then exposed to irradiation dosages ranging from 515 to 1848 Mj/m^2 in Eastern Oregon.	202
5.25. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm dispersion of 162 nm carbon black and then exposed to irradiation dosages ranging from 515 to 1848 Mj/m^2 in Eastern Oregon.	203

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1.1. Bond disassociation energies and maximum wavelengths that contain the required amount of energy to cleave functional groups commonly found in wood.....	12
2.1. Compounds used to reduce the effects of weathering, the reason for inclusion, and concentrations used.....	39
2.2. Vacuum and pressure conditions used to impregnate southern yellow pine sapwood with various compounds.....	40
2.3. Target and average gauge retention data for the materials used to improve weathering of southern yellow pine sapwood.....	43
2.4. Irradiation dose, number of days in the field, and climatic conditions experienced by each sample set.....	44
3.1. Compounds assessed for their ability to reduce weathering of loblolly pine sapwood.....	199
3.2. Vacuum and pressure conditions used to impregnate southern yellow pine sapwood with various surface protection compounds.....	60
3.3. Exposure time, irradiation dose, and average relative humidity for loblolly pine samples exposed for approximately one year in Klamath Falls, Oregon.....	63
4.1. Compounds assessed for their ability to reduce weathering of loblolly pine sapwood.....	129
4.2. Target and average gauge retentions of potential anti-weathering compounds in loblolly pine sapwood.....	131
5.1. Pigments assessed for their ability to reduce weathering of loblolly pine sapwood.....	180
5.2. Vacuum and pressure conditions used to impregnate loblolly pine sapwood with various pigment systems.	180
5.3. Climatic conditions during each exposure period.....	184

EVALUATION OF VARIOUS CHEMICAL TREATMENTS TO PREVENT THE ABIOTIC DETERIORATION OF SOUTHERN PINE SURFACES THROUGH OUTDOOR SCREENING TRIALS

1. WEATHERING PROCESSES OF WOODEN SURFACES AND ITS PREVENTION, CHALLENGES AND OPPORTUNITIES: AN INTRODUCTION

1.1 Abstract

Weathering is the most important cause of premature replacement of outdoor wooden structures. The underlying, self-sustaining free radical reactions involved in weathering are initiated by UV light and oxygen leading to the degradation of lignin. The surface is further degraded through erosion by removal of degradation products and checking. While these mechanisms have been understood since the 1980's, effective treatments that prevent weathering of wood surfaces have not been forthcoming. Treatments investigated thus far are reviewed. While treatment with inorganic UV inhibitors such as chromic acid are promising, these treatments are not environmentally or economically viable. The review suggests that a more innovative approach to address the weathering of wood surfaces is needed.

1.2 Introduction

Outdoor living spaces are an important component of many residential structures. This is evident by the large percentage of new, single family homes within the United States (U.S.) that have an outdoor living area included in the original design and by the large number of home owners that add or significantly change these structures during their tenure. A 1999 study showed that eighty-five percent of new single family homes included an outdoor living area and an estimated 4.2 percent of households added a deck to their existing home each year. The study also indicated that over 45 percent of homeowners added or significantly altered the outdoor living spaces associated with their home during their residence, mostly as

do-it yourself projects (Shook and Easton 2001). This has resulted in a U.S. decking materials market estimated to be worth 5.4 billion dollars per year in 2000, with deck boards and railings representing 2/3 of that market (Principia Partners 2001). Builders participating in a mail survey indicated that the most important attributes when choosing a decking material were durability, long life and visual appeal of the material (Shook and Easton 2001). Conversely, the survey indicated that strength, waste and initial costs were the least important attributes.

Chemical pressure impregnated (CPI) materials were used to construct the majority of decks in 2000, consuming five billion board feet of timber. Forty-four percent of this material was used in applications where it was visible to the end user, while the remainder was used in the substructure. Other materials used for decks include naturally durable materials such as western red cedar (*Thuja plicata* D.Don), redwood (*Sequoia sempervirens* D.Don) and durable tropical timbers. The majority of the naturally durable materials are used in the Pacific region. CPI materials in this region must be incised prior to treatment, reducing the aesthetic appeal of the material and encourage the use of durable woods.

Truini (1996) reported that the average deck is upgraded, expanded, repaired or replaced eleven years after its initial installation. The majority of these decks were not repaired or replaced because of biological attack. Instead, weathering that resulted in discoloration (graying), splitting and warping of the deck boards, was the primary reason for premature repair or replacement of these structures (Williams 2005).

The weathering attributes of treated wood materials encouraged the development of wood/polymer composite products (WPCs) and synthetic polymer lumber products as alternative decking materials. The popularity of these products resulted in the sale of 85 million board feet of non-wood alternative decking materials in 2000, representing an estimated 6 percent of the market share even though these materials cannot be used in structural applications (Principia Partners 2001). The market share of these products is

expected to grow by 10% annually between 2007 and 2011, with an anticipated market value of \$5.5 billion annually by 2011 (Freedonia Group 2007), although the recent downturn in the housing market has slowed growth. Non-wood alternatives carry a price premium of approximately \$3.23 and \$2.32 per board foot for WPCs and synthetic polymer lumber, respectively, at major retailers on the West Coast, when compared to CPI and naturally durable materials. In addition, WPCs do degrade over time when exposed to outdoor conditions, resulting in fading, warping and slow biological decay of the wood component (Schauwecker, et al. 2006, Matuana et al 2001).

The mechanisms of weathering that result in early replacement of solid wood decking are reasonably well understood. Thus, it may be possible to develop new solid wood decking materials that utilize this knowledge to produce a decking product that remains aesthetically appealing for a longer period of time. This approach to providing durable outdoor living spaces requires preservation of the wood grain and texture since these attributes are among the most desirable features for consumers. New treatment technologies would also promote the continued use of an environmentally sound and renewable resource, while maintaining some of the price advantage enjoyed by traditional solid wood decking materials over the composite alternatives.

1.3 Weathering of Wood

The environmental effects of wood have long been known. The earliest written account of weathering appeared more than 3000 years ago when the Israelites used weathered wood to reduce the pH of alkali water while in the deserts of the Sinai Peninsula (ref. in Feist and Hon 1984). Yet, the chemical changes that occur in wood while being exposed to the elements were not described until the 1820s and systematic studies of weathering reactions were not initiated until the 1950s (Feist and Hon 1984). Since that time, a large body of literature has accumulated describing the changes that occur on wood surfaces over time when exposed outdoors in the absence of decay causing organisms.

The main causal agents of weathering are solar radiation, moisture, oxygen and, to a lesser extent, other environmental chemicals. These inputs result in reactions within the wood that alter the chemical composition of the material over time. Characteristic changes during weathering include surface graying, raised grain, warping and checking. The changes that occur in the wood properties as a result of these reactions will be discussed, followed by a review of the chemical reactions associated with these changes.

1.3.1 Material property changes

Solar radiation absorbed by wood contains enough energy to initiate free radical reactions in cellulose, hemicelluloses and lignin polymers (Williams 2005, Hon 1981, Kamoun, et al. 1999). These reactions occur preferentially within the lignin polymer, since the free radicals can be resonance stabilized within the phenoxy groups, allowing polymer cleavage reactions to take place more readily within this material. This results in reduced polymer chain length. The cleaved polymeric lignin chains are then leached from the wood surface, resulting in a morphologically disorganized surface layer about 100-250 micrometers thick (Kataoka and Kiguchi 2001). This layer is rich in cellulose and appears gray in color. Over time, this material is eroded away through water and abrasion, resulting in the loss of 5-6mm of thickness per century. Denser species erode more slowly than less dense materials (Kalnins 1966, Browne and Simonson 1957, Williams 2005).

A thicker, brown layer is located underneath the gray highly degraded material in weathered wood. The polymers in this layer have also been affected by the photo degradation process, most likely through free radical moieties and visible light, since ultra violet (UV) light can not penetrate to this depth (Williams 2005, Debyshire and Miller 1981). The extent of degradation in this layer is less than that observed in the gray colored material, but the lignin content is substantially reduced when compared to un-weathered wood located a few millimeters below the surface (Feist and Hon 1984). The depth of this layer varies from 120 to 2500 micrometers possibly due to different light sources used by the investigators or due to

differences in wood species, since denser materials are more difficult to penetrate (Hon et al. 1992, Browne and Simonson 1957).

Infrared (IR) spectroscopy can be used to determine the rate of lignin, cellulose and hemicellulose loss from the material surface through time (Figures 1.1 and 1.2). Lignin absorption occurs at 1265 cm^{-1} and 1510 cm^{-1} , while carbonyl absorption, a major product of lignin degradation, occurs at 1720 cm^{-1} and 1735 cm^{-1} . Lignin degradation occurs rapidly during weathering. Hon (1983) found significant reductions in the strength of the lignin peak after ten days of either laboratory or field weathering. Hon also noted that the strength of the carbonyl peak increased significantly in the laboratory weathered materials when the wood was exposed to UV light. However, the resulting IR spectra were significantly different for materials weathered in the laboratory and in the field, with the carbonyl peaks being much stronger for the laboratory weathered materials. Lignin peaks were completely absent from the naturally weathered materials after 40 days of weathering and the carbonyl peak was found to be greatly reduced in strength when compared to the laboratory weathered materials. These results indicate that the degraded polymers were leached from the wood surface. Evans et al (1996) using fourier transformed infrared spectroscopy (FTIR) on weathered radiata pine (*Pinus radiata* D.Don), found detectable levels of lignin loss after only four hours of exposure to the sun and substantial losses after 6 days. These results indicate that even though changes in the wood surface may take months to years to become apparent visually, the underlying chemical changes occur almost instantaneously when wood is exposed to sunlight.

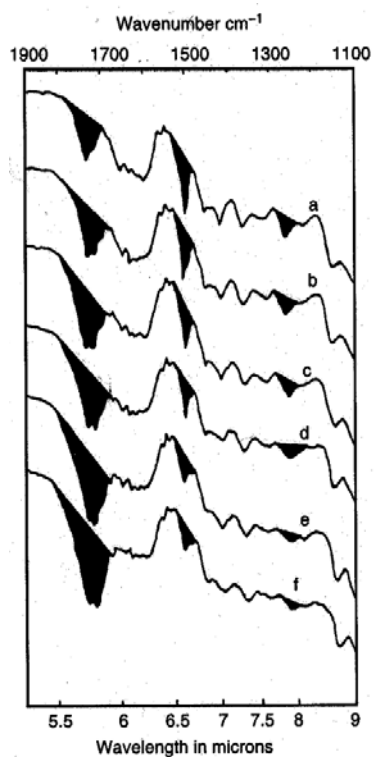


Figure 1.1. Time series of infrared spectra of wood after UV irradiation at atmospheric levels A) control; b) one day; c) four days d) ten days e) 20 days; f) 40 days. Over time the lignin peak (at a wavelength of 7.8 microns) is degraded while the carbonyl peak at a wavelength of 5.75 microns gains strength, indicating that lignin is degraded by UV exposure (Hon 1983).

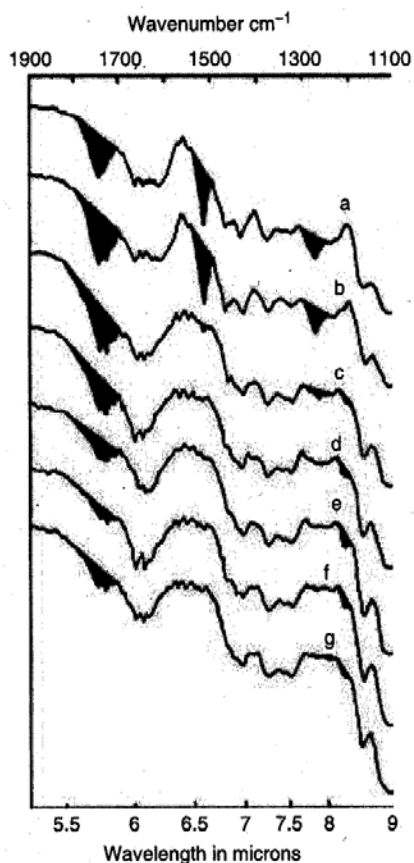


Figure 1.2. Time series of infrared spectra of wood surfaces after outdoor exposure a) control; b) no water leaching c) 30 days; d) 60 days; e) 180 days f) 300 days; g) 480 days. The lignin peak (at a wavelength of 7.8 microns) is lost while the carbonyl peak (at a wavelength of 5.75 microns) is enhanced p yet never to the extent as in laboratory exposed samples indicating that these compounds are leached from the wood (Hon 1983).

Effects on the cellular structure of softwoods and hardwoods as a result of weathering have also been investigated. Although cellulose and hemicelluloses are also degraded during the weathering process, the loss of lignin is most important on the cellular level (Hon and Feist 1986, Chang et al 1982, Hon, 1979, Williams 2005). Lignin acts as a resin within the cellular system, holding the cellulose microfibrils, together to form the cell wall. This means the greatest volume of lignin is located within the S2 cell wall layer (Rowell, et al. 2005). Lignin loss from the S2 layer results in micro cracking parallel to the microfibril angle of exposed cell walls in softwoods (Miniutti 1964). These cracks have been found to initiate at bordered and semi-bordered pit pairs. Cracks initiate in the earlywood through the

enlargement of the aperture, a defect observed after 500 hours of exposure to UV light (Miniutti 1964). Bordered pits were degraded more rapidly than semi-bordered pits in California redwood, while the opposite was noted for longleaf pine (*Pinus palustris* Mill.) (Chang et al 1982, Miniutti 1967). In both cases, pit structures acted as stress concentrators within the softwood cell wall. Unlike softwoods, cell wall checking does not initiate at pits in hardwoods (Evans, et al. 2002). Lignin loss in the S2 layer and the subsequent microcracking results in a weakened cellular structure in all woody materials, allowing individual components of the cell wall to delaminate prior to complete cell disintegration (Borgin et al 1975). Lignin is also lost from other portions of the cell wall, resulting in the progressive thinning, and thus weakening, of the entire cell wall (Evans et al. 2002, Evans 1989).

Lignin in the middle lamella is also the binder connecting individual cells (Rowell, et al. 2005). Lignin is rapidly eroded in this region and in the adjacent S1 cell wall layers (Evans, 1989). Hon and Feist (1986) exposed freshly microtomed transverse, radial and tangential sections to UV radiation for different amounts of time, then examined them using scanning electron microscopy (SEM). Lignin loss caused the wood structure in both hardwoods and softwoods to delaminate after being exposed to 1000 hours of UV light without the addition of water as a leaching agent. These effects were most visible on the transverse and the radial sections. However, weathering effects could also be detected to a lesser extent by examining the tangential sections (Figures 1.3 and 1.4).

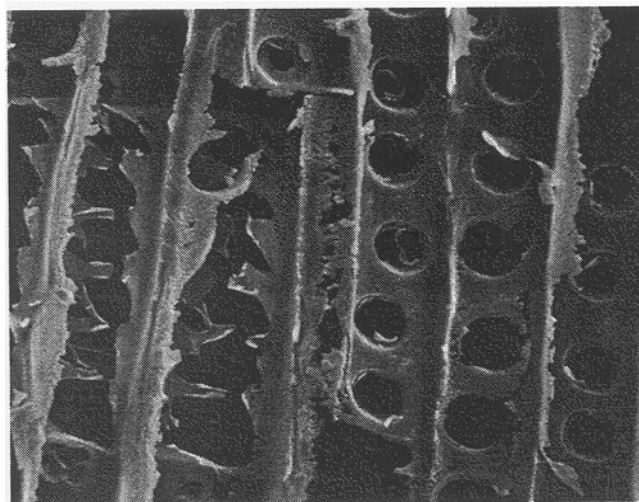


Figure 1.3. Scanning Electron Micrograph (1000x) of the radial face of a southern pine sample after 1000 hours of UV exposure showing the deterioration of intercellular bordered pit pairs (Hon and Feist 1986).

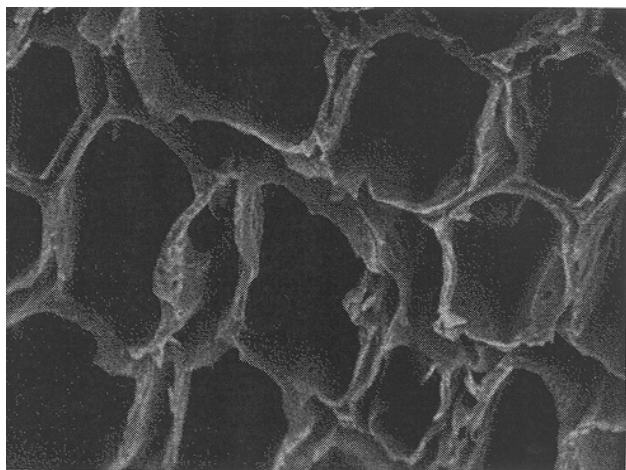


Figure 1.4. Scanning Electron Micrograph (1000x) of the transverse face of a southern pine sample after 1000 hours of UV exposure, displaying the loss of lignin from the middle lamella and the deterioration of the cell wall (Hon and Feist 1986).

Miniutti (1967) found that rays were also affected by weathering, however, their behavior differed markedly from that of normal cells. Softwood ray cells were degraded as easily as the remainder of the material, but extractives found within these structures resisted degradation. Multiseriate rays found in some hardwoods have been shown to be more resistant to weathering than the surrounding material, but intact rays separate from the surrounding wood matrix due to moisture cycling. This causes the rays to lose their

reinforcement function within the cellular structure of the material, leading to more surface cracking as the material shrinks and expands differentially during moisture fluctuations (Kucera and Sell 1987).

The changes that occur on the macroscopic level during weathering are the result of surface changes caused primarily through reduced polymer chain length as well as changes in the bulk properties of the materials. Lignin and cellulose losses reduce tensile strength. Derbyshire et al (1996) investigated the loss of tensile strength by exposing thin samples of six softwood species to different doses of UV light. Both the cellulose and lignin portions of the material were affected by the exposure, suggesting an inverse exponential relationship between tensile strength and UV light exposure. Tests employing different span distances indicated that the early stages of strength loss were caused by structural changes at the material surface, such as microcracking, while the later stages of strength loss were dominated by losses of lignin and cellulose (Derbyshire et al 1996, 1995).

Bulk density differences affect erosion rates since UV light can penetrate less dense materials more easily than denser ones. However, the relationship between wood density and erosion rate is not linear (Sell and Feist 1986). Differences in earlywood and latewood densities result in uneven surfaces after outdoor weathering. These differences are most pronounced during the first seven years of weathering, and are more severe in species that have large, extremely dense latewood bands such as Douglas fir (*Pseudotsuga menziesii* Franco) and loblolly pine (*Pinus taeda* L.) (Williams et al 2001). Erosion rates are also affected by grain direction and exposure orientation. The erosion rates of vertical-grained materials were higher when compared to flat grained materials of the same species (Williams, et al. 2001). Erosion rates of materials exposed at a 45 degree angle were greater than those exposed vertically due to increased UV exposure at the 45 degree angle and because degradation products could be removed more easily. However, differences in erosion rates between samples exposed at 45 degrees and those exposed horizontally was minimal, even

though the UV exposure in the horizontal position was much higher. The lack of difference may be due to accumulation of debris and degradation products on the horizontally exposed material that shielded it from further UV deterioration when compared to the materials exposed at 45 degrees (Williams et al. 2001). Erosion rates also vary seasonally, with the least erosion occurring during the winter months, possibly due to the lower UV exposure during this period when compared to spring and summer irradiation (Evans 1996, Raczowski 1982).

Interactions between the wood surface and moisture also play a crucial role in the macroscopic changes during outdoor weathering. Seasonal changes in relative humidity and precipitation levels result in moisture content fluctuations that cause internal stresses as the material shrinks and swells in an anisotropic manner. Checks or cracks develop on the weakest surface of the material when these stresses exceed the material strength. (Haygreen and Bowyer 1996). This process is further complicated when free water within the cell lumens freezes, causing even greater forces to be exerted on the surrounding wood matrix (Borgin 1969). Extractives within the wood can act as a natural water repellent, resulting in more hydrophobic surfaces; however leaching of extractives and lignin degradation increase hydroscopicity. The hydroscopicity of weathered and un-weathered western red cedar was determined using contact angle measurements which declined significantly after only four weeks of outdoor weathering, demonstrating the loss of water repellent extractives from the surface (Kalnins and Feist 1993).

1.3.2 Chemical reactions involved in the weathering process

The energy required to photodegrade wood products is found in the solar radiation received on the earth's surface. Energy is deposited by the sun in the form of photons and the amount of energy contained is inversely related to wavelength. Photons with wavelengths of 286-3,000 nm can penetrate the earth's atmosphere while the remainder are reflected back into outer space. Five percent of the photons that reach the earth's surface fall into the UV range, (286-380 nm), 45% fall into the visible range (380-780 nm) and 50% fall into the

infrared range (780-3,000 nm). The minimum energy required to break certain chemical bonds can be correlated to different wavelengths (Table 1.1). Photons with wavelengths below 600 nm play an important role in weathering reactions undergone by most natural and synthetic polymers (Evans et al. 2002, Williams 2005, Ranby and Rabek 1975). Although only a small percentage of the photons reaching the earth surface contain enough energy to cause chemical reactions to occur, their number is large enough to initiate chain reactions within cellulose, hemicelluloses and lignin, leading to material breakdown.

Table 1.1. Bond disassociation energies and maximum wavelengths that contain the required amount of energy to cleave functional groups commonly found in wood polymers (Ranby and Rabek 1975).

Bond	Bond dissociation energy (Kcal/mol)	Wavelength (nm)
C-C (Aromatic)	124	231
C-H (Aromatic)	103	278
C-H (Methane)	102	280
O-H (Methanol)	100	286
C-O (Ethanol)	92	311
C-O (Methanol)	89	321
CH ₃ COO-C (Methyl ester)	86	333
C-C (Ethane)	84	340
C-COCH ₃ (Acetone)	79	362
C-O (Methyl ether)	76	376
N-N (Hydrazine)	57	502

The constituents in the wood matrix differentially absorb solar radiation into their chemical components. Cellulose and hemicelluloses both absorb light at 200-300 nm due to their similar backbone structures (Feist and Hon 1984). However, few short wavelength

photons reach the earth's surface, thus the degradation reactions that occur within these materials is less severe. Lignin most readily absorbs light with wavelengths of 280 to 380 nm, but the range extends into the visible range. Lignin has a distinct absorbance peak at 280 nm (Kalnins 1966). The broad range of wavelengths absorbed by lignin and the high energy nature of the photons found at the lower end of this spectrum allow for the rapid and complete degradation of the polymer. Flavonoids, tannins, stilbenes and quinones found in heartwood extractives have also been shown to degrade when exposed to solar irradiation. Photons with wavelengths of up to 500 nm contain enough energy to break the bonds in extractives, reducing the potential protection offered by these compounds against fungal attack and moisture intrusion (Evans et al. 2002).

Light absorption by the three major polymers in wood results in the formation of free radicals, indicating that chemical bonds have been broken. The number of free radicals formed within the material is dependent on the wavelengths of irradiation and temperature (Hon 1981). The free radicals formed within cellulose result from bonds being cleaved at the C1 and C4 positions of the glucose ring (Hon 1976). However, light at shorter wavelengths (280-340nm) can also dehydrogenate cellulose at the C2, C3, C4 and C6 positions. In addition, the carbon-carbon bond between the C5 and C6 carbon atoms can also be cleaved at these wavelengths (Hon, 1976). Hemicellulose is thought to degrade in the same manner as cellulose, but there is little work in this area. Evans et al (1992) reported that xylose and arabinose were leached from wood more readily than the other types of hemicelluloses, but the exact breakdown mechanism is not understood.

Hon (1981) studied free radical formation within lignin model compounds using electron spin resonance (ESR). Model compounds were used since the complete structure of the lignin polymer remains unknown and the ESR spectra from wood derived lignin is extremely complex. The results indicated that phenoxy free radicals were readily produced and resonance stabilized within the polymer. Carbon-carbon bonds adjacent to α -carbonyl

groups were cleaved through a Nairn Type I reaction, indicating that α -carbonyl groups are photosensitizers. However, the Nairn Type I reaction did not occur efficiently.

Free radicals readily react with molecular oxygen to form hydrogen peroxide. The role of oxygen in the weathering process has been investigated using singlet oxygen generators and quenchers. Introduction of singlet oxygen generators such as Rose Bengal or Methylene blue increased the amount of hydroperoxide in the material, while the addition of singlet oxygen quenchers reduced the amount of hydroperoxide present (Hon et al 1982). Hydroperoxides are important in the weathering process since they attack the polymer backbone through hydrogen abstraction reactions, forming more hydroperoxide and another free radical while weakening the polymer. In addition, hydroperoxides easily undergo photolysis in the presence of UV light, forming two free radicals that react with the polymer to form two new peroxides. Evans et al (2002) concluded that these chain reactions led to the rapid increase in the rate of polymer degradation on the surface of the wood, even though only a small proportion of the photons from the sunlight contained enough energy to deteriorate the wood polymers. Feist and Hon (1984) summarized photodegradation of wood in a schematic illustrating the self-perpetuating nature of these reactions (Figure 1.5).

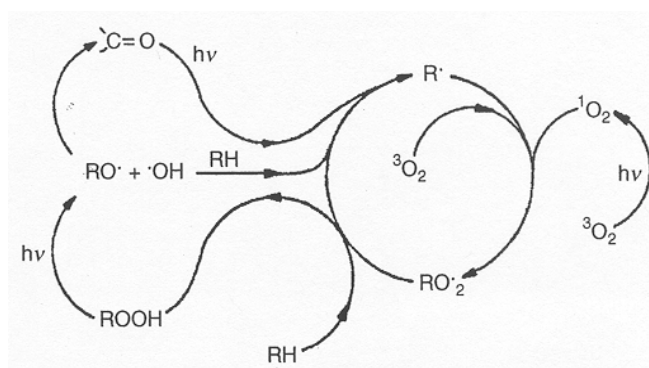


Figure 1.5. Schematic illustrating the photodegradation of wood as described by Feist and Hon 1984.

The weathering reactions from the breakdown of primary polymers result in the formation of a large number of other compounds. The carbonyl content of the wood greatly increases and carboxylic acid is formed as lignin is fragmented and removed. This increases the acidity of the material (Leary 1967). In addition, vanillin, carbon monoxide and dioxide, methanol, formaldehyde, and organic acids have been identified from weathered wood surfaces (Kalnins 1966, Sandermann and Schlumbom 1962). Carbohydrates resulting from the degradation of cellulose and hemicelluloses are also solubilized and removed (Hemmingson and Morgan 1990). The addition of water during the weathering process aids in the removal of these reaction products and also increases the rate of weathering by swelling the cell walls, increasing the access of both the peroxides and light to the cellulose and lignin (Feist and Hon 1984).

1.4 Prevention of Weathering

Weathering can be addressed in a number of different ways. The majority of methods rely on the application of coatings after the wood has been machined into its final shape. These methods of preventing weathering can be grouped into film-forming coatings and penetrating coatings. Film-forming coatings form a continuous, nonporous layer across the surface of the material, while penetrating finishes instead relying on penetrating pigments and water repellents to color and protect the surface. Other systems that do not rely on pigments have also been developed such as reactive metal systems and traditional copper-based wood preservatives. Chemical and physical modifications of the bulk material have also shown promise (Fiest and Hon 1984).

1.4.1 Film forming coatings

Paints are perhaps the oldest and most effective method for preventing wood weathering. Pigments present in these chemicals prevent sunlight from reaching the wood, thus preventing photon-based chain reactions from occurring. The non-porous nature of these

treatments also sheds moisture, preventing the build up of internal stresses that result when differential moisture contents develop within the material. Paints also prevent the leaching of extractives and wood preservatives (Feist and Hon 1984, Nejad and Cooper 2006). Surface discoloration can be further reduced through the addition of mild fungicides, preventing the build up biofilms on the surface that can lead to a gray discoloration of the material (Feist and Hon 1984). However, film forming finishes hide the natural beauty of wood, making them unattractive in some applications. Films can also trap moisture in the wood, creating conditions conducive to fungal decay. Finally these polymer finishes are susceptible to photodegradation and will eventual fail.

Clear film forming finishes, such as clear polyurethanes, provide protection against water intrusion and erosion, while allowing the natural beauty of the wood to show through the protective coating. However, the durability of these systems is limited due to the continued degradation of the wood by sunlight (Black and Mraz 1974, Williams 1983). UV breakdown of the wood results in discoloration and loss of adhesion between the wood and the coating, resulting in premature failures. Clear coatings can be amended with free radical quenchers or UV blockers to improve performance (Williams 2005, Evans et al. 2002).

Paint adhesion, and subsequently its service life, is also affected by the condition of the wood prior to treatment. Williams et al (1987) found that weathering western red cedar for two weeks prior to coating resulting in a 50% loss in paint adhesion when compared to un-weathered control samples. The service life of paint applied to wood that had been pre-weathered for one month was only 6 to 10 months compared to 17 years for paint applied to un-weathered materials (Underhaug et al 1983, Williams and Feist 2001). Paint systems must be applied to the wood immediately after machining in order to obtain optimum performance.

1.4.2 Penetrating finishes

Penetrating coatings provide the same protection from UV light offered by film forming finishes without obscuring the texture of the wood. However, these coatings do not provide the same amount of moisture protection as film forming coatings. Thus moisture gradients will develop within the material and checking will occur over time. On the positive side, the open pore nature of the finish prevents blistering, peeling and the underlying de-bonding of the finish (Williams and Feist 1999). The life span of these coatings is controlled by the cracking of the wood substrate and pigment loss from the wood surface that often leads to bleaching (Sterling et al 2006, Evans et al. 2002). Sterling et al (2006) reported that the performance was highly dependent on the solids content of a product. Feist (1988) also investigated the performance of penetrating finishes and found that the pigment content of the stain was inversely related to the erosion rate of the material. Complete prevention of surface deterioration is impossible because the systems remain semi-transparent, allowing some light to reach the wood surface.

Penetrating finishes are often composed of a water repellent, a moldicide, and a number of chemicals such as pigments and hindered amine light stabilizers that prevent weathering. These active chemicals are then suspended or dissolved in either an organic solvent or water (Williams and Feist 1999). The water repellents used in these products provide some dimensional stability to the wood. These hydrophobic compounds, mainly waxes and resins, increase the contact angle between the surface of the wood and the water droplet to over 90 degrees, preventing water from being sorbed by the surface. The water should then either evaporate or run off, but there is no physical barrier between the wood and the water. Water repellents have also been shown to prevent the leaching of degradation products from the surface, thereby slowing the erosion rate (Minemura et al 1983). Water repellents tend to break down as the wood weathers, resulting in a highly hydrophilic surface. This change normally occurs within the first 21 months after application (Morrell et al 2001).

Reapplication of water repellents to weathered surfaces cannot produce the same degree of protection, since the water repellent cannot bond as readily to the compromised surface (Voulgardis and Banks 1981). Water repellents do not provide complete protection from water intrusion, since water vapor can still enter the material, causing it to swell. Never the less, water repellents are an integral component of clear or semi- transparent systems since these components are not destroyed by the weathering of the underlying wood like their film forming counterparts.

Penetrating finishes in organic solvents appear to be more durable than water borne systems; however, the use of solvent borne systems is declining due to restrictions on the release of volatile organic compounds (VOC's) (Morrell et al 2001, Jacobsen and Evans 2006). Allowing the wood surface to weather for a short amount of time prior to staining has been shown to increase the amount of stain retained by the material (Arnold et al 1992), although there was no link between increased chemical uptake and extended service life (Arnold et al 1992, Morrell et al 2001). Significant interactions between wood preservatives and stains can affect finish performance, but the effects are formulation specific (Nejad and Cooper 2006).

1.4.3 Inorganic surface treatments

Different chromium containing solutions were first investigated as pretreatments to clear finishes in siding applications (Black and Mraz 1974). Some chrome treatments greatly extended the service life of clear finishes, giving service lives in excess of 7 years. The most effective formulations were ammonium chromate acid, ammoniacal copper-arsenate, ammoniacal copper-chrome-arsenate, cupriethylene diamine, copper and iron molybdate and copper ferricyanide. However, a number of these formulations tinted the wood a brown or green color. In addition, the authors noted that the treatments containing ammonia gave the wood a blotchy appearance, although the blotches could be removed with water and light sanding.

More permanent treatments using this same technology, but without the application of a clear coat were developed later by applying aqueous chromic acid solutions (Feist and Ellis 1978). The chemical was applied by a dip or spray treatment, and then the wood was baked, converting the hexavalent chrome into the less toxic trivalent state. This fixed the chromium salts to the wood by forming large complex polymers that were highly resistant to photooxidation. These treatments also imparted water repellency and dimensional stability to the substrate, reducing surface erosion (Fiest 1979, Williams and Feist 1988). These formulations produced slight reductions in strength due to cellulose degradation (Williams and Feist 1984).

The chemical reactions involving chromic acid and wood components to form a weather resistant surface have been studied extensively. Chromium forms covalently bonded compounds with lignin, stabilizing the polymer when exposed to UV light (Pizzi 1990a, de Lange et al 1992). Schmalzl et al (1995, 2003) used guaiacol acid as a model compound for lignin and found that hexavalent chromium formed a complex mixture of highly insoluble, thermally stable guaiacol oligomers. These thermally stable oligomers were tightly held in cellulose, hemicellulose and lignin polymeric complexes that were cross-linked with trivalent chromium, forming complex, high molecular weight polymers on the wood surface. These materials acted as a screen against UV radiation. Chromic acid has also been shown to interact with the polysaccharides, forming transition complexes with cellulose and hemicellulose as CrO_4^{-2} , resulting in decarboxylation of the cellulose (Pizzi 1990b, de Lange et al 1992).

Although chromic acid showed great promise for protecting wood surfaces against the effects of UV light and water, this technology was never commercialized due to worker risks posed by hexavalent chromium and due to questions regarding the environmental fate of the material. In an effort to reduce the health risks associated with hexavalent chromium, chromium nitrate formulations were developed. These treatments reduced the effects of

weathering when used as a pretreatment on plywood panels coated with a film forming finish, but were less effective when exposed outdoors in above ground settings (William and Feist 1988). Iron (III) formulations have also been studied. For example, iron (III) nitrate complexes with guaiacyl moieties, a model lignin compound, provided dimensional stability and fungal resistance (Ntshilele et al 1994). These treatments also reduce micro-checking of pits when exposed to artificial weathering (Chang et al 1982). However, these systems were ineffective in field trials (Evans and Schmalzl 1989, Evans et al 1992), possibly because the iron did not interact with the carbohydrates (Ntshilele et al 1994).

Tin, potassium permanganate and manganese are among the inorganic systems that have also been investigated for surface protection (Schmalzl and Evans 2003). Schmalzl and Evans (2005) reported that veneers treated with oxidative manganese, potassium permanganate or manganic acetate retained lignin on the surface after 35 days of outdoor weathering, suggesting that these compounds complexed with the lignin and reduced UV absorption. Tetraethyl titanate or tetraisopropyl titanate treatments experienced significantly reduced lignin content but little strength loss. The results suggest that these compounds complexed with the cellulose, protecting it from UV light. However, none of these treatments were as effective as chromic acid. While titanate-containing treatments warrant further research, the authors suggested that their inability to color the wood reduced their potential effectiveness. Zirconium based treatments have also been investigated, but have not proven effective (Schmalzl and Evans 2003).

1.4.4 Effects of conventional wood preservatives on weathering

The majority of materials exposed to unfiltered solar radiation are also susceptible to biological decay and are usually treated with chemical agents intended to prevent fungal attack. The majority of these systems contain combinations of copper compounds plus an organic co-biocide to prevent fungal attack, but many also contain water repellent systems to provide dimensional stability. The effects of these compounds on weathering is formulation-

specific. Ammoniacal copper quat (ACQ) and copper ethanolamine treatments produced slightly reduced lignin losses from the surface during artificial weathering (Liu et al 1994, Zhang and Kamdem 2000), while chromated copper arsenate (CCA) formulations had little effect on weathering. Separate tests on CCA distribution on the surface of the material after 9 years of exposure indicated that the copper and arsenic components were lost preferentially when compared to the fixed chromium components (Zahora 2000). Evans et al (2003) examined the effect of CCA on surface checking in relation to the long term appearance of the material. CCA treated materials had fewer, yet longer checks than the untreated controls. Materials treated with water had checking patterns similar to those seen in CCA, indicating that this difference maybe due to the uncontrolled re-drying from very high moisture contents experienced by the material after treatment but the differences were not statistically significant. Didecyldimethyl ammonium chloride (DDAC) formulations increased lignin losses from board surfaces (Jin et al 1991)

Water repellents have also been included in some wood preservative formulations to increase dimensional stability and reduce preservative leaching. Unlike brush or dip applied water repellents that only penetrate a short distance inward from the surface, water repellents applied using vacuum / pressure processes are much more uniformly distributed in the wood. This improved distribution can allow water to bead off the treated material for a much longer time than when these systems are topically applied. Southern pine lumber treated with CCA and a water repellent and exposed to field conditions in North Carolina beaded water from the surface for three years, greatly improving the dimensional stability of the boards, reducing swings in moisture content and reducing surface checking (Zahora 1995). Water repellents were lost from the outer portions of the material after 9 years of exposure resulting in raised grain and some surface checking, but the surface checking was still less than that seen in CCA treated materials without water repellent. In addition, the dimensional stability of the materials with water repellent was greatly improved. These results indicated that even though

water repellents do not prevent surface erosion or discoloration, they stabilize the wood, preventing the development of visibly unappealing deep checks (Zahora 2000). Similar results were observed with other species / chemicals combinations with and without a water repellent system (Barreal 1988, Futong and Zahora 2000, Evans et al 2000).

1.4.5 UV Absorbers and hindered amine light stabilizers

Synthetic polymers have used different hindered amine compounds (HALS), hindered phenolic antioxidants (PAO), and UV light absorbers (UVA) as photostabilizers for the past 40 years. These compounds increase the durability of polymer-based products, such as vinyl siding, when exposed outdoors, reducing fading and embrittlement over time. These technologies have also been incorporated into different coatings to protect the polymeric binder from photodegradation and have also been investigated as clear finishes for protecting wood. Dibenzoylresorcinol, a UVA compound that prevents the formation of free radicals by absorbing UV light and desorbing it as heat, has been shown to reduce the production of gaseous and volatile photodegradation products during artificial weathering (Kalnins 1966). Chang and Chou (1999) found that different UVA compounds reduced the effects of UV exposure on both the wood substrate and the coating itself. Conversely, Hon et al (1985) found that UVA compounds did not prevent wood discoloration under acrylic coatings. In addition, the combination of UVA and HALs prevented photodegradation in acrylic based polymer coatings applied to wood by preventing high concentrations of free radicals (Rogez 2004). However, HALs or PAOs by themselves were not effective when added to film forming coatings used on wood products (Chang and Chou 1999). Yet Chou et al (2007) reported that aromatic polyurethane and aliphatic polyurethane coatings containing 2% hydroxyphenyl benzotriazole, an ultraviolet light absorbing polymer, significantly reduced the photo yellowing of both the film and China fir (*Cunninghamia lanceolata* Lamb.) after artificial weathering.

More promising results have been obtained when UV absorbers and hindered amine light stabilizers were bonded directly to the wood polymers. Grafting UVA compounds directly

to the surface of uncoated western red cedar reduced erosion in accelerated weathering trials and enhanced finish performance when coated with a clear polyurethane finish (Williams 1983). Ungrafted UVA compounds protected the wood for a short period of time before being leached from the surface, allowing the weathering process to resume. However, the grafting process required large energy inputs since the wood and the treating solution must be heated above 100 °C for the reactions to occur, making treatment uneconomical. Another UVA compound, 2-hydroxy-4(2,3-epoxypropoxy)- benzophenone (HEPBP) has also been investigated on scots pine (*Pinus sylvestris* L.), sugi (*Cryptomeria japonica* D.Don), and black poplar (*Populus nigra*) for this application. HEPBP could be permanently incorporated into the wood either through grafting or through the formation of a homopolymer. The resulting material had weight losses equal to those seen in chromic acid treated samples and lower tensile strength losses during the first 50 days of outdoor weathering when weight gains during treatment exceeded 1.5%. In addition, the HEPBP treated materials experienced less discoloration than those treated with chromic acid, turning yellow instead of a dark green color. However, the reaction times and treatment temperatures required for HEPBP treatment are cost prohibitive for industrial applications (Kiguchi and Evans 1998). Even if the processing parameters could be improved, the UV absorbers themselves are currently prohibitively expensive for use in traditional wood products.

1.4.6 Cell wall modification and lumen fill treatments

Chemical modification or bulking alters wood properties by either chemically modifying the hydroxyl groups found within the wood (chemical modification) or by filling the cell lumens (bulking) with a monomer that is then polymerized, resulting in weight gains in excess of 7%. Both of these processes result in a tougher, more dimensionally stable, and decay resistant final product. However, these processes also alter the weathering properties of the wood.

A variety of methods have been developed to chemically modify the cell wall material, to increase dimensional stability and reduce hygroscopicity (Rowell 2005). The most

developed and economically important method is acetylation, whereby hydroxyl groups are blocked through a reaction between acetic anhydride and hydroxyl groups. This process modifies the wood substrate and produces acetic acid as a byproduct. Acetylation is typically continued until weight gains of 10-20% are achieved. These levels have been shown to reduce checking and erosion compared to untreated aspen (Feist et al 1991), as well as reduce the amount discoloration on radiata pine exposed to accelerated weathering methods (Plackett et al 1992). Smaller weight gains can have unexpected effects on wood properties (Rowell 2005). Acetylation of Scots pine to weight gains of 5-10% actually increased the rate of weathering under field conditions (Evans et al 2000).

Improved weathering in acetylated wood has been attributed to the blocking of phenolic hydroxyl groups where free radicals and peroxides are most easily generated (Kalnins 1966). More recent studies have found that acetic anhydride bonds more readily with cellulose and hemicelluloses than with lignin, suggesting that acetylation protects the cellulose components of the wood, while leaving the lignin vulnerable to photodegradation (Feist et al 1991, Evans et al 2000, Kalnins 1984, Torr et al 1996). A number of the other chemical modification techniques have also been investigated, but only benzylation at extremely high weight gains protected both the cellulose and lignin components (Evans et al 2002).

The lumen filling treatments replace the void spaces in the wood with a polymer matrix that limits fluid movement and reduces the ingress of water vapor. The wood is impregnated with monomers, most often methyl methacrylate, and then these compounds are polymerized, in situ, preventing the compounds from being removed via leaching. These systems reduce checking by limiting fluctuations in moisture content and also harden the wood surface to reduce erosion (Rowell et al 1981).

Combinations of chemical modification and lumen filling treatments have been investigated to determine if both checking and color change can be controlled. Acetylation

followed by lumen filling with methyl methacrylate increases the weathering durability of the wood. Butylene oxide, butyl-isocyanate and methyl isocyanate cell wall treatments in combination with methyl methacrylate lumen filling treatments have also been reported to reduce weathering effects (Rowell et al 1981).

1.4.7 Influence of wood processing on weathering

Weathering characteristics such as checking and warping are influenced by a number of gross wood anatomy features such as grain direction and growth rate. These variables can either be improved upon or exacerbated by the processing steps undertaken to transform a log into a final product. The orientation of the growth rings to the exposed surface has been shown to greatly impact the number of checks formed on the exposed surface. Orienting growth rings parallel to the surface, as in flat sawn materials resulted in nine times the number and length of checks after 33 months of outdoor exposure compared to materials where the growth rings were oriented perpendicular to the exposed surface, as seen in radially cut boards (Sandberg 1999). These differences in surface checking may reflect differences in the shrink and swell coefficients of the earlywood and latewood components of each growth ring. Latewood and earlywood move at different rates as water is absorbed and desorbed by the material, resulting in internal stresses (Boutelje 1962). Earlywood and latewood in radially cut materials are oriented in series, allowing these stresses to equilibrate so that the forces do not exceed the strength of either the earlywood or the latewood. However, the earlywood and latewood in flat sawn materials are in parallel, limiting the movement of any given layer and resulting in the development of stresses that can exceed the strength of any given layer. The resulting stress relief leads to check formation (Sandberg 1999). These differences are further exacerbated by drying rate differences between earlywood and latewood, resulting in even greater stresses as the material dries unevenly, further increasing the surface checking process (McCurdy and Keey 2002). Increased checking has also been shown to occur in juvenile wood and sapwood when compared to relatively stable heartwood (Wiedenhoeft and

Miller 2005, Haygreen and Bowyer 1996). While these anatomical features help explain surface check development, it is not feasible to cut only radial boards or boards containing no juvenile wood or sapwood, since the amount of waste generated in the radial sawing is significant and large trees of potential environmental importance would be required.

While radially sawn material has an advantage in weathering, it is also possible to improve checking characteristics of flat sawn decking. Radially oriented surfaces made from flat sawn, short rotation materials that were resawn and laminated exhibited significant improvements in surface appearance after 2 years of outdoor exposure. In addition, surfaces can be sculpted with a beading pattern that makes checks less obvious (Preston 2008). Furthermore, kerfing the underside of flat sawn deck boards has been shown to reduce cupping after one year of exposure, although increased checking was associated with this process. The number of kerfs had a significant impact on wood performance, with one 20mm deep kerf down the center of the board being most effective (Ratu et al 2007). Installation practices have also been investigated to determine if different fastener systems or placing the growth rings concave or convex to the exposed surface affect checking of flat sawn materials. Fastener type had no effect on checking after six months in the field, while board orientation greatly influenced the number of surface checks, with the convex oriented material experiencing less checking than the concave oriented boards (Urban and Evans 2005). This suggests that weathering characteristics of flat sawn materials can be greatly improved using machining and installation techniques.

1.5 Future Directions

Wood has played an important role as a building material in the United States and around the world both in structural and decorative applications. However, in the last 25 years, wood has fallen out of favor for decorative, exterior applications due to the amount of maintenance required. Wood remains the material of choice for decks and other outdoor living structures where the structural qualities of the material play a larger role. However, wood

plastic composites and other materials are making inroads into this area, threatening the position of solid wood products. Much of this growth has come because of the perceived reduced maintenance requirements and increased long term aesthetic appeal. Increased scarcity of non-renewable materials along with public awareness of such issues as global climate change and the need for conservation, create opportunities to reintroduce wood as a beautiful, durable, environmentally friendly and cost effective building material for outdoor applications.

In order to take full advantage of this opportunity, previous knowledge of the wood weathering process must be combined with our understanding of polymer chemistry and wood anatomy to create new durable products that are environmentally sound and visually appealing. A systems approach will be the most effective method for developing new products that combine chemical protection, through the strategic use of UV light stabilizers, water repellents, and wood preservatives, with other technologies that take full advantage of natural wood properties.

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A New Look at the Weathering Performance of Solid-Wood Decking Materials

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2. A NEW LOOK AT THE WEATHERING PERFORMANCE OF SOLID-WOOD DECKING MATERIALS

2.1 Abstract

Greater reliance on renewable building materials has increased the need for wood surfaces that can be exposed outdoors without checking or weathering. In the past, wooden support members were generally covered with other materials, but these members often remain exposed in new structures. Biocide treatments allow wooden members to remain structurally sound, yet weathering quickly reduces the aesthetic appeal of wood in these applications. While many treatments have been investigated to prevent discoloration and checking, none have proven to be environmentally and economically feasible. The potential of several alternative approaches to reduce weathering and biotic degradation were explored on loblolly pine samples impregnated with pigments, water repellents, organic UV inhibitors or organic biocides and exposed outdoors in Eastern Oregon. Replicates harvested after predetermined solar radiation doses were assessed for checking and color change. Pigments provided the greatest protection against discoloration, while wax based water repellents provided the greatest protection against checking. Interestingly, the results also suggested that formulation properties such as particle size and shape and melt point played important roles in determining the ability of a material to protect the wood surface against weathering.

2.2 Introduction

Public awareness of resource scarcity and environmental protection has steadily increased during the past three decades. This awareness has been heightened by the public debate of issues such as global climate change, the impending end of the petroleum era, and the responsible management of old growth/native forest ecosystems. Heightened environmental responsibility has also been driving consumer preferences for building products that present a smaller ecological footprint. One material that has the potential to meet the

demand for green building products is plantation-grown timber. This material is near carbon-neutral, is easily machined, and has aesthetic appeal (CSIRO, 2006; Buchana and Levine, 1999; Buchanan and Honey, 1994). However, one of the greatest drawbacks associated with wood is poor resistance to weathering when exposed outdoors. Wood is inherently sensitive to ultraviolet light and wet/dry cycling, and the much higher proportions of juvenile wood in the plantation resource exacerbates these problems (William, 2005; Haygreen and Bowyer, 1996).

The chemical and anatomical changes that occur within wood exposed to ultraviolet light have been studied extensively (Williams, 2005). Models indicate that the destruction of wood polymers is driven primarily by self-sustaining free radical reactions, leading to the preferential depolymerization of lignin, leaving behind a weak, disorganized surface of cellulose fibers, appearing white to gray in color (Evens et al, 2002; Fiest and Hon, 1984; Kataoka, and Kiguchi, 2001). Further, it is believed that the destabilization of the wood surface along with moisture cycling leads to the development of checks that mar the surface and create avenues for moisture collection and microbial growth (Haygreen and Bowyer, 1996; Derbyshire et al, 1995, 1996).

Controlling the undesirable consequences of exterior exposure has been extensively studied, yet few promising treatments that do not negatively alter the natural aesthetic appeal of the material have been forthcoming. One promising process developed during the 1970s was chromic acid treatment (Williams, 2005; Black and Mraz, 1974). This treatment resulted in a very stable, albeit green-tinted surface (Feist and Ellis, 1978). However, concerns over the use of hexavalent chromium make this treatment impractical. Other treatments that have shown some promise include iron oxide-based chemistries and the grafting of UV absorbers onto the wood surface (Ntsihlele et al, 1994; Chou et al 2007). None of these methods completely prevents the degradation of both the lignin and the cellulose polymers (Evans et al 1992). Thus, if wood is to play a role in exterior applications, other treatments must be

developed. The objective of this study was to evaluate the effects of selected water repellents and UV inhibitors on resistance of wood to photodegradation in order to gain a basic understanding of how the properties of these treatments affect the weathering characteristics of wood.

2.3 Methods

Water repellents, pigments, and organic UV-light inhibitors were chosen as the three major classes of compounds for this investigation. In an effort to examine some of the many variables within each group, a number of compounds with specific attributes of interest were chosen (Table 2.1). Clear, flat sawn southern yellow pine sapwood samples (10 mm thick, 85 mm wide, and 155 mm long) were prepared from nominal 1" x 4" stock. Two matched samples from each parent board were assigned to be treated with each compound of interest. This allowed for comparisons between chemical treatments across the natural range of wood characteristics. Stable treating solutions were formulated at the concentrations found in Table 2.1. The wood samples were weighed prior to being impregnated using a uniform vacuum/pressure cycle (Table 2.2). After treatment, the samples were weighed to determine chemical uptake and then reconditioned to a moisture content of 9% using a climate chamber set at 25 °C and 50% relative humidity. However, the positive control samples treated with chromic acid were not treated using the vacuum/ pressure method. Instead, the chemical was painted on the surface. These samples were conditioned along with the other samples. This deviation was necessary due to the toxic nature of the chromic acid. The samples were end-sealed using a marine epoxy resin. Baseline colorimeter measurements were made on the exposed face using a Konica Minolta Chroma Meter (Ramsey, NJ) and a jig to center the colorimeter over the samples.

Table 2.1. Compounds used to reduce the effects of weathering, the reason for inclusion, and concentrations used.

Class	Compound	Purpose	Application Concentration (ppm)
Pigment	Red iron oxide suspension with a particle size of 700 nm	Baseline for particle size and crystal shape comparison	1000
Pigment	Red iron oxide suspension with a particle size of 190 nm	Particle size on surface discoloration	1000
Pigment	Yellow iron oxide suspension with a particle size of 190 nm	Crystal shape on surface discoloration	1000
Pigment	Titanium dioxide with a particle size of 130 nm	Compound and particle size on discoloration	1000
Pigment	Titanium dioxide suspension with a particle size of 195 nm	Compound and particle size on discoloration	1000
UV stabilizer	Hydroxyphenylbenzotriazole Class	UV absorber	1000
UV stabilizer	Hindered amine light stabilizer (HAL)	Free radical scavenger	1000
Water repellent	Oil in water emulsion with a wax melt point of 34–38 °C	Melt point and wax on water repellency	20,000
Water repellent	Oil in water emulsion with a wax melt point of 54–58 °C	Melt point and wax on water repellency	20,000
Water repellent	Oil in water emulsion with a wax melt point of 65.5–75 °C	Melt point and wax on water repellency	20,000
Water repellent	Silicate with a particle size of 8–20 nm	Particle size and silicates on water repellency	20,000
Water repellent	Silicate with a particle size of 20–100 nm	Particle size and silicates on water repellency	20,000
Water repellent	Water dispersed acrylic polymer	Control water ingress by binding to the surface of the wood	4000

Table 2.1 (Continued).

Biocide	DCOIT	Known to control mold and prevent biological discoloration	1000
Positive control	Chromic acid	Known to control surface discoloration	30,000
Negative control	Untreated	Baseline for checking and discoloration	NA

Table 2.2. Vacuum and pressure conditions used to impregnate southern yellow pine sapwood with various compounds

Cycle	Time (min)	Pressure/ Vacuum
Initial vacuum	5	25 mmHg
Pressure	10	150 psi
Final vacuum	5	25 mmHg

2.3.1 Exterior Exposure

The samples were mounted on aluminum supports with the growth rings oriented concave face upwards. Each sample was secured to the rack by placing one 4.5 mm diameter screw into each corner of the sample. This limited cupping and warping, forcing stress relief to occur through check development.

Sixteen samples per treatment were exposed in the eastern Oregon high-elevation desert at a site near Klamath Falls (Lat: 42.22, Long: -121.78, elevation of 1250 m) on racks pitched at 45° pointing due south (Figure 2.1). Solar irradiation data were collected daily from an AgriMet weather station operated by the Bureau of Reclamation located at the site. Natural precipitation was augmented with non-chlorinated irrigation water between June and the end of October by spraying the samples for 15 min per day at sunrise using sprinklers mounted to the upper edge of the racks. Approximately 0.668 m³ of water was delivered to the samples

per day. Two samples per treatment were harvested at the end of each 454 MJ/m^2 irradiation interval. This irradiation interval corresponded to the maximum amount of solar energy that the site received in the two weeks surrounding the summer solstice.



Figure 2.1. Samples mounted on 45° racks and pointed due south in Klamath Falls, Oregon, prior to the installation of the sprinkler heads.

The harvested samples were reconditioned to a moisture content of 9% in a dark climate chamber. The conditioned samples were then scanned using a 600dpi Canon color scanner (Lake Success, NY). Each image was then stored as a .jpg file and the checking characteristics of the samples were analyzed using a custom software package developed by the University of British Columbia and updated by Mississippi State University (Evans, 2008; Li and Nicholas, 2008). Colorimeter measurements were taken using the Konica Minolta Chroma Meter and the results were compared with the baseline measurements made prior to exposure.

2.4 Results and Discussion

Gauge retentions for each sample were calculated using the actual chemical concentration used and the chemical uptake of each sample (Table 2.3). Chemical retentions within the pigment and UV stabilizer classes were not statistically different at an alpha level of

0.05 allowing for the comparison of checking and color fading data within these treatment groups. Retentions of the low melt point wax were statistically different from some of the other treatments in this group; however, since the average retention was within two kg/m^3 of the others, it was included in the comparisons. The results also indicated that gauge retentions were below the target retentions for all of the treatments. This systematic error indicates that the parent boards may have originated from trees that were less permeable than the average southern pine specimen.

Table 2.3. Target and average gauge retention data for the materials used to improve weathering of southern yellow pine sapwood.

Class	Compound	Target retentions (kg/m³)	Gauge retention (kg/m³)*
Pigment	Red iron oxide suspension with a particle size of 700 nm	0.75	0.55 (0.53-0.57)
Pigment	Red iron oxide suspension with a particle size of 190 nm	0.75	0.56 (0.54-0.58)
Pigment	Yellow iron oxide suspension with a particle size of 190 nm	0.75	0.56 (0.54-0.58)
Pigment	Titanium dioxide with a particle size of 130 nm	0.75	0.55 (0.52-0.58)
Pigment	Titanium dioxide suspension with a particle size of 195 nm	0.75	0.52 (0.51-0.53)
UV stabilizer	Hydroxyphenylbenzotriazole Class	0.75	0.56 (0.53-0.59)
UV stabilizer	Hindered amine light stabilizer (HAL)	0.75	0.55 (0.52-0.59)
Water repellent	Oil in water emulsion with a wax melt point of 34–38 °C	15.00	9.77 (8.74 – 10.80)
Water repellent	Oil in water emulsion with a wax melt point of 54–58 °C	15.00	11.13 (10.59-11.66)
Water repellent	Oil in water emulsion with a wax melt point of 65.5–75 °C	15.00	11.30 (10.27-12.32)
Water repellent	Silicate with a particle size of 8–20 nm	15.00	11.52 (11.25-11.80)
Water repellent	Silicate with a particle size of 20–100 nm	15.00	11.41 (11.04-11.77)
Water repellent	Water dispersed acrylic polymer	3.00	2.11 (1.97 – 2.25)
Biocide	DCOIT	0.75	0.50 (0.38-0.54)
Positive control	Chromic acid	3% solution brushed on surface	NA
Negative controls	Untreated	NA	NA

(*) values in parentheses represent upper and lower confidence interval limits using an alpha value of 0.05.

Actual irradiation doses received by the samples were within 7% of the targeted quantities except for irradiation period six where the samples were removed after

approximately one year of exposure. The amount of exposure time required to achieve a specific irradiation dose varied with season. The samples were installed in August and the time required to achieve a specific irradiation dose increased with the onset of winter and then decreased again as summer arrived (Table 2.4). Surface discoloration occurred rapidly as predicted by Evans et al. (1996), while the low relative humidity at the site (Table 2.4) kept biological discoloration of the surfaces to a minimum. The low relative humidity combined with the daily water sprays allowed for the rapid development of checks in all of the materials. Checks were predominately found in the latewood bands (Figure 2.2) and their number generally increased over time, while check length and width remained uniform. This may be explained by the greater stiffness of cell walls in the latewood portion of the growth ring, when compared to the thinner cell walls in the earlywood.

Table 2.4. Irradiation dose, number of days in the field, and climatic conditions experienced by each sample set

Irradiation Period	Irradiation Dose (Mj/m²)	Time in the Field (days)	Harvest dates	Average Relative Humidity (%)
1	486.80	19	September 8 2008	52.10
2	939.38	42	October 1 2008	50.02
3	1363.52	78	November 6 2008	57.64
4	1886.12	152	January 19 2009	69.90
5	2337.25	201	March 9 2009	71.58
6	6096.12	357	August 12 2009	67.15

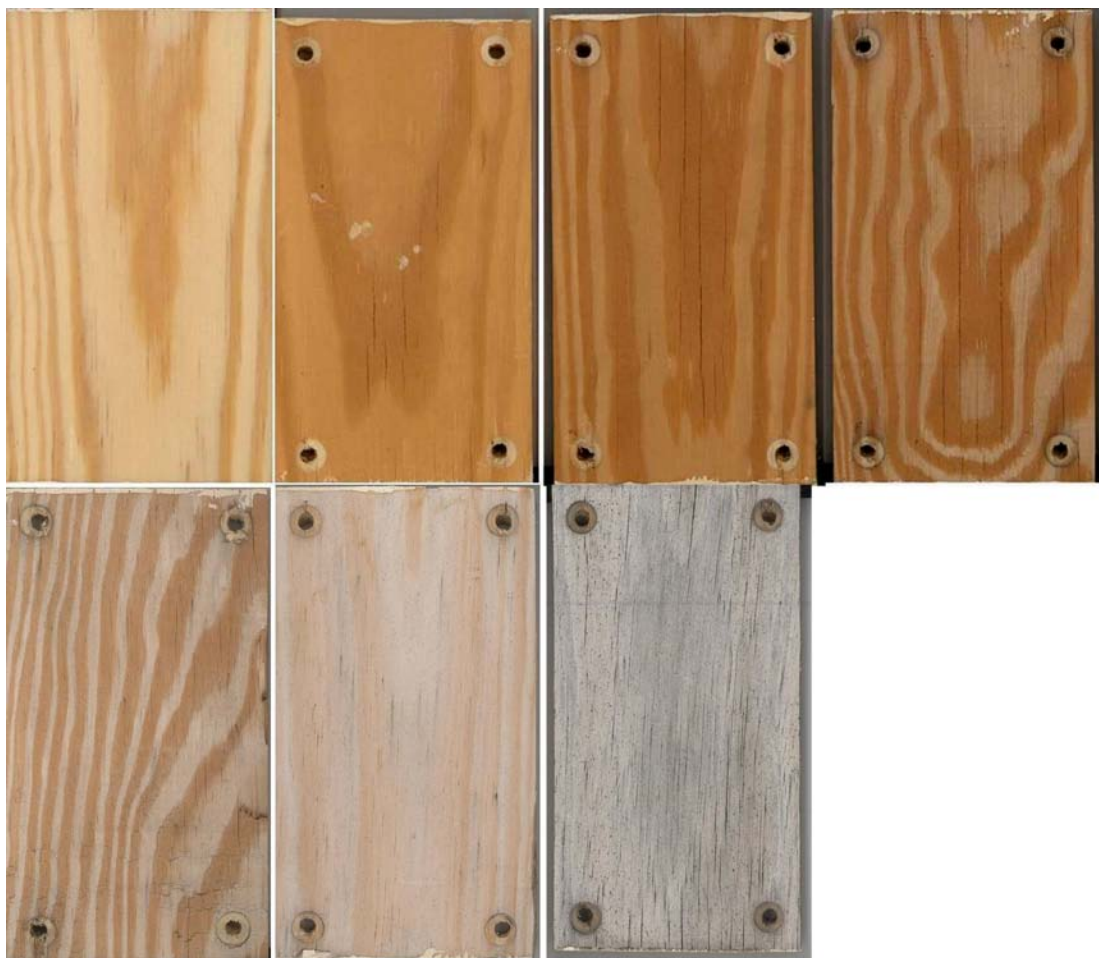


Figure 2.2. Progression of checking and discoloration within southern pine samples exposed to 0, 486.80, 939.38, 1363.52, 1886.12, 2337.25 or 6096.12 MJ/m^2 of irradiation (left to right), respectively.

Checking and total color change results were analyzed by treatment class. Pigments provided the greatest fade resistance and the least protection from checking, while samples treated with the organic biocide (DCOIT) checked the least.

The effects of each class of compounds were evaluated to gain an understanding of how the selected properties affected weathering. Samples treated with red iron oxide pigments experienced the least amount of color change within the pigments group (Figure 2.3). The results suggest that crystal shape plays an important role in preventing solar energy from reaching the wood surface. Particle size also appeared to play a role in preventing discoloration, perhaps because of preferential loading of larger particle size materials on the

wood surface where the compound was needed. The larger particle size materials protect the substrate from a broader portion of the solar spectrum, thus reducing the amount of free radical reactions that can occur. Water repellents did not significantly affect color change, even though some protection would be expected from the silicate particles. It is likely that the silicate particles were too small to block a significant portion of the solar spectrum. The performance of UV absorbers indicates that it might be more fruitful to prevent solar energy from reaching the wood surface than to remediate the free radicals that are produced by it. This can be deduced from the data showing that hydroxyphenylbenzotriazole compounds imparted more protection than hindered amine light stabilizers (HALs) compounds although the data also suggest that HALs provided longer lasting protection than hydroxyphenylbenzotriazoles (Figure 2.4).

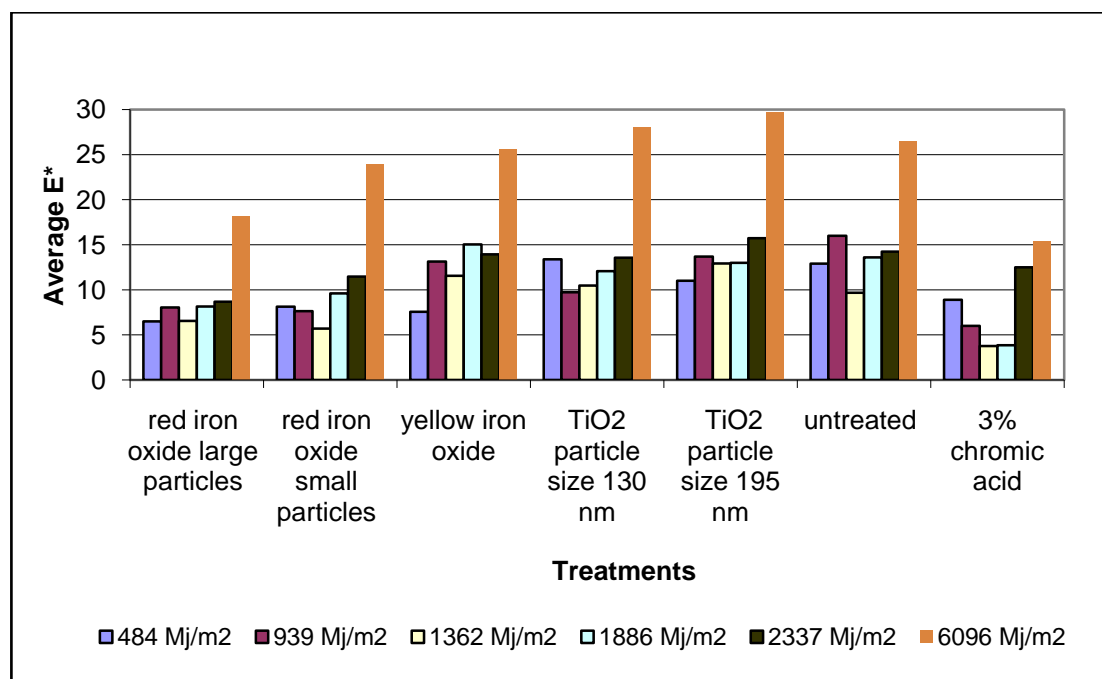


Figure 2.3. Effects of pigments on total color change through time for southern pine samples exposed to sunlight. Untreated and samples treated with 3% chromic acid are included as negative and positive controls.

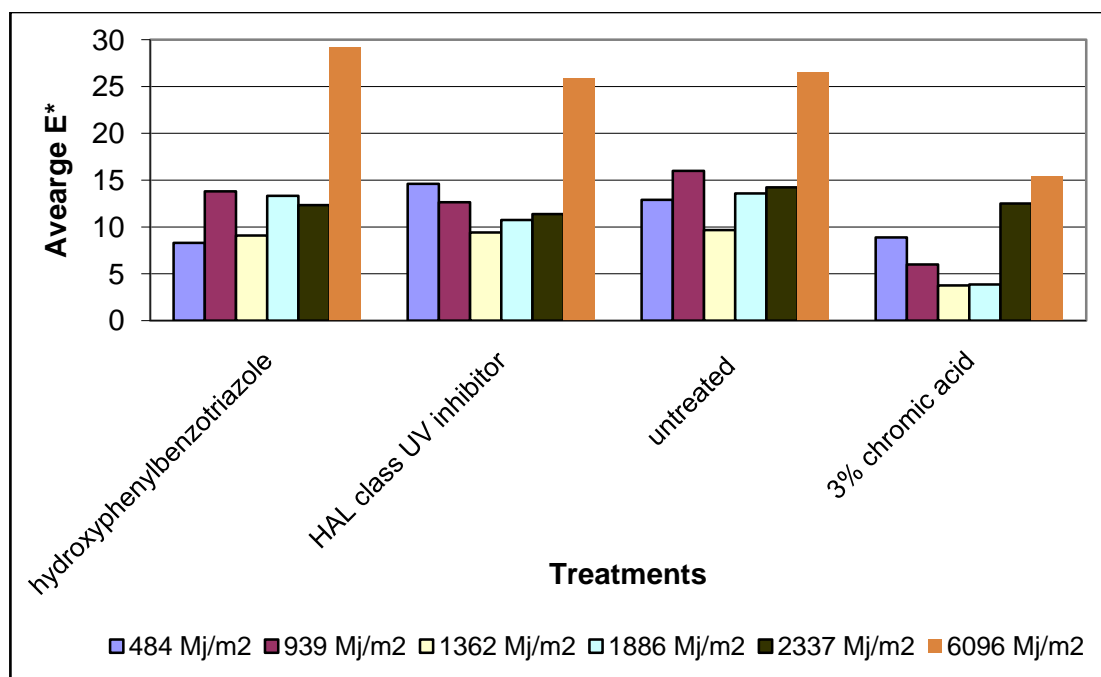


Figure 2.4 Effect of UV stabilization on total color change through time for southern pine sapwood exposed to sunlight. Untreated and samples treated with 3% chromic acid were included as negative and positive controls.

Both color change and checking generally increased over time, but there was little correlation between the two physical property changes, suggesting that different environmental factors were contributing to checking and color change. Checking was affected by seasonal changes at the site. A majority of the treatments were associated with a strong rise in the average number of checks that developed during the fall, winter and early spring months, when occasional snow and rain events at the test site were interspersed with drying winds. This observation suggests that surface checking early in the weathering process is primarily controlled by water ingress and moisture cycling. However, the large spike in the number of checks observed during the last 156 days of exposure suggests that removal of lignin from the surface of the substrate later in the weathering process results in a significant increase in the number of checks that develop on the surface. These observations suggest that water repellents will out-perform other treatments early in the weathering process, while compounds that prevent lignin degradation may provide better long term protection.

Silicate water repellents produced the most hydrophobic surfaces during the initial 1362 Mj/m² of irradiation, indicating that these compounds could be useful wood stabilizing agents (Figure 2.5). Yet the performance of wax based systems surpassed the silicates as the amounts of precipitation and irradiation increased. These results suggest that while the silicates adhered to the surface of the cell walls, the wax based systems penetrated the cell walls, preventing the cells walls from swelling. Absorption of the wax-based systems into the cell walls may have also reduced the rate of depletion through leaching or other forms of degradation.

The melt point of the wax-based water repellents affected performance. Initially, the low melt-point wax offered better protection against checking than the higher melt-point material, presumably because it melted and spread more evenly over the surface during conditioning. However, samples treated with the lower melt-point wax experienced more checking than those with higher melt-point waxes with continued exposure. Increased checking may be caused by the continued absorption of the low melt-point wax into the wood, moving it away from the surface where it is needed. Alternatively, the lower melting point wax may have been more sensitive to UV degradation. The acrylic resin treatment gave similar results to the low melt point wax, although the acrylic resin appears to be much more efficient than the wax since only one fifth of the wax retention was achieved similar checking results. Acrylic treated samples rapidly lost their ability to prevent checking with continued irradiation exposure, indicating that the material had broken down after exposure to sunlight or that it had been removed from the surface through water ingress. UV stabilizers, especially the HAL class, did not greatly influence color change, but did limit checking during the first 1886.1 Mj/m² of irradiation. This may reflect their oilborne nature, which would act as a water repellent.

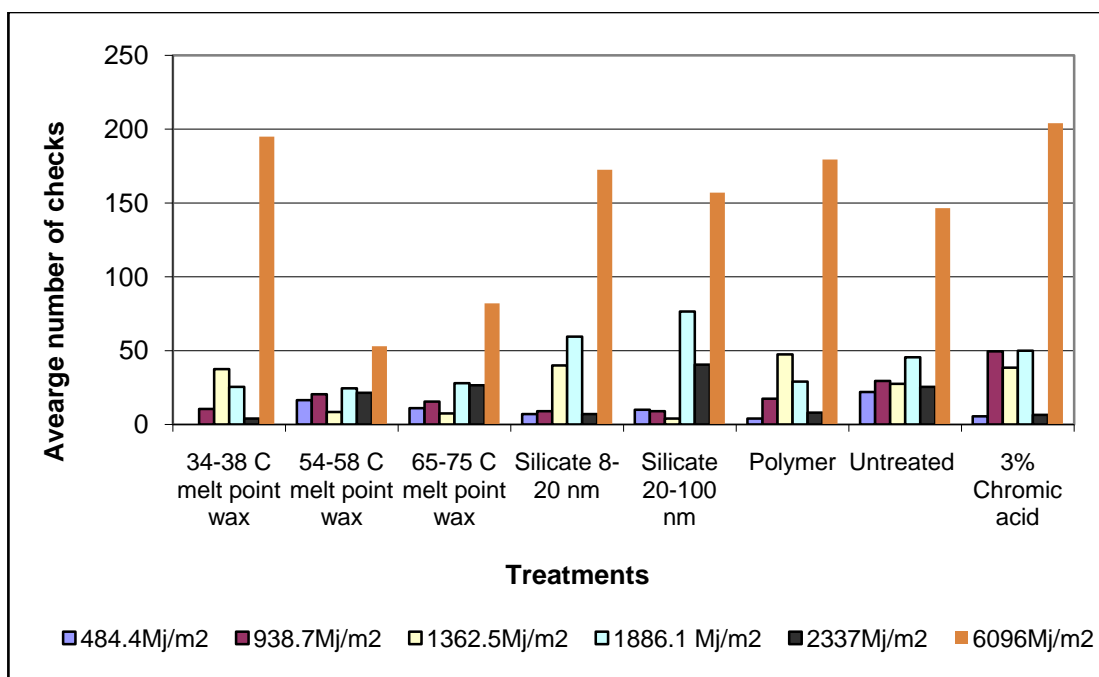


Figure 2.5. Effect of water repellent treatment on average number of checks through time on pine sapwood samples in an exterior exposure. Untreated and samples treated with 3% chromic acid were included as negative and positive controls, respectively.

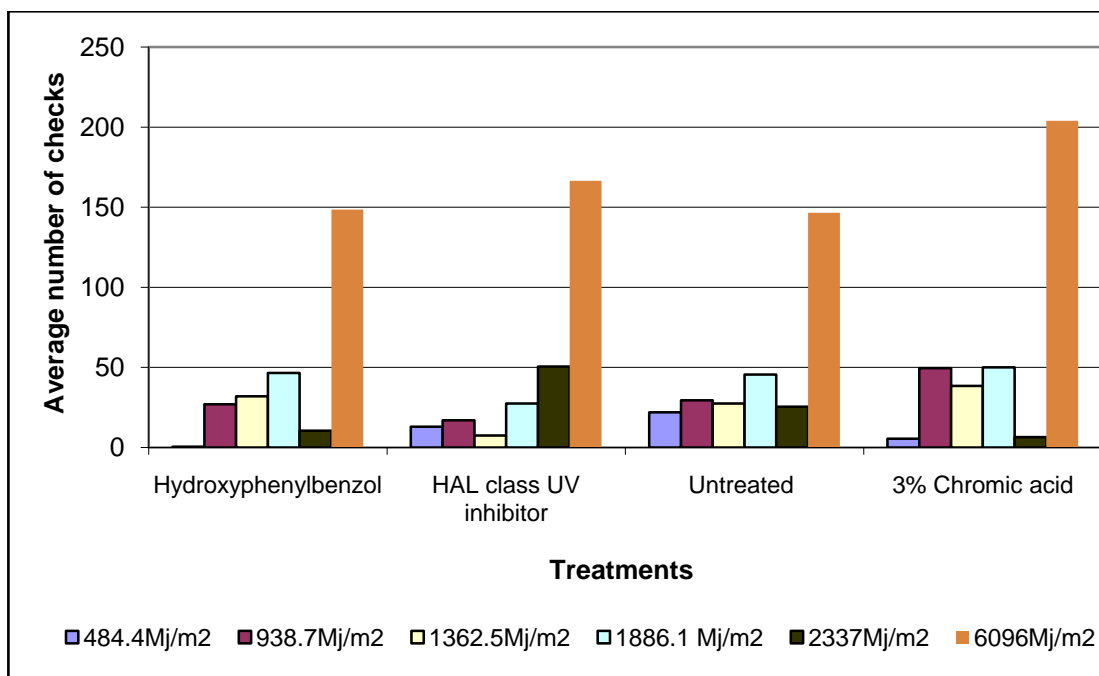


Figure 2.6. Effect of UV stabilization treatments on average number of checks through time on pine sapwood samples in an exterior exposure. Untreated and samples treated with 3% chromic acid were included as negative and positive controls, respectively.

Average check width and length were also investigated to assess differences between treatment effectiveness. No significant changes in checking were detected between treatments or over the duration of the study (Figures 2.7 and 2.8). The absence of effect may be due to the reconditioning process undertaken after the samples were returned from the field. This may have allowed checks to close slightly, making changes less obvious.

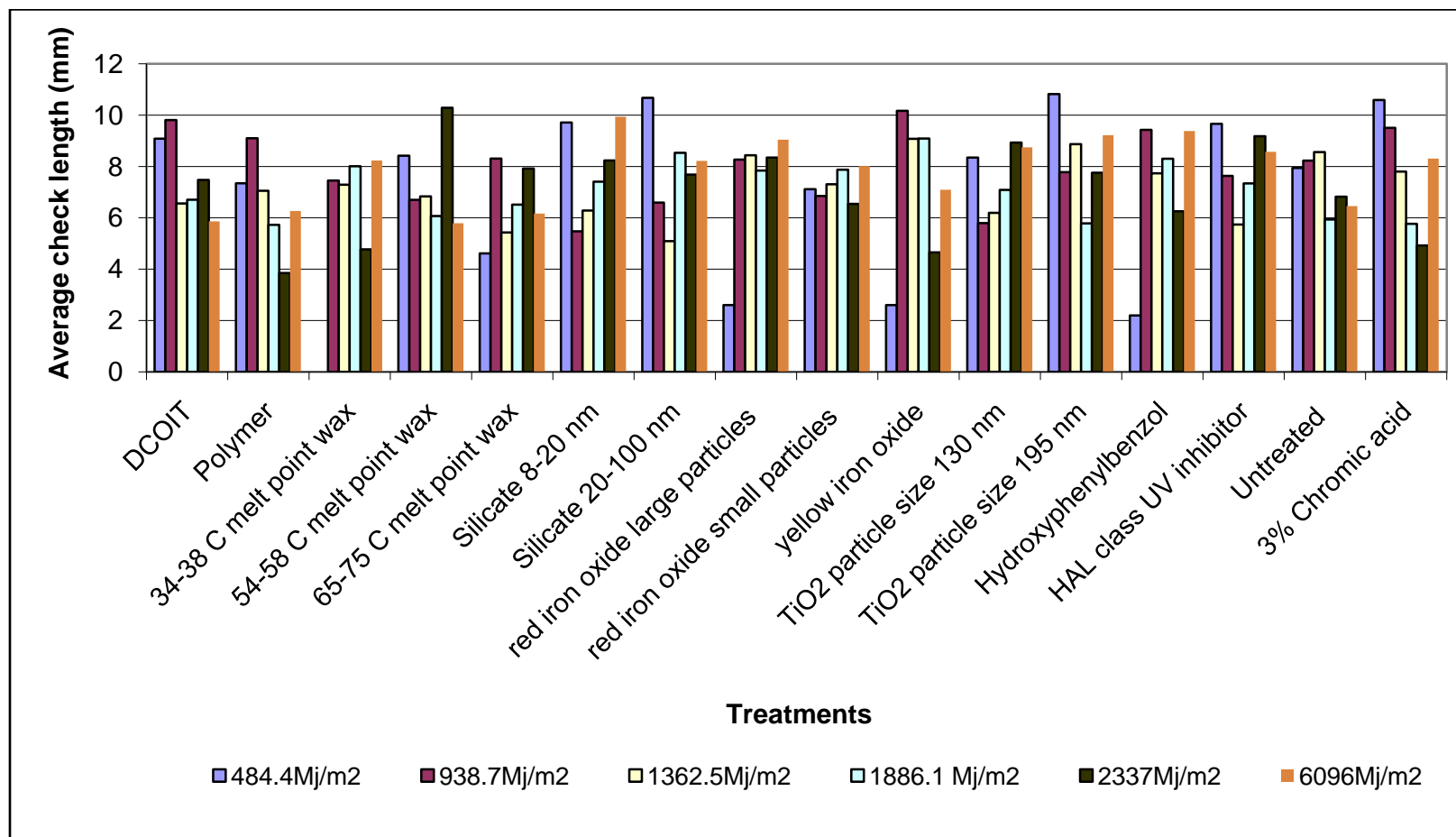


Figure 2.7. Effect of treatment on average check length for pine samples exposed to different levels of UV radiation.

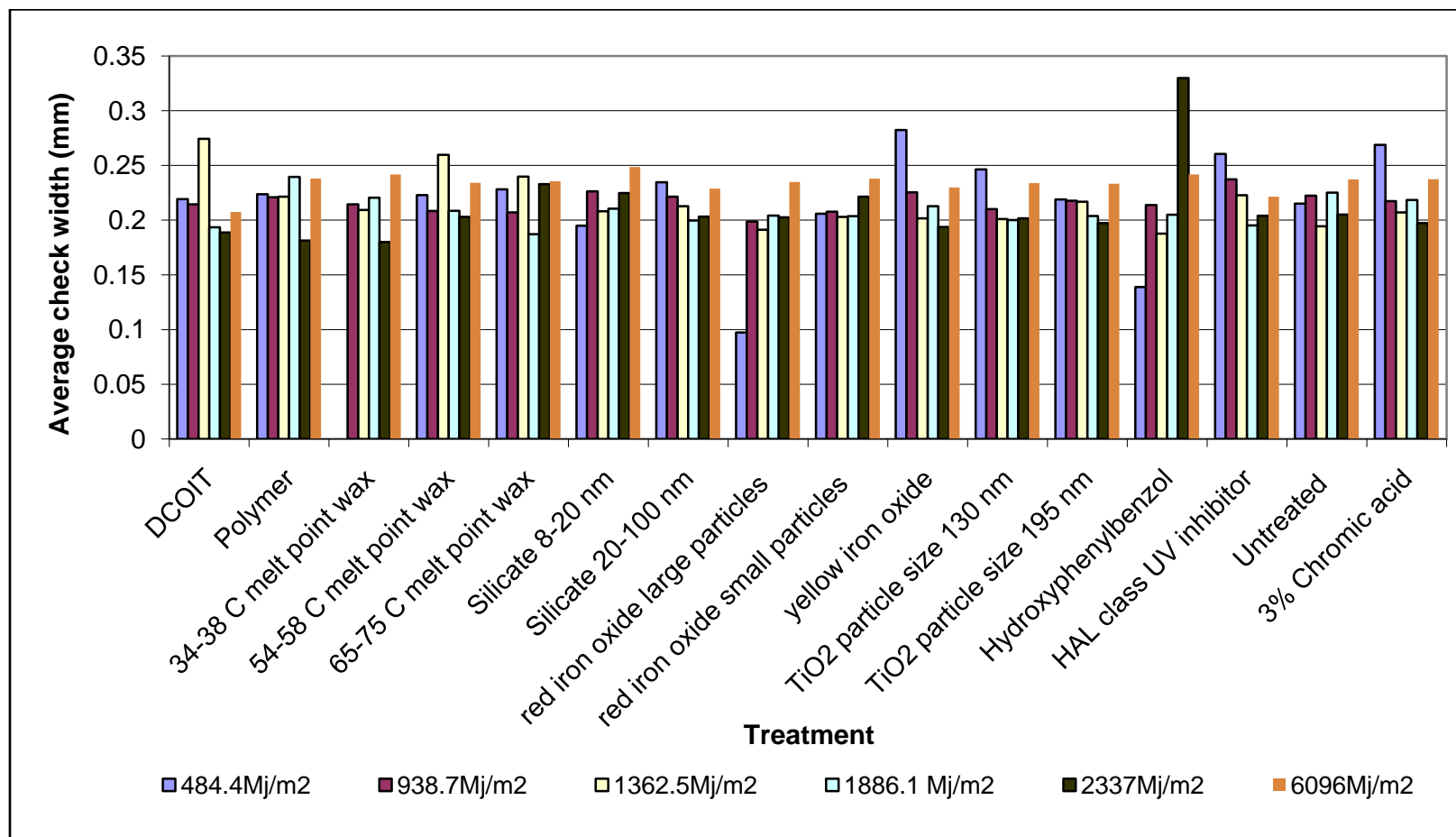


Figure 2.8. Effect of treatment on average check width for pine sapwood samples exposed to different levels of UV radiation

2.5 Conclusion

While none of the treatments completely prevented discoloration or checking, some markedly reduced susceptibility to damage. Pigments provided better fade resistance than the other treatments investigated and silicates initially produced the most hydrophobic surfaces while waxes provided better long term protection. The results also highlighted the importance of individual properties within a group of treatments. This was most clearly illustrated with the various iron oxide and wax water repellent treatments. Individual properties such as particle size and shape for the iron oxides or the wax melt point had dramatic effects on treatment performance. While no individual treatment provided complete protection, the results suggest that incorporation of combinations of carefully selected components can impart reasonable degrees of surface protection in wood.

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FTIR Analysis of Wood Surfaces Treated with Prospective Surface Protectants and Exposed
Outdoors for Various Exposure Periods

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3. FTIR ANALYSIS OF WOOD SURFACES TREATED WITH PROSPECTIVE SURFACE PROTECTANTS AND EXPOSED OUTDOORS FOR VARIOUS EXPOSURE PERIODS

3.1 Abstract

Visual appeal is often as important as structural integrity when building materials are selected for outdoor applications. The poor performance of wood as a result of discoloration and checking has led to the increased use of alternative materials for such applications as outdoor cladding and decking. The underlying chemical reactions leading to discoloration and checking on wooden surfaces have been extensively studied. Lignin de-polymerization is the critical process leading to weathering of wood surfaces. The potential for using different classes of surface protection agents to prevent lignin loss from wood surfaces was assessed on loblolly pine samples impregnated with pigments, water repellents, organic UV inhibitors or an organic biocide. These samples were exposed to predetermined doses of solar radiation in Eastern Oregon and then evaluated for chemical changes that occurred on the surface using FTIR. While lignin loss was complete in all of the samples after one year of exposure, some treatments provided longer protection than others. The greatest protection was provided by the organic UV light inhibitors, while red iron oxides and a petroleum based water repellent with a melt point of 54-58 °C also provided protection against lignin degradation.

3.2 Introduction

Graying and checking of wood that is exposed outdoors make this material less attractive for outdoor cladding, decking and structural applications. Visual appearance of the exposed surface is often as important as the structural integrity in these applications. This favors other materials such as metal, stone or synthetic polymer building materials that do not discolor or crack with time (Williams 2005; Evans et al 2002; Truini 1996; Principia Partners 2001).

The underlying chemical reactions associated with wood weathering were extensively studied at the United States Forest Products Laboratory in the 1980's (Feist and Hon 1984; Hon and Feist 1986). These investigations suggested that surface degradation was a bleaching process. Self-sustaining bleaching reactions were initiated through the absorption of sunlight, resulting in the formation of free radicals (Hon 1981). Molecular oxygen from the atmosphere and these free radicals then combined to form hydroperoxide, a compound capable of destroying the molecular bonds found in the backbone of the lignin and hemicellulose polymers (Hon et al 1982). Degradation of the lignin and hemicellulose polymers left only cellulose on the wood surface, giving rise to the gray fibers often associated with wood exposed outdoors (Kalnins 1966; Browne and Simonson 1957). The continued bleaching process weakens the exposed surface and the remaining cellulose fibers are eroded by wind or rain, resulting in the formation of checks, raised grain and the loss of cross section from the member (Sell and Feist 1986; Williams 2005).

The earliest approaches to limit weathering of wood surfaces included selection of timbers of species with good weathering characteristics, or coating the wood surface prior to exposure (Feist and Hon 1984). Neither of these methods is completely effective. The selection of high density woods or woods with large amounts of extractives only slows check formation and loss of cross section (Sell and Feist 1986). Coating wood with a polymer is only effective as long as the polymer coating remains intact and adheres well to the underlying wood (Feist and Hon 1984; Nejad and Cooper 2006; Black and Mraz 1974; Williams 1983). However, coatings can become brittle over time since they are also attacked by sunlight, causing them to crack and peel. This exposes the wood to the effects of the surrounding environment. In addition, the application of a polymer coating has the disadvantage of hiding the natural beauty of the wood (Williams 2005).

Black and Mraz (1974) investigated a large number of chemistries for protecting wood surfaces from weathering without obscuring the natural pattern, color and texture of the wood.

Chrome-based chemistries were most effective at preventing weathering, with chromic acid showing the most promise of all of the chemistries investigated (Feist and Ellis 1978). Unfortunately, the hazardous nature of chromic acid has prevented it from being used commercially for this application. Iron oxide-based chemistries and grafting of UV absorbers onto the wood surface have also shown some promise, yet none of these methods completely prevented surface degradation (Evans et al 1992; Ntshile et al 1994; Chou et al 2007). Thus, there is still a need for improving the protection of wood surfaces from the action of sunlight, oxygen and water. This report assesses the ability of selected surface protection agents to limit chemical changes on surfaces of southern pine lumber exposed outdoors for one year.

3.3 Methods

Water repellents, pigments, organic UV-light inhibitors and organic biocides were chosen as the four major classes of compounds for this investigation (Table 3.1). Clear, flat sawn loblolly pine sapwood (*Pinus taeda*) samples (10 mm thick, 85 mm wide, 155 mm long) were prepared from nominal 1"x4" stock. One sample from each of 10 parent boards was assigned to be treated with each compound of interest. This allowed for comparison between chemical treatments across the natural range of wood characteristics. The wood samples were weighed prior to being impregnated using a uniform vacuum/pressure cycle (Table 3.2). After treatment, the samples were weighed to determine chemical uptake and then reconditioned to 9% moisture content in a climate chamber set at 25 °C and 50% relative humidity. The samples were end-sealed using a marine epoxy resin.

Table 3.1. Compounds assessed for their ability to reduce weathering of loblolly pine sapwood.

Category	Compound	Purpose	Application Concentration (ppm)
Pigment	Red iron oxide suspension (particle size of 190 nm)	Particle size on surface discoloration	1000
Pigment	Yellow iron oxide suspension (particle size of 190 nm)	Crystal shape on surface discoloration	1000
Pigment	Red iron oxide suspension (particle size of 700 nm)	Baseline for particle size and crystal shape comparison	1000
Pigment	Titanium dioxide (particle size of 130 nm)	Compound and particle size on discoloration	1000
Pigment	Titanium dioxide suspension (particle size of 195 nm)	Compound and particle size on discoloration	1000
UV stabilizer	Hydroxyphenylbenzotriazole Class	UV absorber	1000
UV stabilizer	Hindered amine light stabilizer (HAL)	Free radical scavenger	1000
Water repellent	Oil in water emulsion (wax melt point of 34–38 °C)	Melt point and wax on water repellency	20,000
Water repellent	Oil in water emulsion (wax melt point of 54–58 °C)	Melt point and wax on water repellency	20,000
Water repellent	Oil in water emulsion (wax melt point of 65.5–75 °C)	Melt point and wax on water repellency	20,000
Water repellent	Silicate (particle size of 8–20 nm)	Particle size and silicates on water repellency	20,000
Water repellent	Silicate (particle size of 20–100 nm)	Particle size and silicates on water repellency	20,000

Table 3.1 (Continued).

Category	Compound	Purpose	Application Concentration (ppm)
Water repellent	Water dispersed acrylic polymer	Control water ingress by binding to the surface of the wood	4000
Biocide	DCOIT	Known to control mold and prevent biological discoloration	1000
Positive control	Chromic acid	Known to control surface discoloration	30,000
Negative control	Untreated	Baseline for checking and discoloration	NA

Table 3.2. Vacuum and pressure conditions used to impregnate southern yellow pine sapwood with various surface protection compounds.

Cycle	Time (min)	Pressure/ Vacuum
Initial vacuum	5	25 mmHg
Pressure	10	150 psi
Final vacuum	5	25 mmHg

3.3.1. Outdoor Exposure

The samples were mounted on aluminum supports so that the wood growth rings were oriented concave face upwards. Each sample was secured to the rack using a 4.5 mm diameter screw in each corner of the sample. The screws limited cupping and warping, forcing stress relief to occur through check development. Six samples per treatment were exposed in the eastern Oregon high-elevation desert, at a site near Klamath Falls (Lat: 42.22, Long: – 121.78, elevation of 1250 m) on racks pitched at 45° that pointed due south (Figure 3.1). Solar irradiation data were collected daily from an AgriMet weather station operated by the Bureau

of Reclamation and located at the site. Natural precipitation was augmented with non-chlorinated irrigation water between May and the end of October by spraying the samples for 15 min per day at sunrise using sprinklers mounted to the upper edge of the racks. Approximately 114 L of water was delivered to the samples per day. One sample per treatment was harvested at the end of each 454 Mj/m^2 irradiation interval. This irradiation interval corresponded to the maximum amount of solar energy that the site received in the two weeks surrounding the summer solstice. The harvested samples were reconditioned to a moisture content of 9% and examined for changes in the chemical composition of the surface using Fourier transformed infrared (FTIR) spectroscopy.



Figure 3.1. Samples mounted on 45° racks in Klamath Falls, Oregon, showing sample configuration and orientation, but prior to the installation of the sprinkler heads.

3.3.2 *FTIR Spectroscopic Analysis of Wood Surfaces*

Specimens ($\sim 2 \text{ mm} \times 10 \text{ mm} \times 20 \text{ mm}$) were removed from each sample using a carving knife. Three specimens from different earlywood and latewood bands were selected from each sample. The spatial location of the specimens was chosen at random. Two FTIR instruments were used to collect the spectra, a ThermoNicolet Avatar 370 spectrometer and a Perkin Elmer Spectrum One FTIR Spectrometer; both instruments were operated using a single bounce attenuated total reflection (ATR) probe. The crystal used in association with the

ThermoNicolet device was a Smart Performer ZnSe crystal, while the Perkin Elmer device was operated using a MIRacle (Pike Technologies inc. 2009) ATR adapter fitted with a composite diamond crystal. Sixty scans were collected per specimen. After collection, the spectra were baseline corrected and all six spectra collected from one sample were averaged to produce a composite spectrum representing the entire sample using Omic 7.4 software (Thermo Fisher inc. 2007). Composite spectra from matched samples collected after each irradiation interval were overlaid and changes in the chemical composition of the surface were observed.

Regions of the spectra relevant to the photodegradation of wood were quantified using the Omic 7.5 Software package. Individual peak heights were measured and the resulting data normalized using the large cellulose and hemicelluloses C-O stretching peak located at 1033 cm^{-1} . Loss in peak height was expressed as a percent loss, using the unexposed reading as a baseline. The carbonyl region was treated differently from the other regions of interest due to overlapping peaks in this portion of the spectra. The region between 1750 and 1700 cm^{-1} was normalized within a treatment and Fourier self deconvolution was applied to resolve overlapping peaks, allowing for the analysis of esters (1736 cm^{-1}), carboxylic acid (1726 cm^{-1}) and conjugated ketones (1716 cm^{-1}). Peak height was recorded and used to study the degradation process of hemicelluloses and the development of the degradation byproduct carboxylic acid over time (Fabiya et al 2011).

3.4 Results and Discussion

Actual irradiation doses received by the samples were within 7% of the targeted quantities, except for period six where samples were arbitrarily removed after approximately one year of exposure. The amount of exposure time required to achieve a specific irradiation dose varied with season. The time required to achieve a specific irradiation dose increased with the onset of winter and then decreased again as summer arrived (Table 3.3). Surface discoloration occurred rapidly as predicted by Evans et al. (1996), while the low relative

humidity (Table 3.3) kept biological discoloration of the surfaces to a minimum. The low relative humidity combined with the daily water sprays allowed for the rapid development of checks in all of the materials. Checks were predominately found in the latewood bands (Figure 3.2) and their number generally increased over time, while check length and width remained uniform. This may be explained by the greater stiffness of cell walls in the latewood portion of the growth ring, when compared to the thinner cell walls in the earlywood.

Table 3.3. Exposure time, irradiation dose, and average relative humidity for loblolly pine samples exposed for approximately one year in Klamath Falls, Oregon.

Irradiation Period	Irradiation Dose (Mj/m²)	Time in the Field (days)	Average Relative Humidity (%)
1	484.4	19	52
2	938.7	42	50
3	1362.5	78	58
4	1886.1	152	70
5	2337.3	201	72
6	6096.1	357	67



Figure 3.2. Examples of progressive check and discoloration development on loblolly pine samples exposed to 0, 487, 939, 1363, 1886, 2337 and 6096 MJ/m^2 of irradiation (A-G).

The two FTIR spectrometers used for this investigation were calibrated by comparing spectra obtained from the same untreated non-exposed control sample. Even though the crystals utilized by the two instruments were different, the resulting spectra generated by the two instruments were well correlated (Figure 3.3). One slight deviation between the two instruments was detected in the region between 1700 and 1550 cm^{-1} . The instrument utilizing the ZnSe crystal appeared to be slightly less sensitive in this region than the instrument utilizing the composite diamond crystal, yet both instruments clearly resolved the two shoulder peak in this area located between 1650 and 1600 cm^{-1} . As a result, no distinctions will be made when discussing spectra from the two instruments.

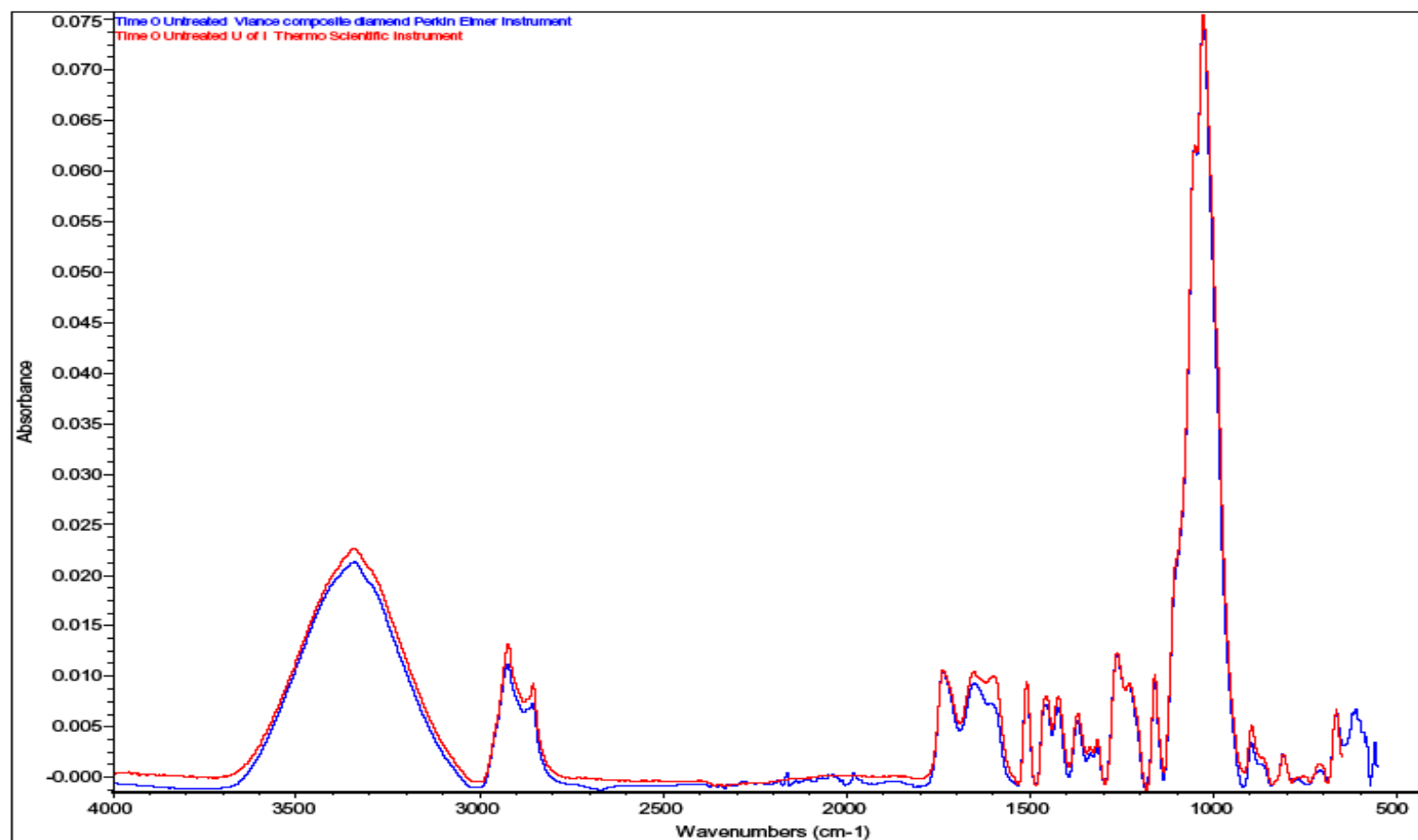


Figure 3.3. Comparisons between FTIR spectra of the untreated unexposed southern pine samples collected using Perkin Elmer and Thermo-Scientific instruments showing good agreement along most of the spectra.

Dramatic changes occurred in the FTIR spectra of the untreated control samples with weathering exposure (Figure 3.4 and 3.5). In most cases, peak intensity declined over time, although this was not always the case. A twin peak located between 3000 and 2800 cm^{-1} lost definition over time, suggesting that aliphatic groups (C-H stretch of CH_2 and CH_3) associated with wood extractives had been removed from the wood surface (Mayo et al 2004). In the fingerprint region of the spectra, the peak at 1740 cm^{-1} (carbonyl-ester) followed the pattern observed by Anderson et al (1991), initially increasing in strength and peaking after 939 MJ/m^2 of irradiation. This peak degraded over the remaining four sampling periods and disappeared after one year of exposure. Anderson et al (1991) suggested that this peak is associated with deacetylation of hemicellulose. The initial increase in peak intensity may be associated with the photo oxidation of hemicellulose to produce carboxylic acid that increased the absorbance at this wavelength. Deconvolution of the carbonyl region indicated that the peak at 1736 cm^{-1} (ester peak) steadily decreased, suggesting that the hemicellulose was degraded over time (Figure 3.6). The peak at 1726 cm^{-1} associated with carboxylic acid, a degradation product associated with the depolymerization of lignin and hemicellulose initially increased, then declined as lignin and hemicellulose were depleted from the surface supporting a theory by Anderson et al (1991; Fabiyi et al 2011; Leary 1967). The conjugated ketone peak (1716 cm^{-1}) followed a pattern similar to the carboxylic acid peak, suggesting that the concentration of cellulose on the wood surface increased as the lignin and hemicelluloses were degraded. However, this peak was also degraded with increased exposure suggesting that the cellulose polymer was also negatively affected by exposure to solar irradiation, although at a reduced rate compared to the other polymers.

The neighboring peak centered between 1660 and 1590 cm^{-1} followed a similar pattern to that of the unconjugated carbonyl peak, initially increasing and then decreasing after the second sampling. However, this peak was never completely lost. Tolvaj and Faix (1995) suggested that this peak was associated with the aromatic stretching of lignin and the

absorption of water by the cellulose polymer. This suggests that even though the lignin ether linkage peak located at 1513 cm^{-1} was lost early in the weathering process, degraded lignin components were still present on the wood surface (Stirling and Morris 2009). The peak located at 1600 cm^{-1} associated with lignin was lost immediately after exposure, while the second peak, at 1466 cm^{-1} also associated with lignin, was lost over a longer period of time. The primary lignin peak located at 1513 cm^{-1} (substituted aromatic) was also sharply reduced but remained discernable until the third sampling period, when the samples had received in excess of 1363 MJ/m^2 of irradiation (Anderson et al, 1991; Stirling and Morris, 2009).

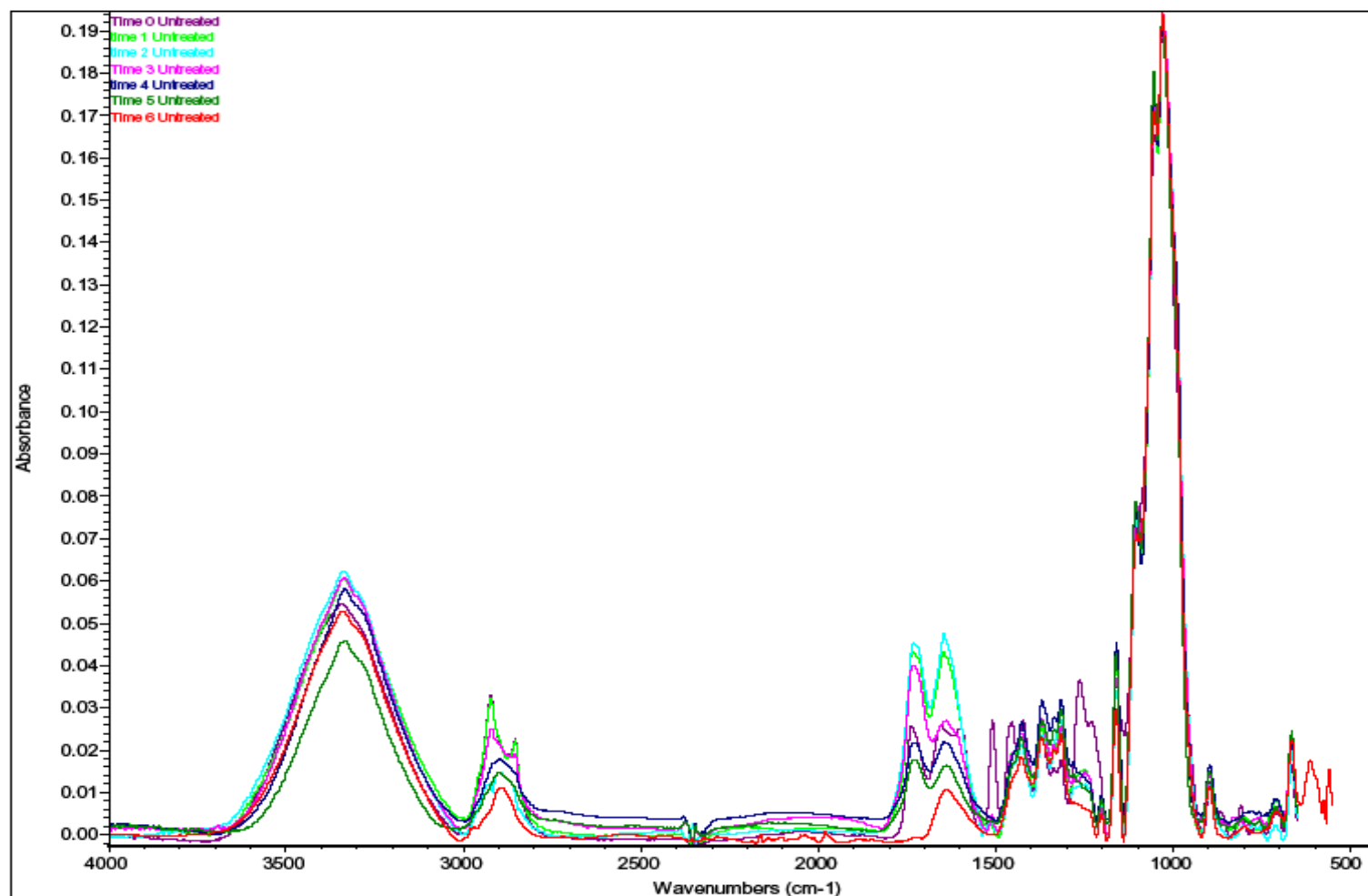


Figure 3.4. FTIR spectra collected from untreated southern pine samples after being exposed outdoors to irradiation dosage increments of 454 MJ/m² showing degradation of peak intensity in many regions with increased exposure.

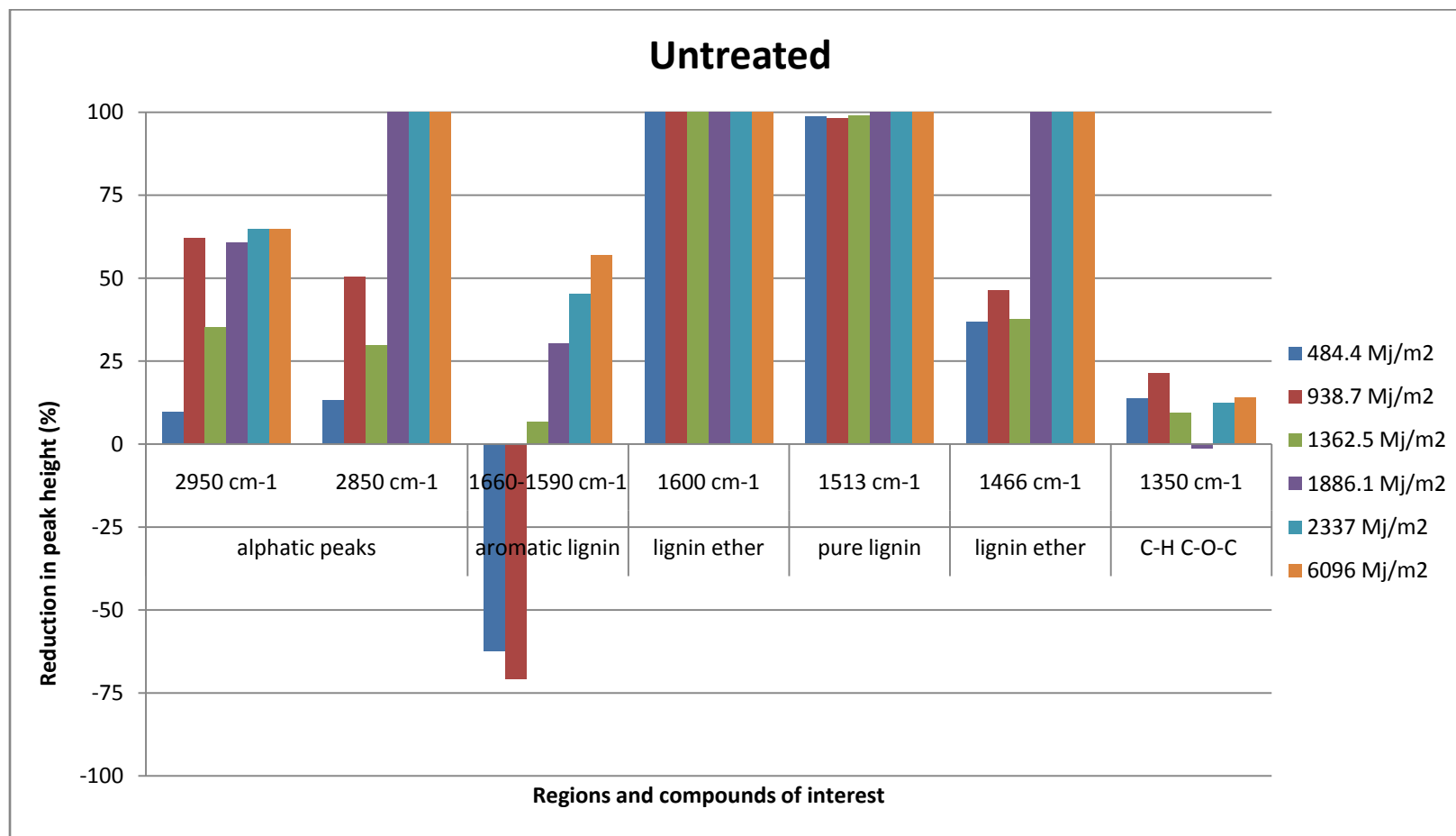


Figure 3.5. Reduction in peak intensity in FTIR spectra from untreated southern pine samples after being exposed outdoors to irradiation dosage increments of 454 MJ/m².

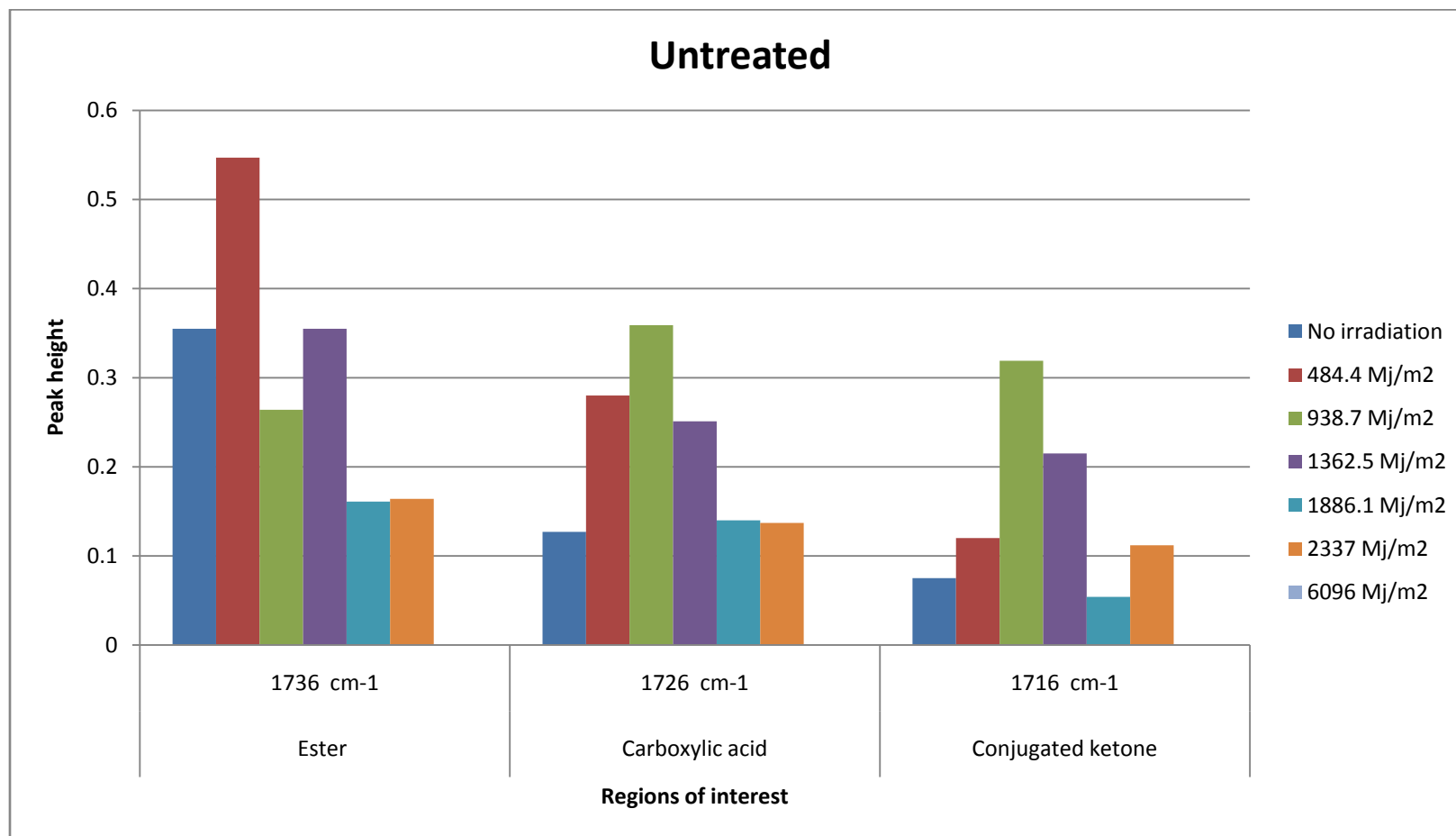


Figure 3.6. Changes in the carbonyl region of FTIR spectra collected from southern pine after being exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

FTIR spectra of the positive controls treated with 3% chromic acid solution indicated that this treatment provided some protection against weathering (Figures 3.7 and 3.8). The aliphatic C-H peaks (3000 and 2800 cm^{-1}) lost definition over time, but at a slower pace than in the untreated samples. Chromic acid treatment also affected the degradation behavior of lignin and hemicellulose. The carbonyl band at 1740 cm^{-1} did not show the initial increase that occurred in the untreated samples and was previously observed by Anderson et al (1991), but intensity did decrease over time. Deconvolution of the peak indicated a significant drop in the ester peak, after 939 MJ/m^2 of irradiation, suggesting that the application of chromic acid protected the acetyl ester regions in hemicellulose for a relatively short period of time (Figure 3.9). Carboxylic acid and conjugated ketone peaks followed the same general pattern as observed in the untreated sample, yet at a reduced intensity, suggesting that the chromic acid treatment sequestered the production of carboxylic acid. The peaks associated with lignin behaved similarly to the pattern observed for the untreated control samples, but the pure lignin peak was still visible after 1886 MJ/m^2 of irradiation. This was a substantial improvement over the untreated controls and helps to explain why chromic acid is such an effective surface protection agent.

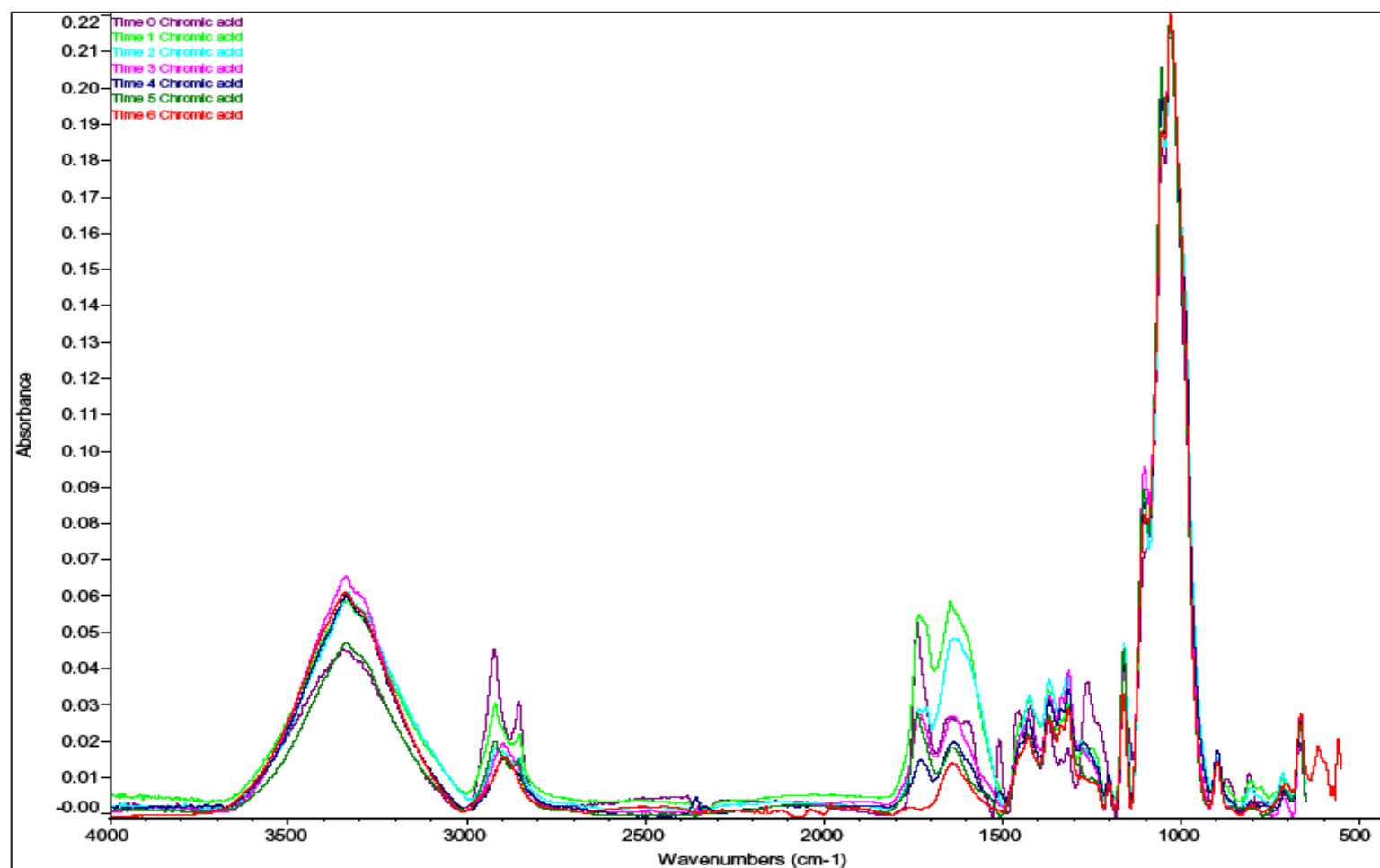


Figure 3.7. FTIR spectra collected from 1% chromic acid treated southern pine samples after outdoor exposure to irradiation dosage increments of 454 MJ/m² showing losses in peak intensity in some regions, but at much slower rates than found with untreated controls.

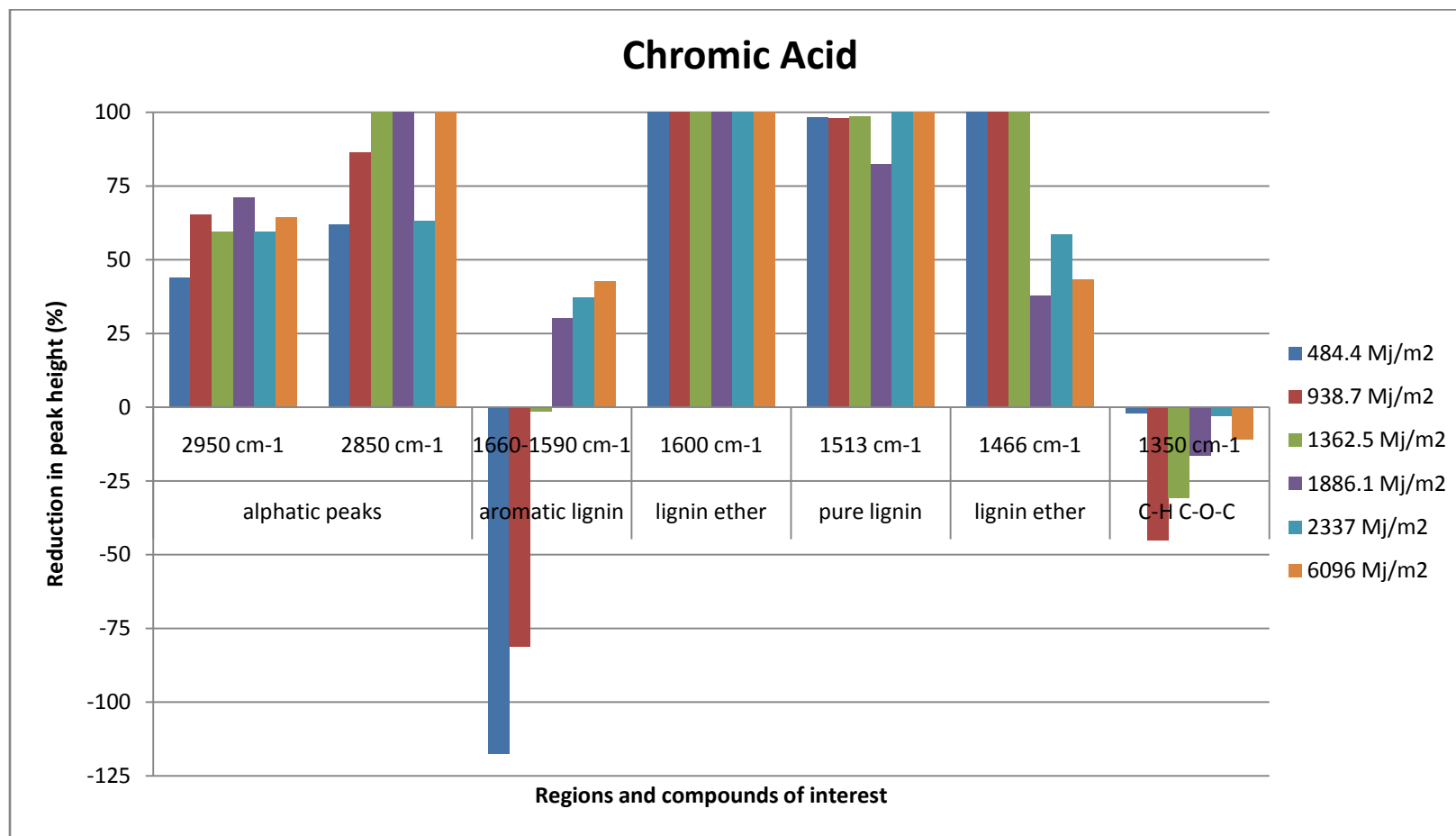


Figure 3.8. Reduction in FTIR peak intensity for chromic acid (3%) brushed southern pine samples after being exposed outdoors to irradiation dosage increments of 454 MJ/m².

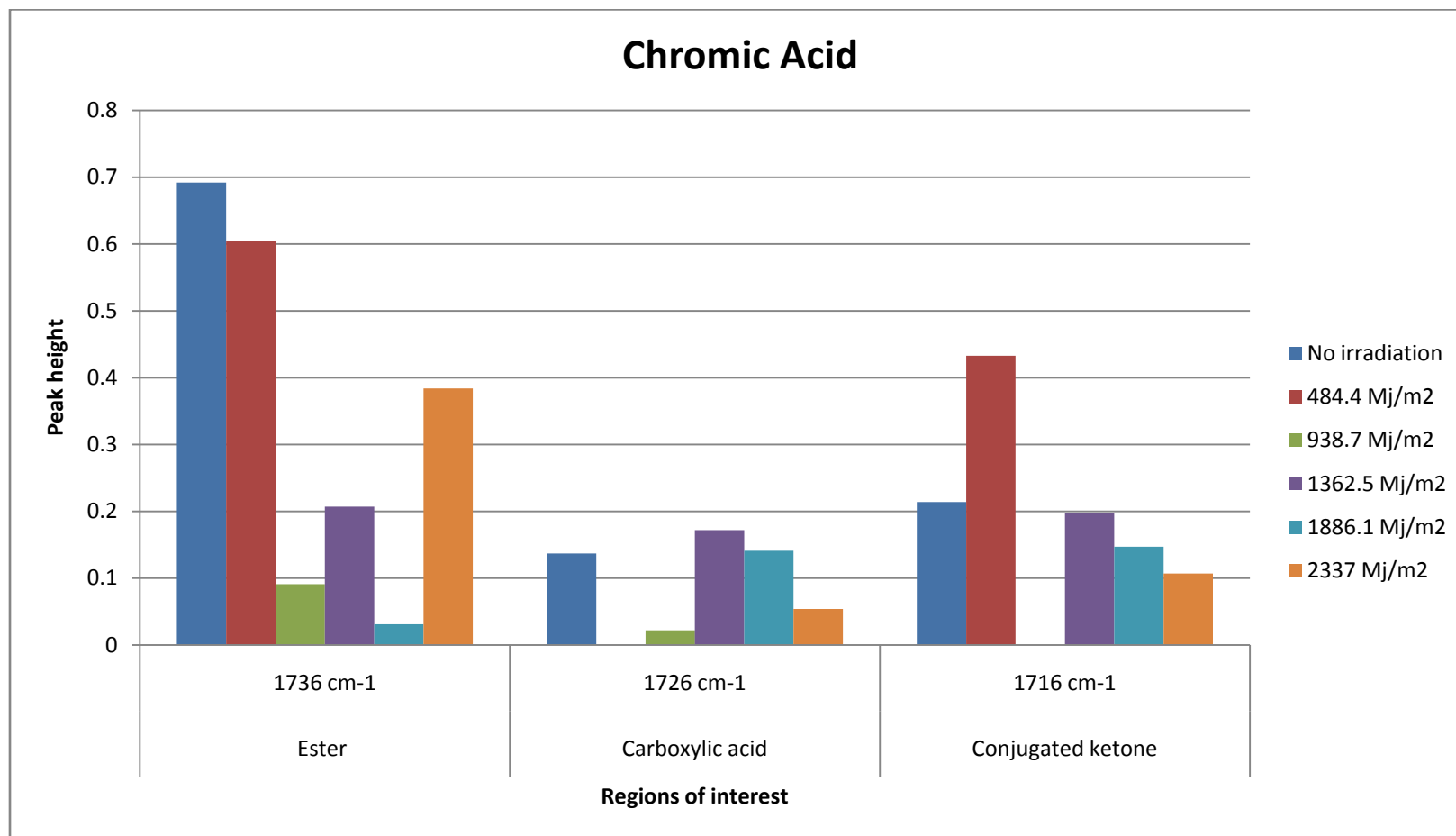


Figure 3.9. Changes in the carbonyl region of FTIR spectra collected from southern pine samples brushed with chromic acid (3%) and after exposure outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

Spectra for all iron oxide-based treatments contained large initial aliphatic peaks that were lost within the first exposure period, regardless of the pigment source. These peaks were associated with the carrier system used to hold the pigments in suspension during application and were rapidly lost from the wood surface (Figures 3.10-18). The largest differences between the untreated and iron oxide treated samples were observed with a red iron oxide suspension with a mean particle size of 190 nm (Figures 3.10-12). This treatment amplified the initial absorbance in the unconjugated carbonyl region (1740 cm^{-1}), but the strength of this peak decreased to the height observed in the untreated controls after exposure to 487 MJ/m^2 of irradiation. Deconvolution suggested that the initial spike in the unconjugated carbonyl region was associated with a strong signal from the ester and carboxylic acid absorption peaks (Figure 3.12). These peaks degraded rapidly after exposure, suggesting that this treatment did not protect the hemicellulose as the raw spectra would suggest. Deconvolution of the carbonyl region suggested that treating samples with iron oxide prevented the buildup of carboxylic acid, possibly slowing the loss of lignin. The neighboring peak attributed to the aromatic stretching of lignin and the absorbance of water by cellulose was also affected by iron oxide. These samples did not experience an initial rise in absorbance as witnessed in the unexposed samples. Instead, peak absorbance decreased gradually, suggesting that lignin was still being lost from the surface. This premise was confirmed by the loss of the pure lignin peak located at 1513 cm^{-1} . A further difference observed in spectra from this treatment was the shape of the peak located at 1280 cm^{-1} . Although this peak was degraded as quickly as in the untreated samples, the peak lacked the shoulder observed on the untreated control.

Samples treated with a yellow iron oxide differed from the red iron oxide in crystal shape while the second red iron oxide differed from the first in particle size (700 nm). Spectra collected from these treatments differed only slightly when compared to the untreated control (Figures 3.13-18). The peak located at 1740 cm^{-1} did not initially increase for either treatment

as was observed in the untreated controls, suggesting that these treatments reduced the amount of carboxylic acid produced in the degradation process or that it was rapidly converted to other degradation products. Deconvolution of the carbonyl peak supported the theory that the production of carboxylic acid was controlled using these treatments. In addition, the yellow iron oxide treatment stabilized the concentration of cellulose on the surface (1716 cm^{-1}), yet both treatments followed the trend observed in the 190 nm red iron oxide treatment, indicating that hemicelluloses were rapidly lost from the surface. These treatments also resulted in the accelerated loss of the pure lignin peak when compared to the untreated controls, suggesting that these treatments offered little protection to the wood. The inability of the yellow iron oxide to protect the wood may be attributed to a crystal shape that may have been less efficient at reflecting solar radiation, while Mie's solution to Maxwell's equation offers an explanation for the poor performance of the large particle size red iron oxide. Mie's solution suggests that spheres with larger particles sizes reflect light less efficiently than smaller spheres, thus allowing more UV radiation to reach the lignin (Levinson et al, 2005a and b). An alternative explanation is that the larger particle size of the second red iron oxide may have prevented penetration into the cell wall were it was needed to protect the polymers.

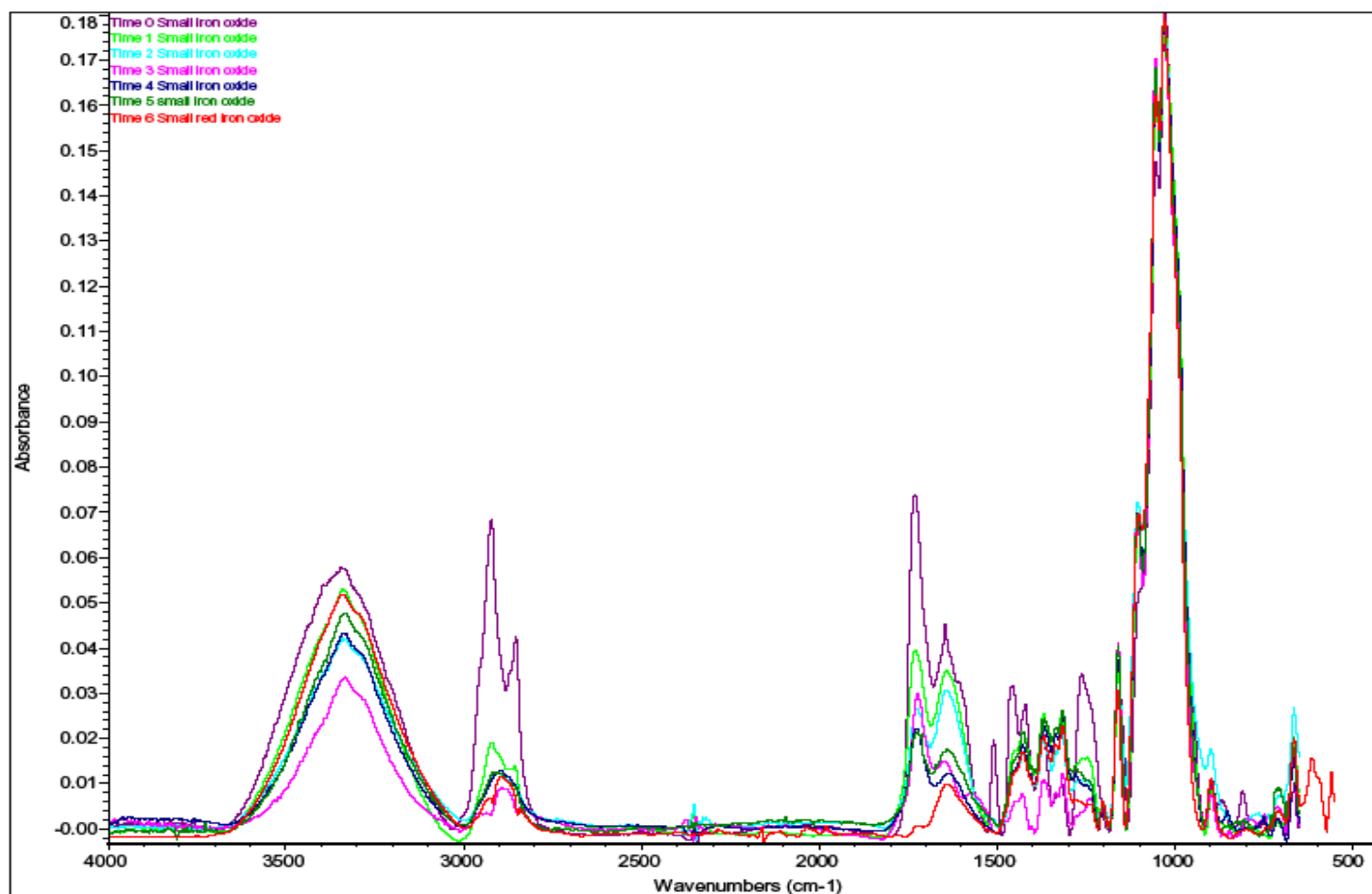


Figure 3.10. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 190 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

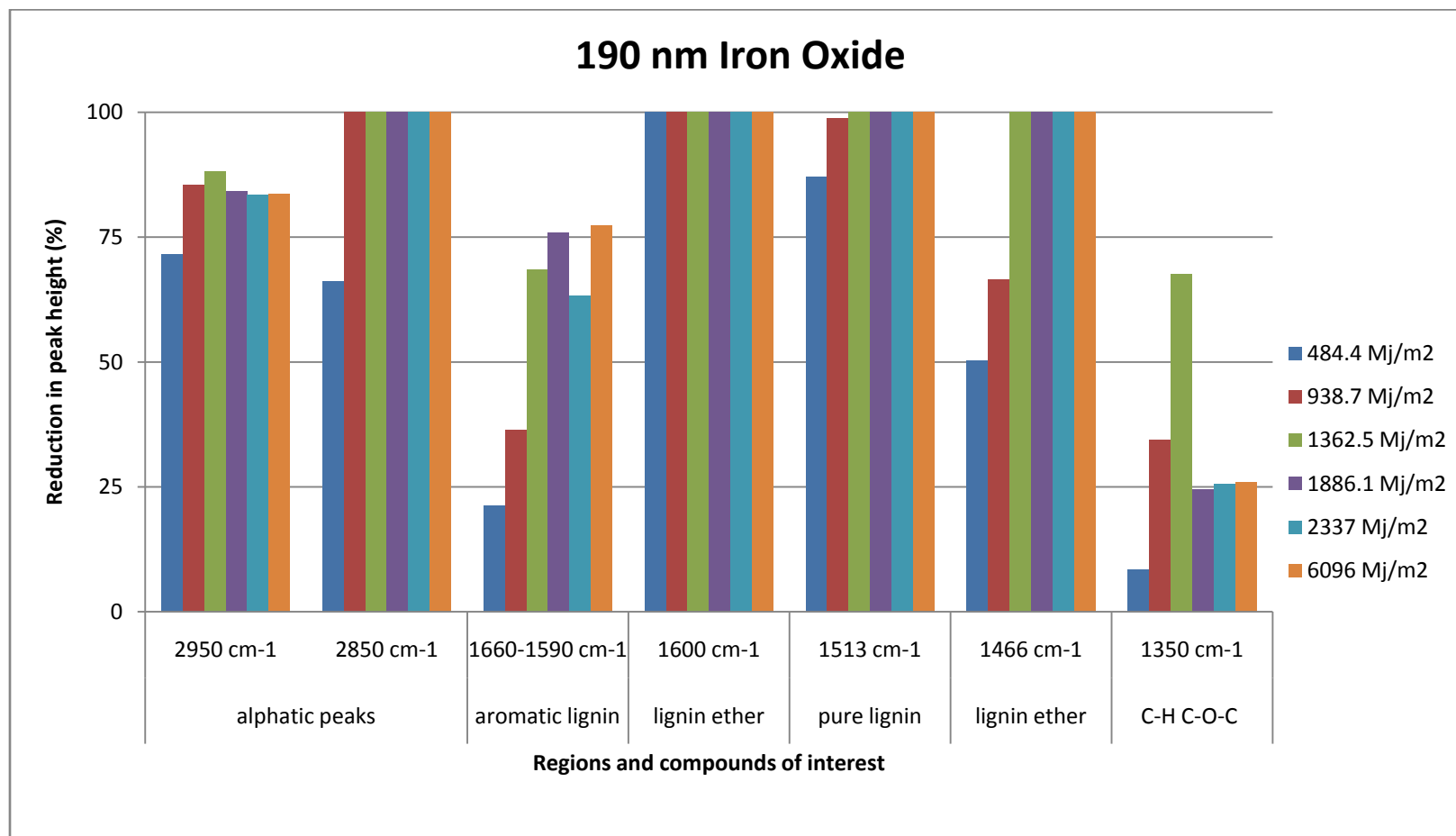


Figure 3.11. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 190 nm red iron oxide particles after being exposed outdoors to irradiation dosage increments of 454 MJ/m².

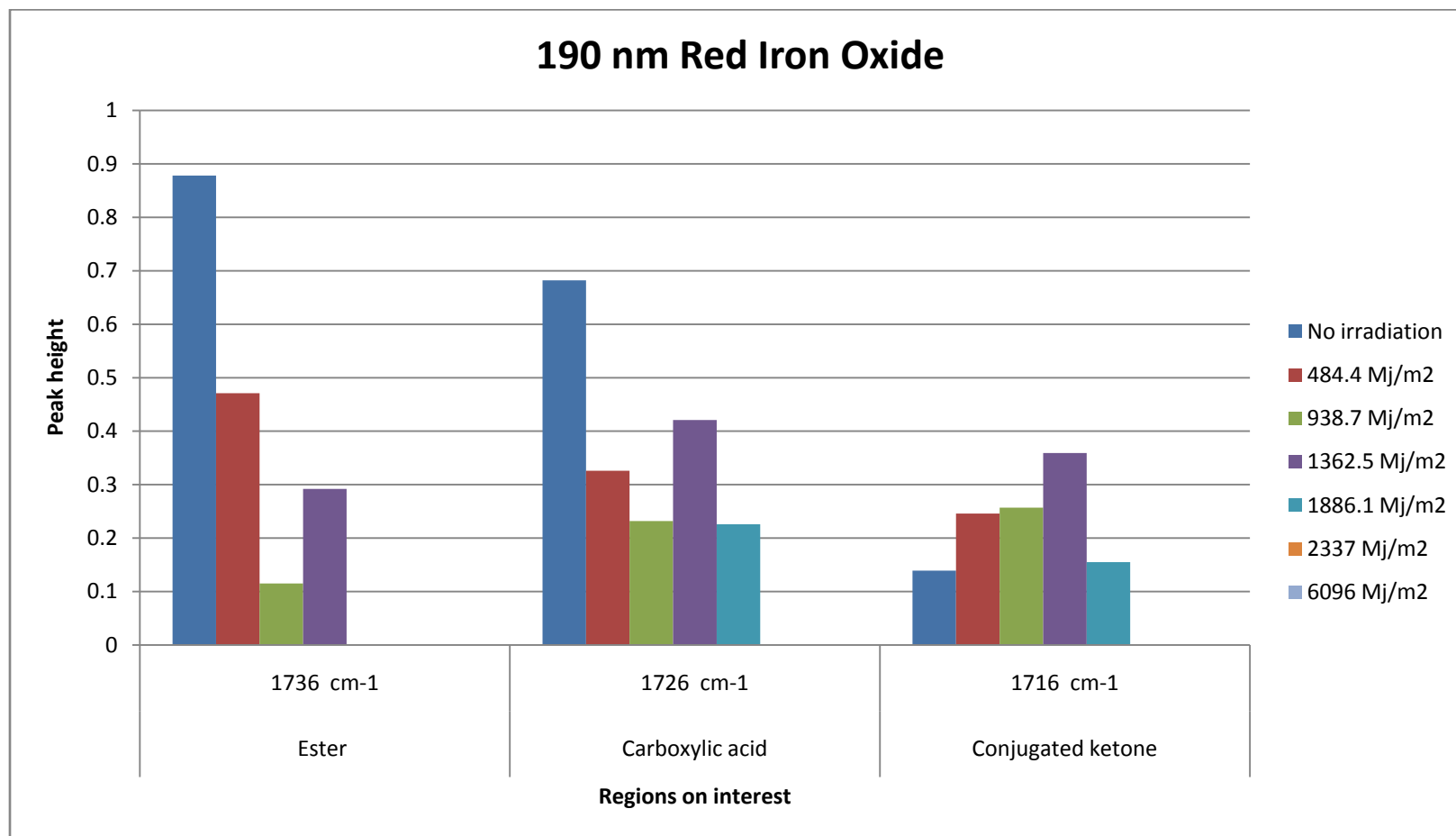


Figure 3.12. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 1000 ppm solution of 190 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

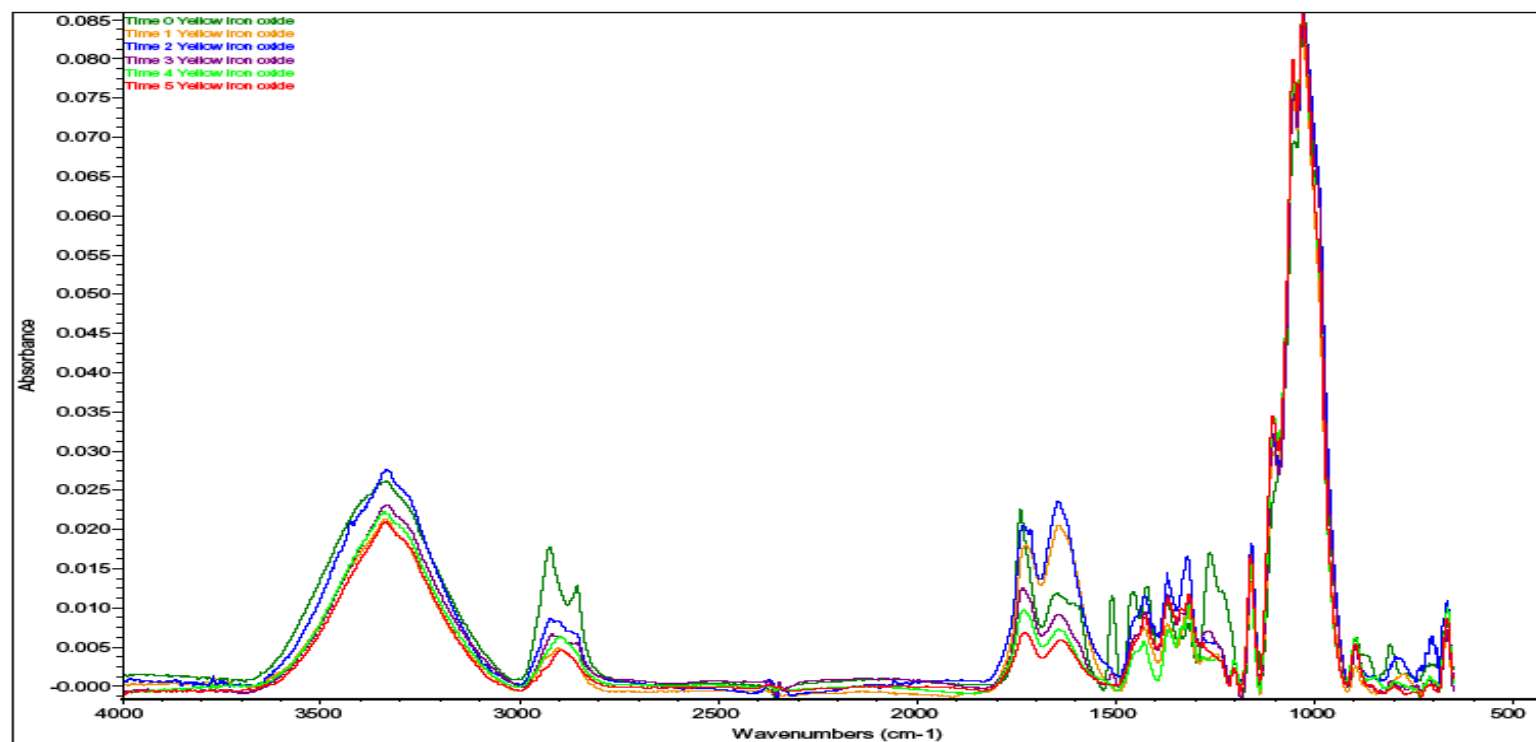


Figure 3.13. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 190 nm yellow iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

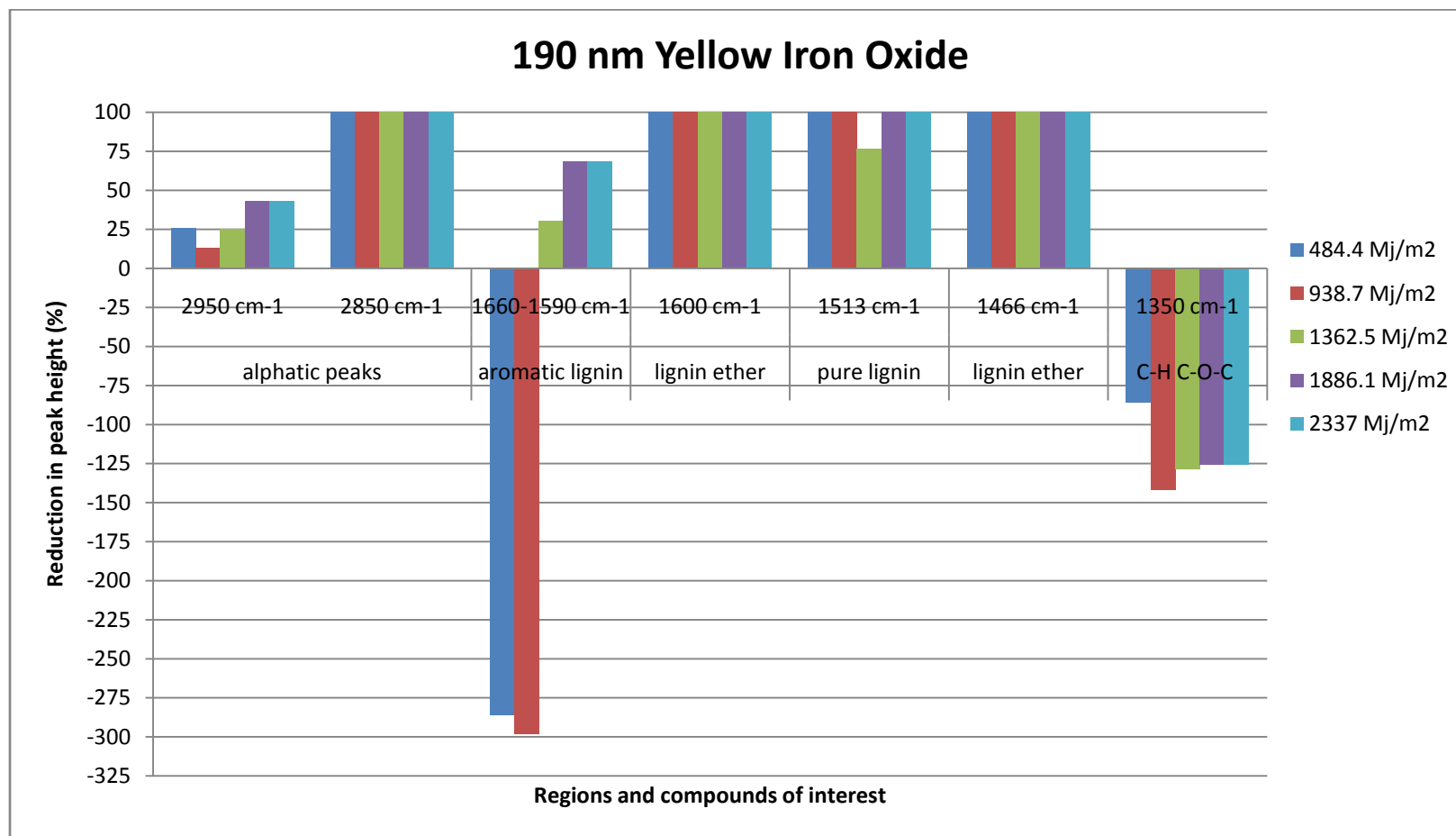


Figure 3.14. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 190 nm yellow iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m².

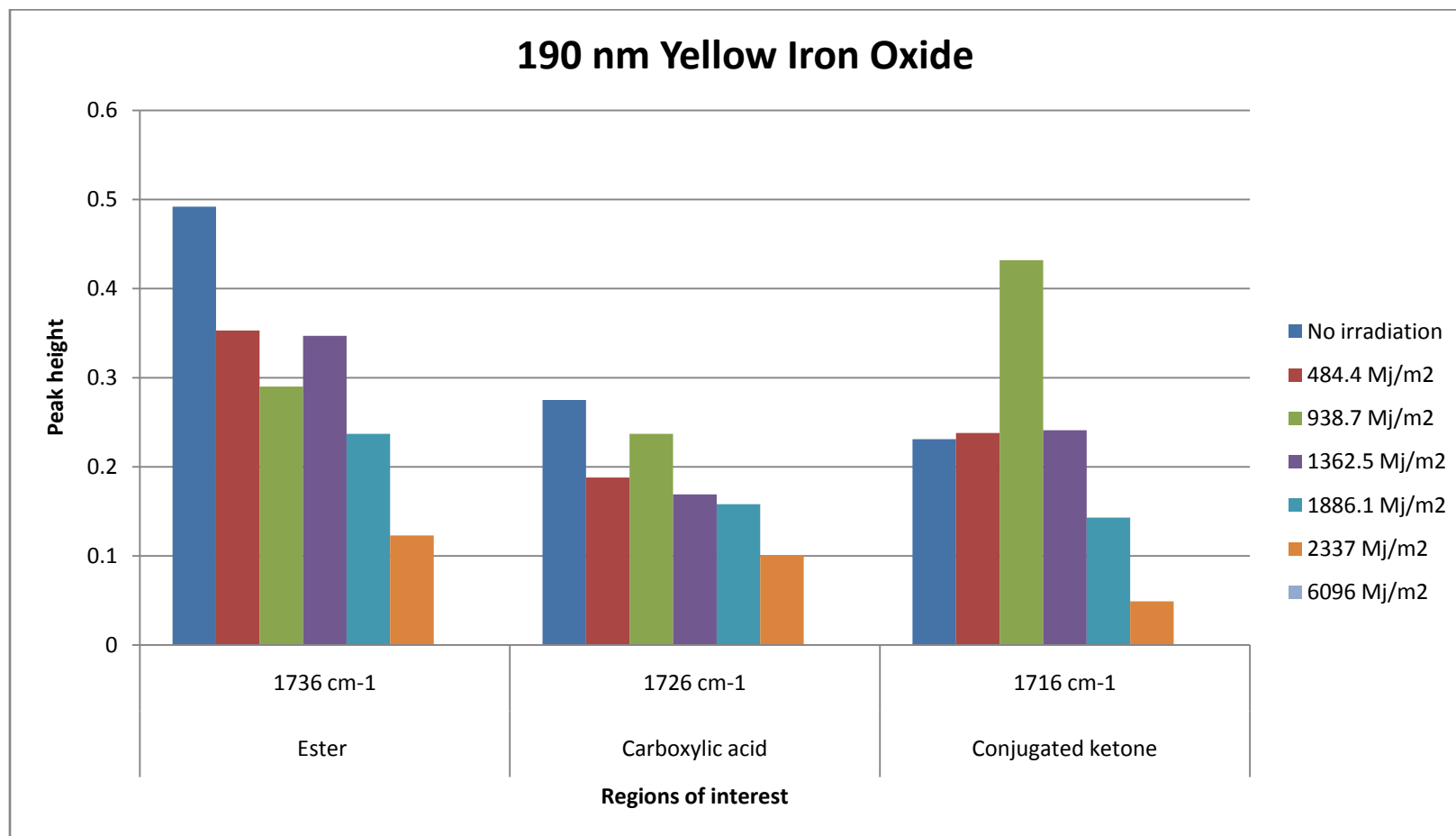


Figure 3.15. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 190 nm yellow iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

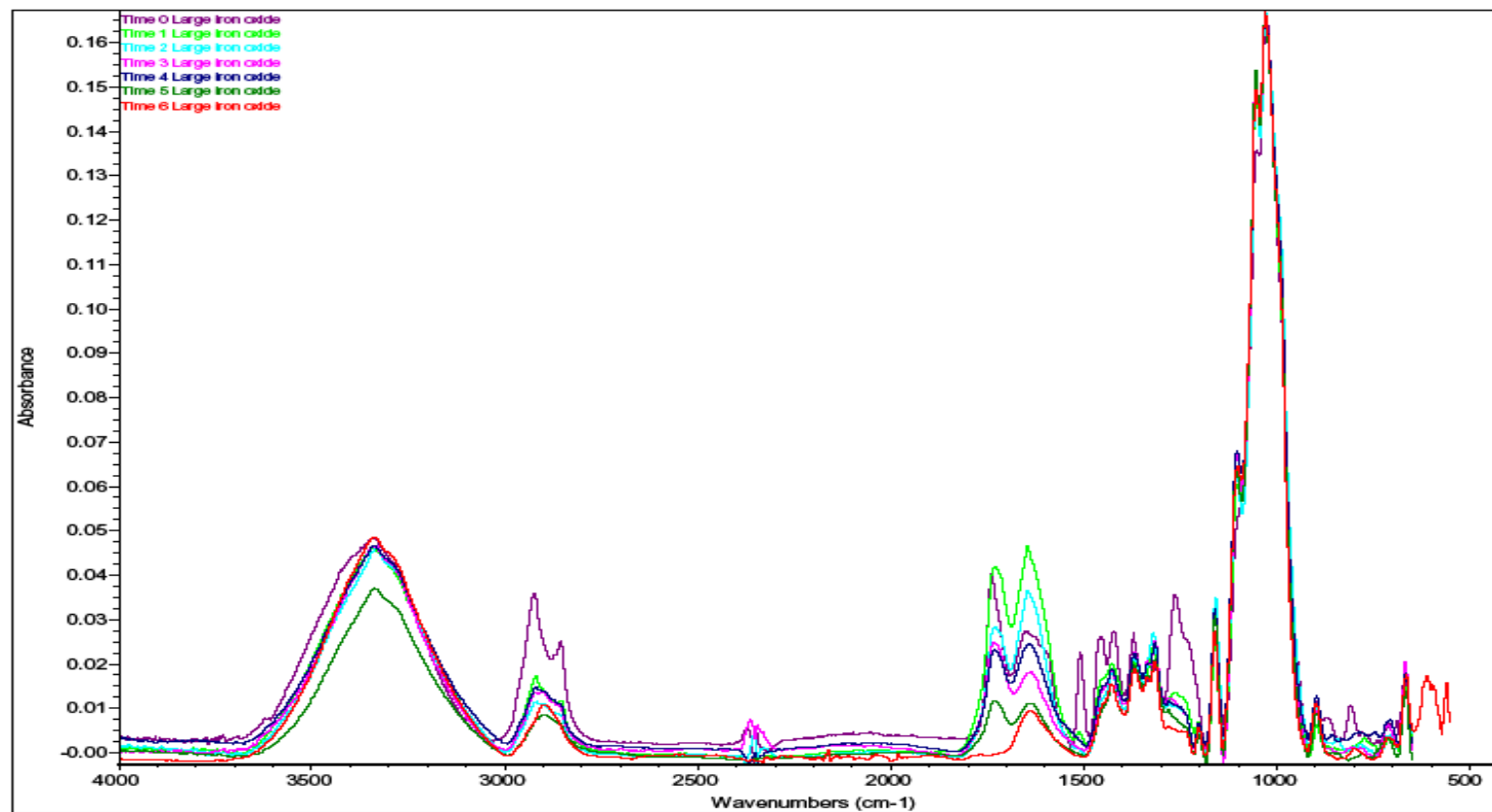


Figure 3.16. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 700 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

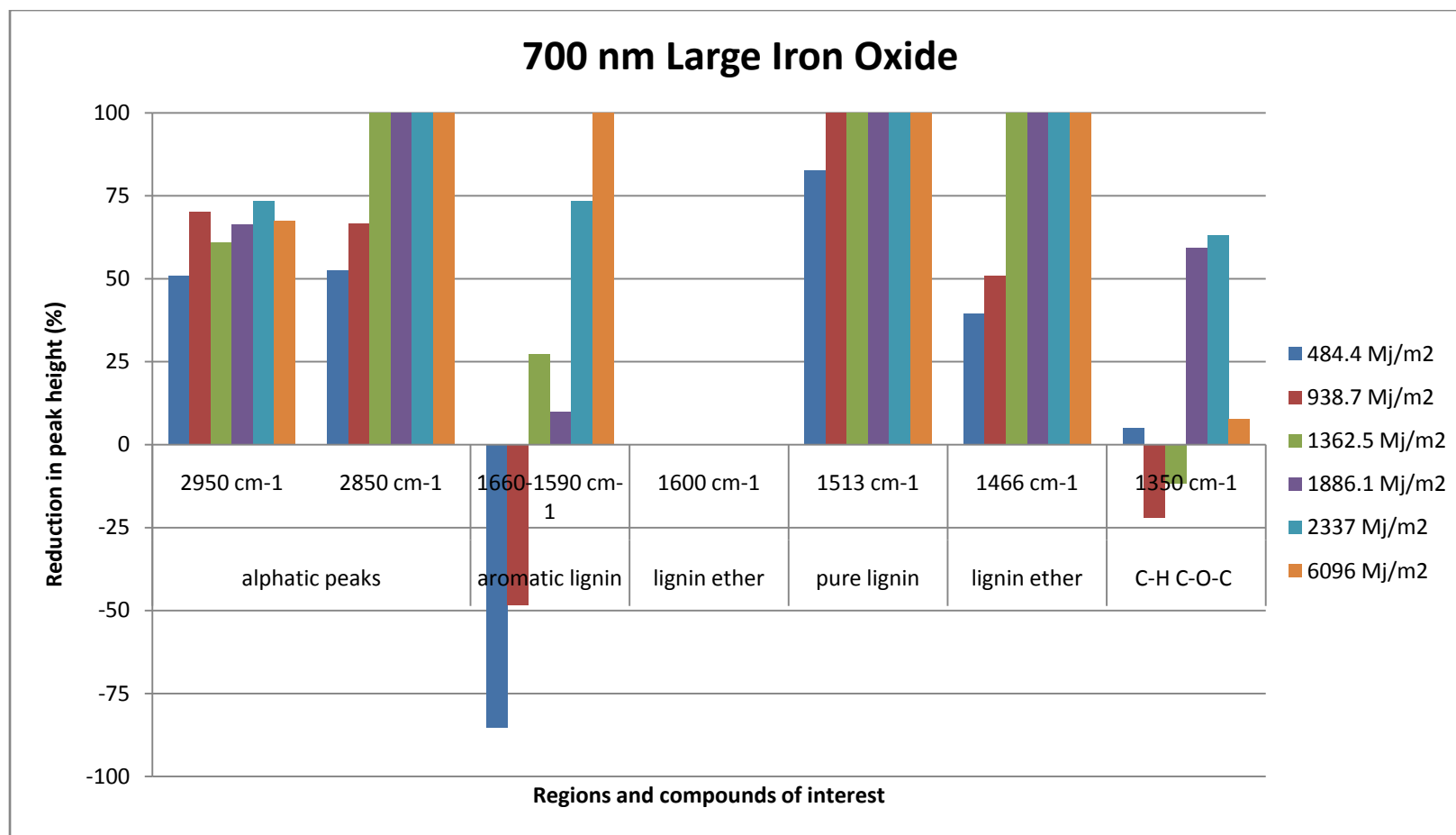


Figure 3.17. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 700 nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m².

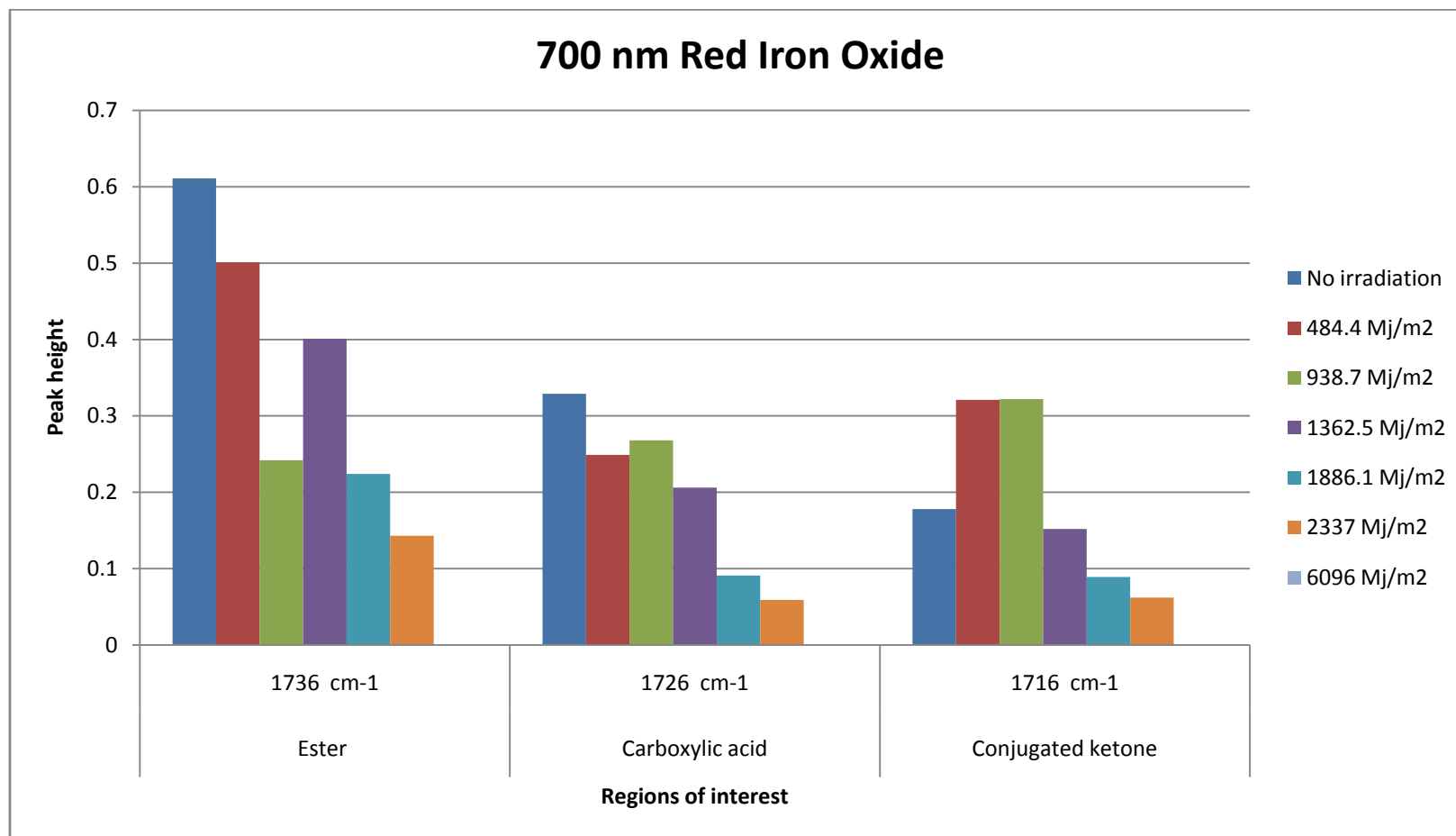


Figure 3.18. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 700nm red iron oxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

FTIR spectra indicated that neither titanium dioxide treatment protected the aliphatic compounds on the surface as evidenced by the loss of the peaks between 3000 and 2800 cm^{-1} (Figures 3.19-23). However, the aliphatic peak reappeared in the 130 nm treatment after one year of exposure, suggesting that these samples were exposed to an environmental contaminant. The spectra generated from these samples were still used for this analysis because the remainder of the peaks fell in line with expectations. The peak located at 1740 cm^{-1} decreased steadily over time, suggesting that the hemicellulose was being removed from the surface, although a small peak was still present in the spectra for samples treated with the 130 nm particle size material. Deconvolution indicated that hemicellulose loss was slowed through the application of titanium dioxide, although deconvolution suggested that the larger particle size material provided longer lasting protection than the smaller particle size material (Figures 3.21 and 3.24). This region of the spectra also suggested that carboxylic acid formation was not altered by the application of titanium dioxide, in contrast to the longevity of the pure lignin peak. Examination of the pure lignin peak located at 1513 cm^{-1} and the surrounding aromatic peaks indicated that compound size affected the ability to protect lignin from degradation. However, the spectral data suggests that smaller particles provided more lignin protection than larger particles, as evidenced by the time required to lose the pure lignin peak, even though both the 130 and 195 nm titanium dioxide particle were small enough to prevent ultraviolet light from reaching the wood surface. Thus the performance differences were most likely due to the ability of the titanium dioxide particle to interact with the polymer.

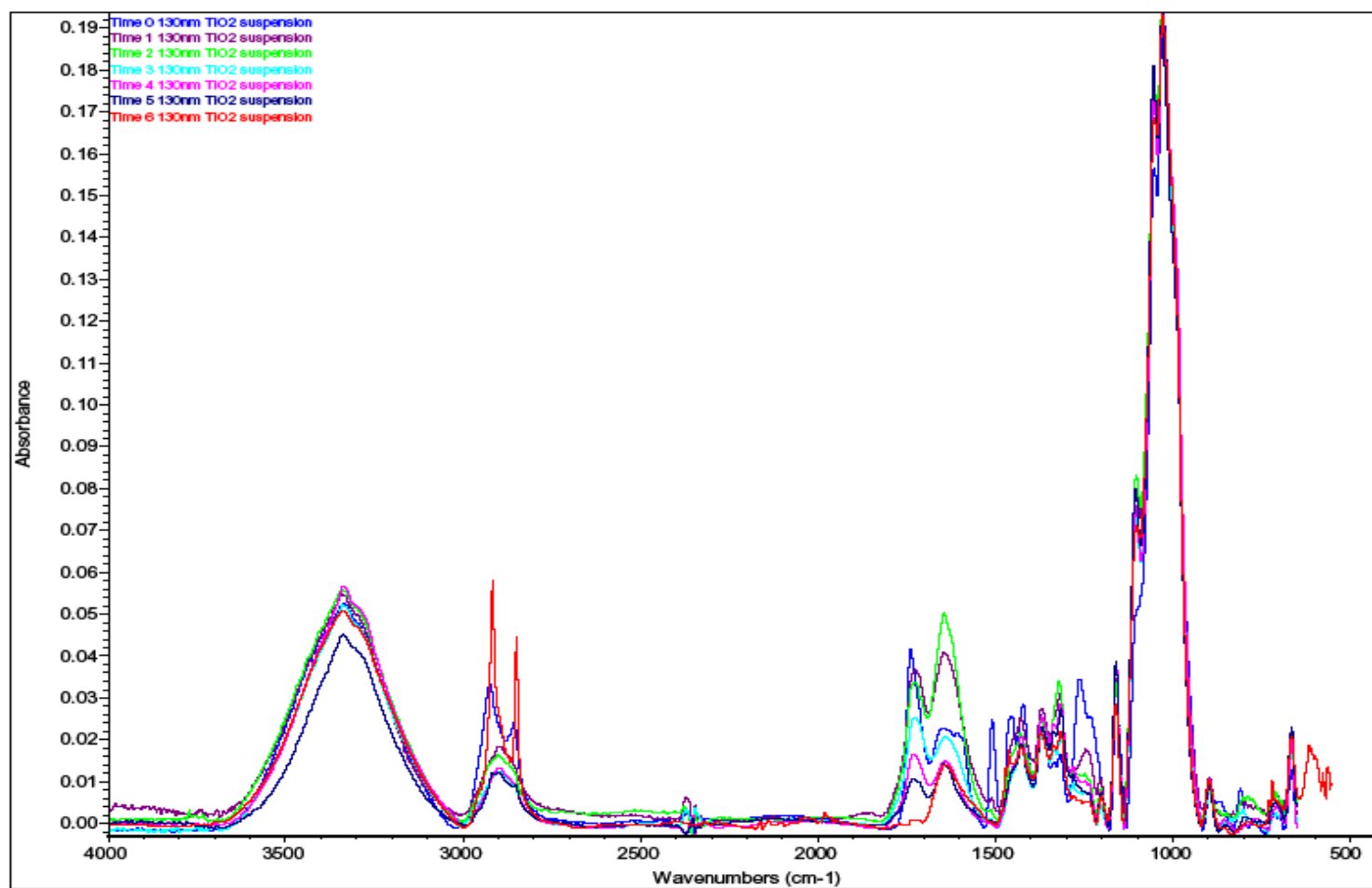


Figure 3.19. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 130 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

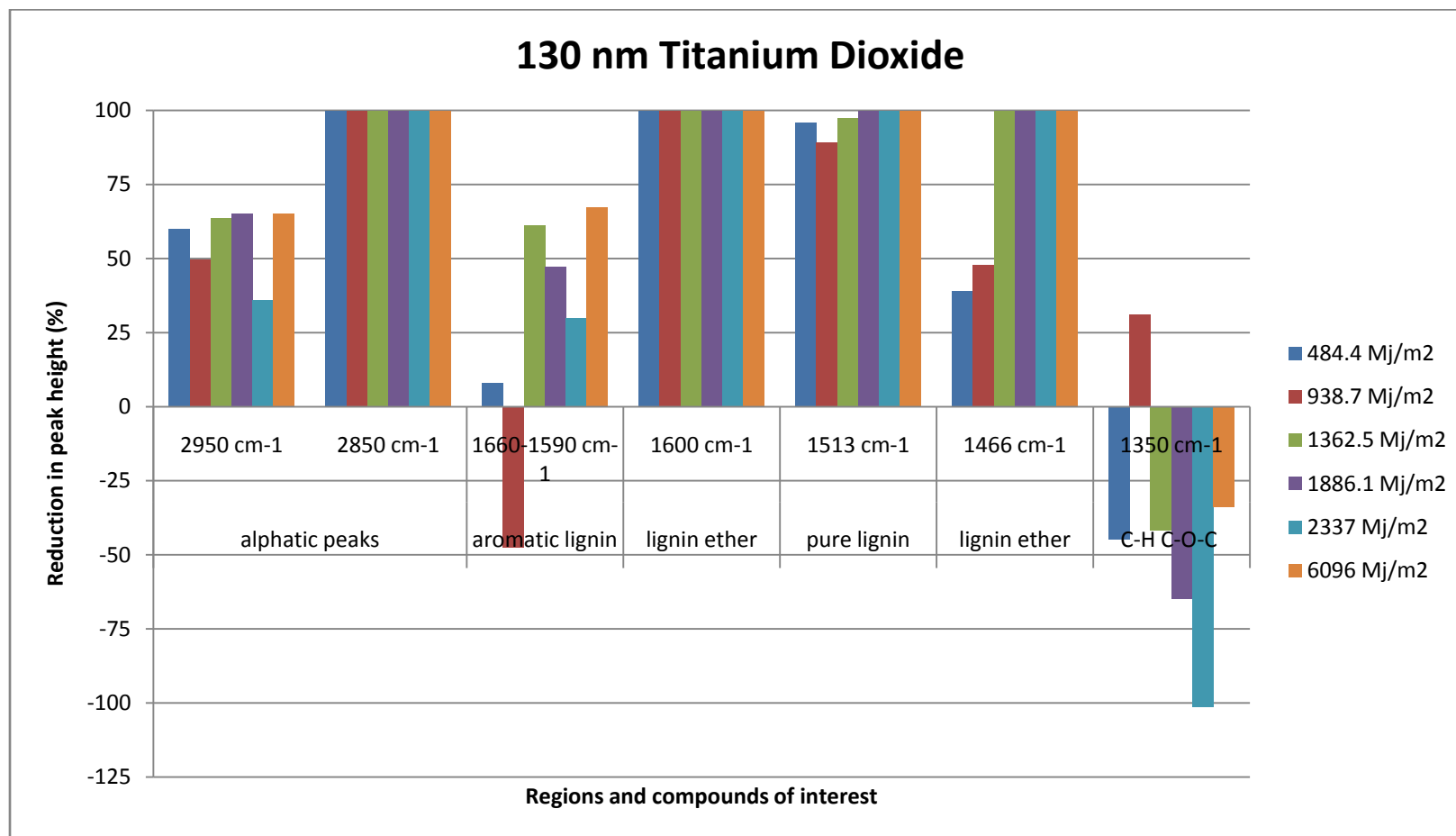


Figure 3.20. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 130 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

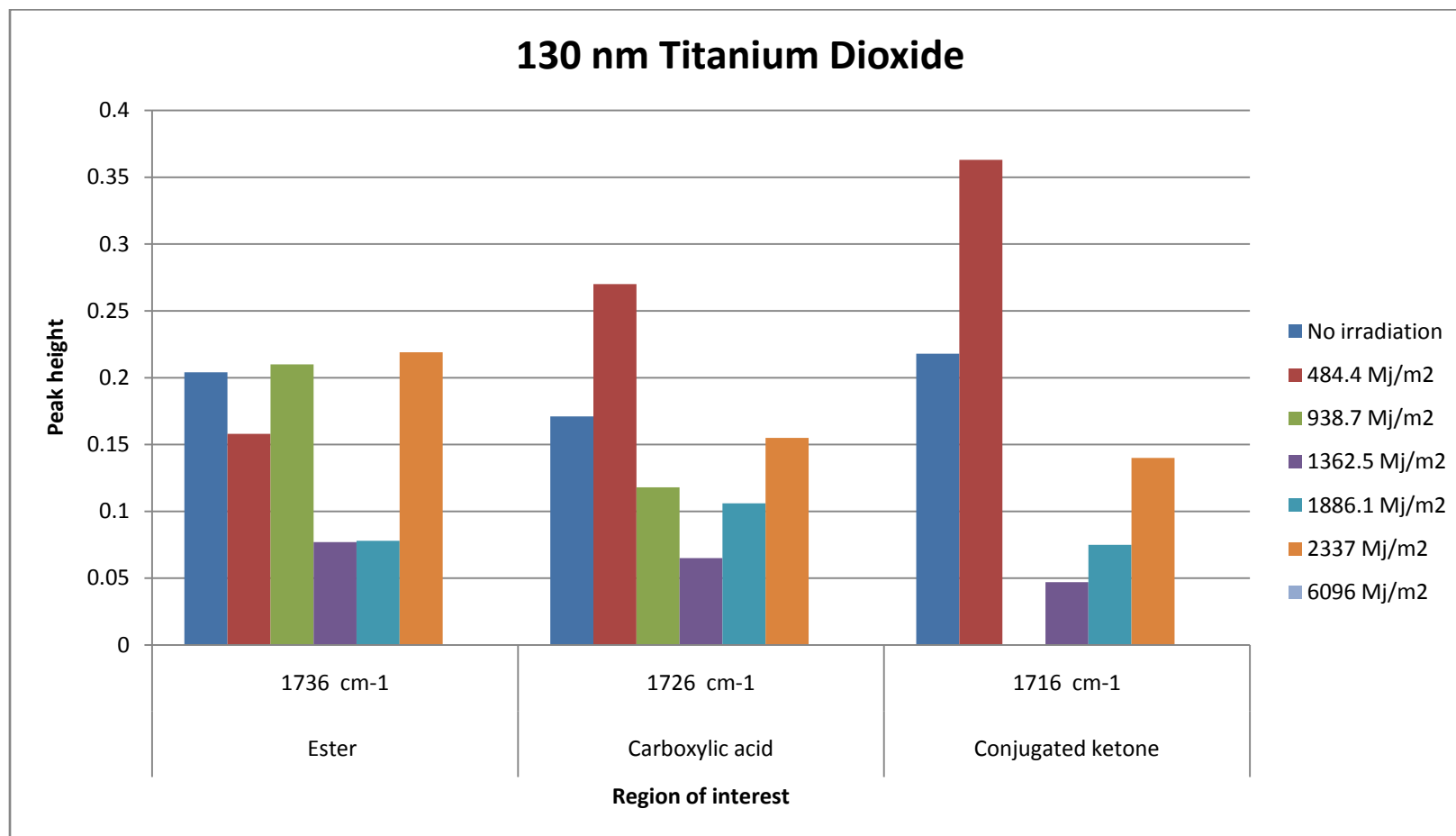


Figure 3.21. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 130 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 Mj/m^2 . Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

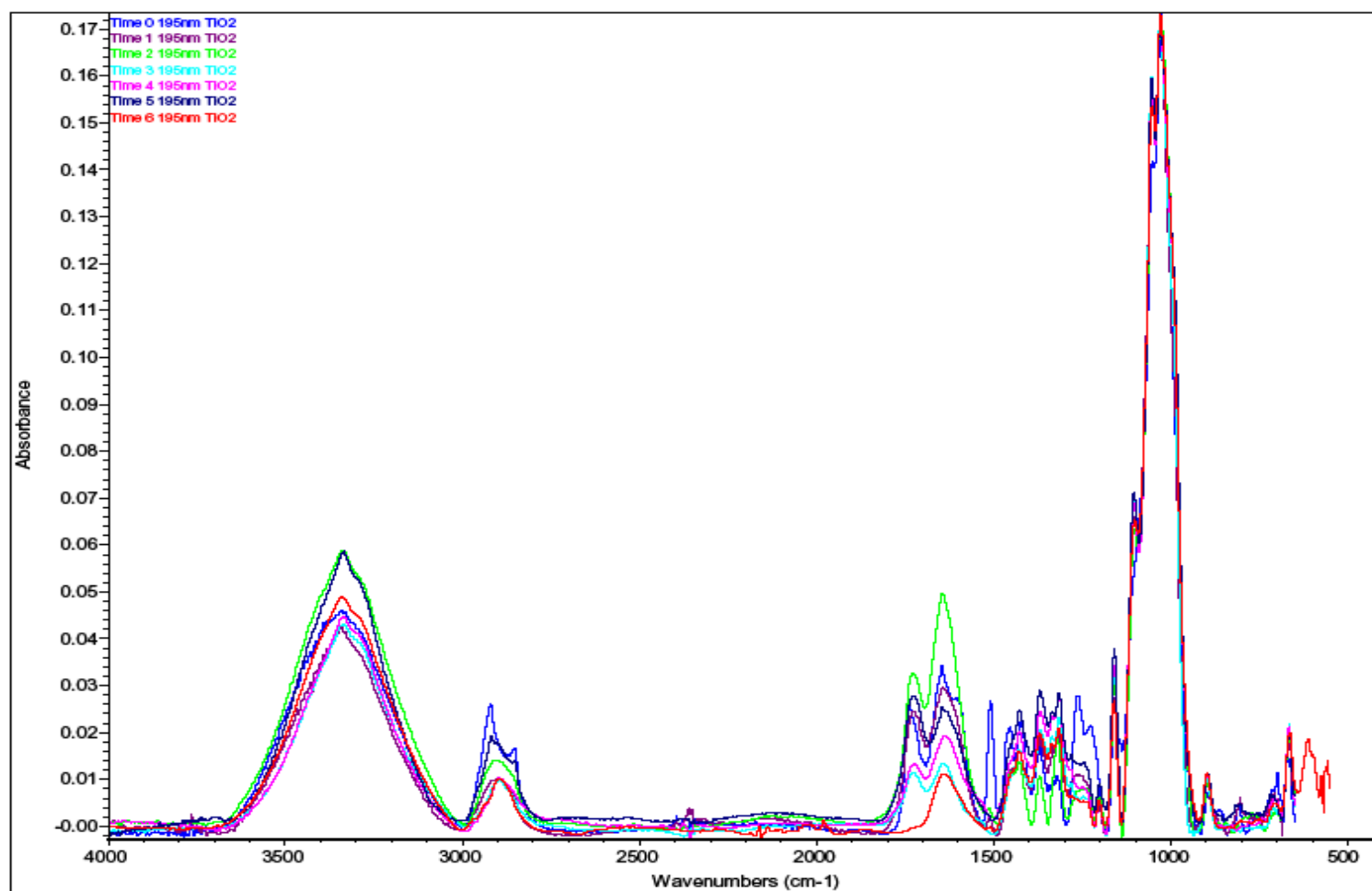


Figure 3.22. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 195 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

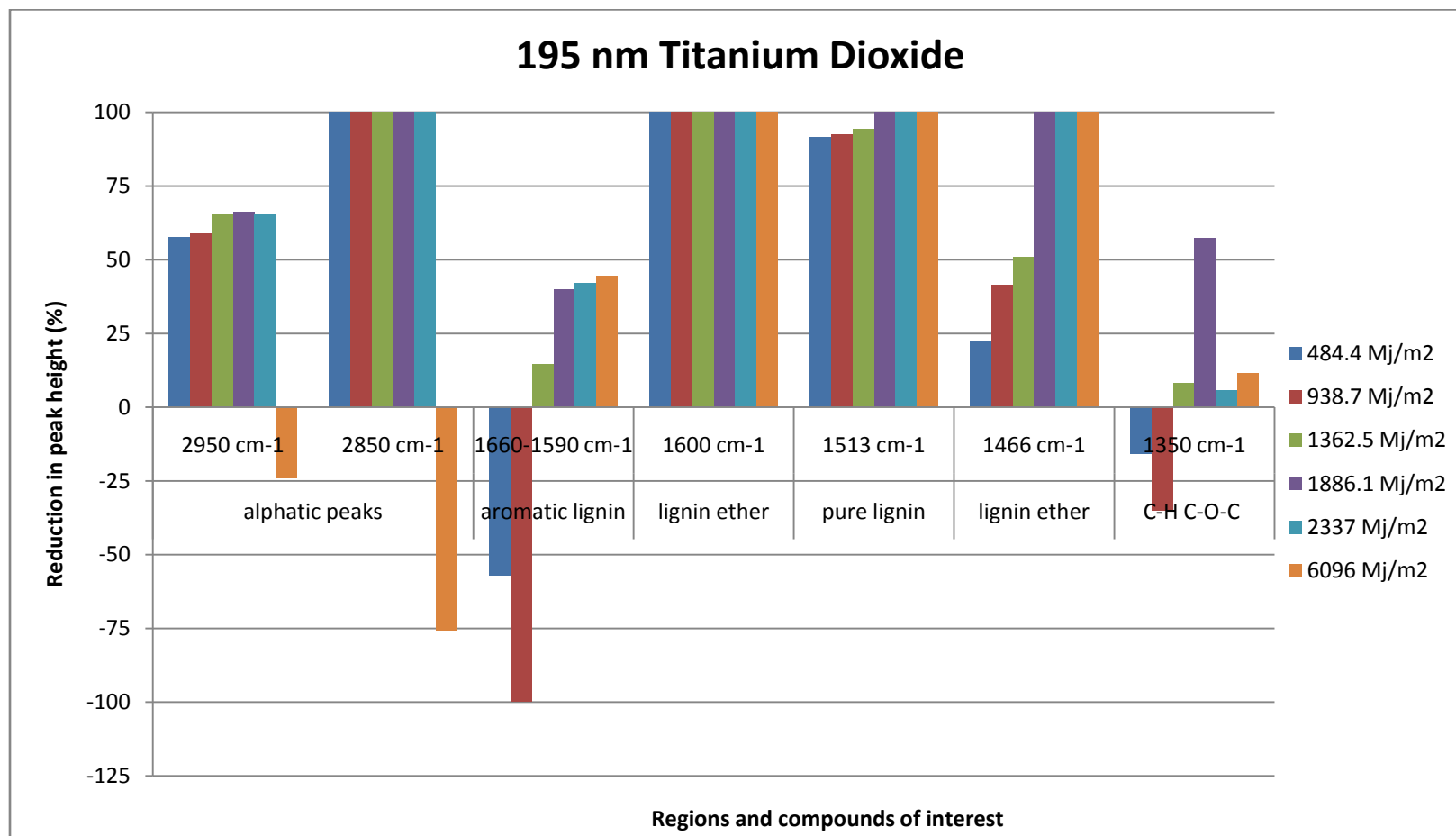


Figure 3.23. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 195 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m².

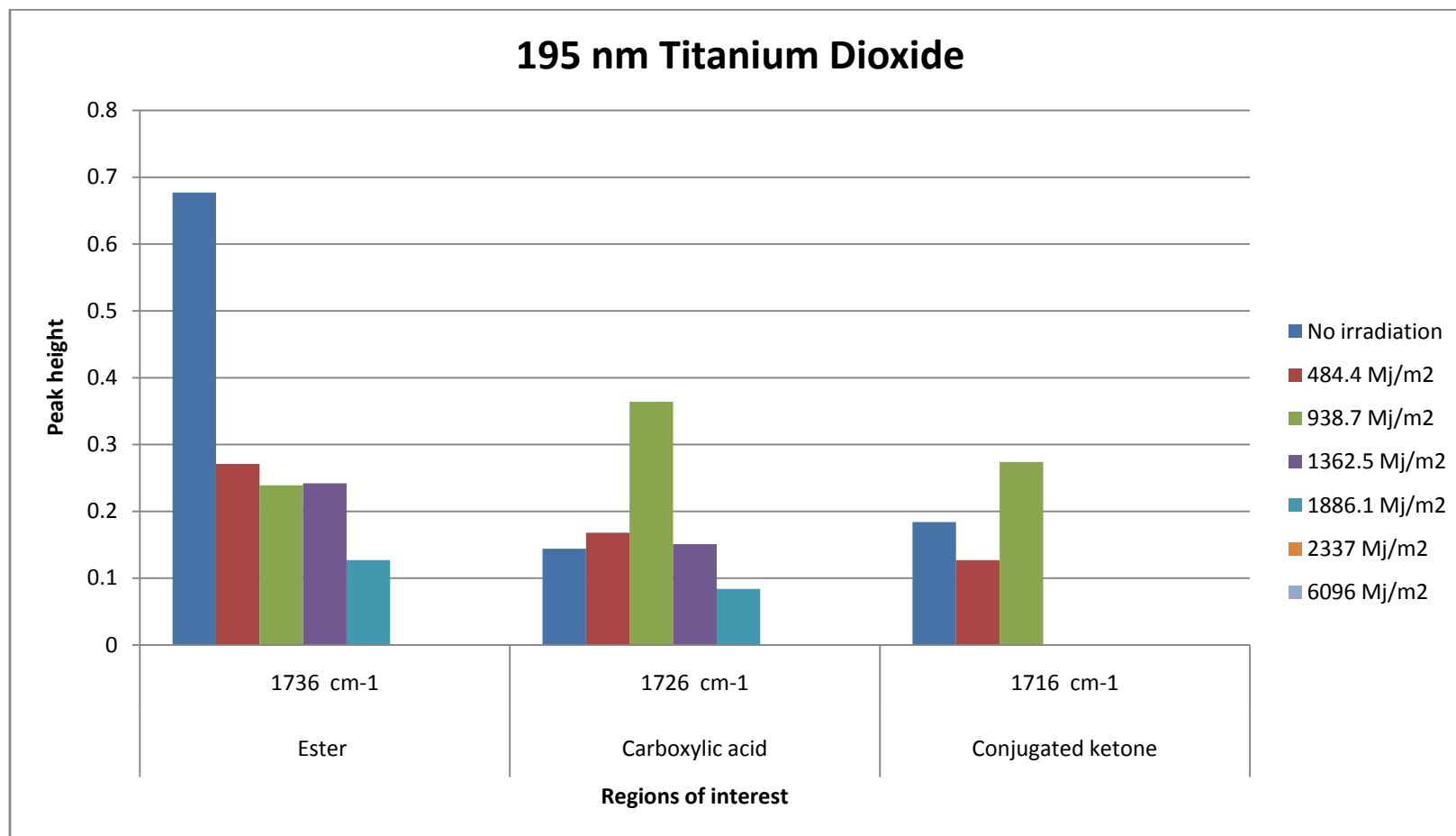


Figure 3.24. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 195 nm titanium dioxide particles and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

Application of wax-based water repellents resulted in a strong increase in the absorption at 3000 to 2800 cm^{-1} prior to exposure (Figures 3.25-33). However, the intensity of the twin peaks located in this range decreased over time, indicating that wood extractives and the water repellents were lost from the surface. In addition, each of the water repellents had a unique affect on the fingerprint region. The application of a wax with a melt point of 34-38 °C resulted in a stronger unconjugated carbonyl peak for the first 1886 Mj/m^2 of exposure followed by a rapid reduction (Figures 3.25 and 3.26). Deconvolution suggested that these changes were caused by the stabilization of the ester and carboxylic acid regions for the first 1363 Mj/m^2 of irradiation (Figure 3.27). This suggested that short chain petroleum-based waxes may have stabilized hemicellulose for a prolonged period of time. The aromatic stretch peak located between 1660 and 1590 cm^{-1} increased more substantially than the untreated control samples after the first and second sampling periods, but the height of the initial peak was similar to the untreated control. This suggests that the application of a wax-based treatment did not slow lignin degradation, but only prevented removal of lignin degradation products from the wood surface. The FTIR data for the pure lignin peak supports the premise that this treatment did not prevent the destruction of the lignin polymer. This observation is also supported by a secondary aromatic peak located at 1450 cm^{-1} , which declined at a much slower rate in the samples treated with the wax than in the untreated controls. These results indicate that the wax prevented removal of lignin degradation products from the wood surface by preventing water ingress.

Spectra from samples treated with a wax-based water repellent with a melt point of 54 to 58 °C, showed losses in absorption of the aliphatic region over the one year exposure period, suggesting that a majority of this treatment was lost from the surface of the samples due to erosion and water solubility (Figures 3.28 and 3.29). However, the finger print region indicated that this treatment offered more protection than the lower melting point wax. Although the height of the unconjugated carbonyl peak was reduced by half after the first

487 Mj/m^2 of irradiation, the peak was not completely lost over the one year exposure period. Deconvolution of this region suggested that the large drop experienced early on was due to the loss of esters, possibly imparted onto the samples by the treatment, while the treatment controlled the production of carboxylic acid during the remainder of the exposure period, suggesting that this compound may have provided protection to the lignin (Figure 3.30). Similarly, the pure lignin peak and the aromatic stretch peak located at 1450 cm^{-1} degraded at slower rates than in the untreated controls suggesting that this wax offered more weathering protection than the lower melt point wax. Increasing the melt point of the wax further to $65.5\text{--}75\text{ }^{\circ}\text{C}$ did not improve wood protection, but this wax was less sensitive to loss from the samples (Figures 3.31 and 3.32). FTIR spectral analysis suggested that this higher melt point wax also provided some protection to the hemicellulose since the unconjugated carbonyl peak was still visible after one year of exposure. Deconvolution indicated that, while ester concentration declined quickly it was never lost completely from the surface. The treatment also controlled the amount of carboxylic acid produced (Figure 3.33). However, this treatment did not prevent lignin degradation and loss from the wood surface. This was evident through the rapid loss of the peak at 1513 cm^{-1} and the loss of the aromatic stretching peaks after a large initial increase in absorption in the peak located between 1660 and 1590 cm^{-1} . These results suggest that, although the waxes were included as water repellents, wax chain length also influenced how the wax interacted with and protected the cell wall polymers.

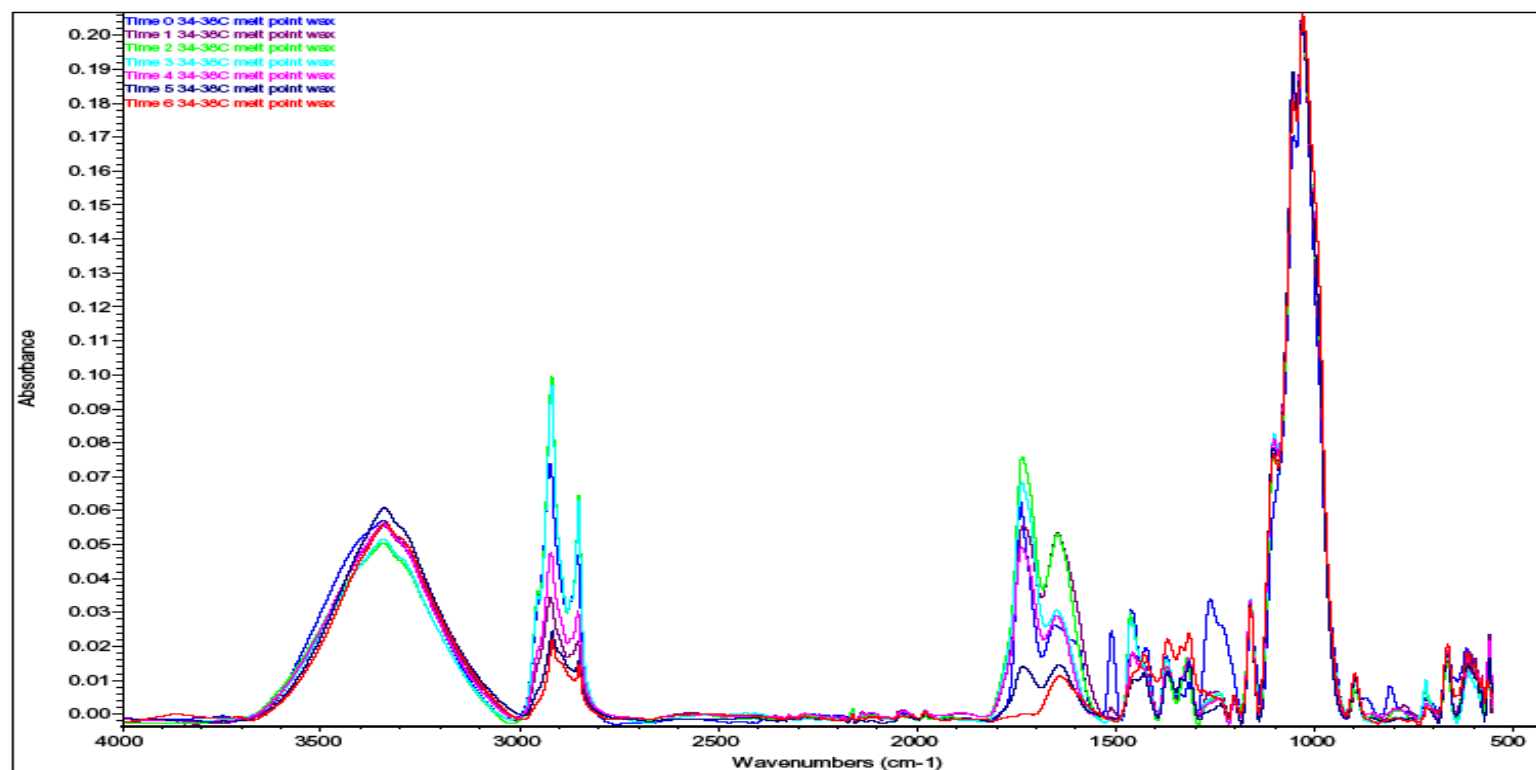


Figure 3.25. FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C. Spectra were collected after the samples had been exposed outdoors to 6 irradiation dosage increments of 454 MJ/m².

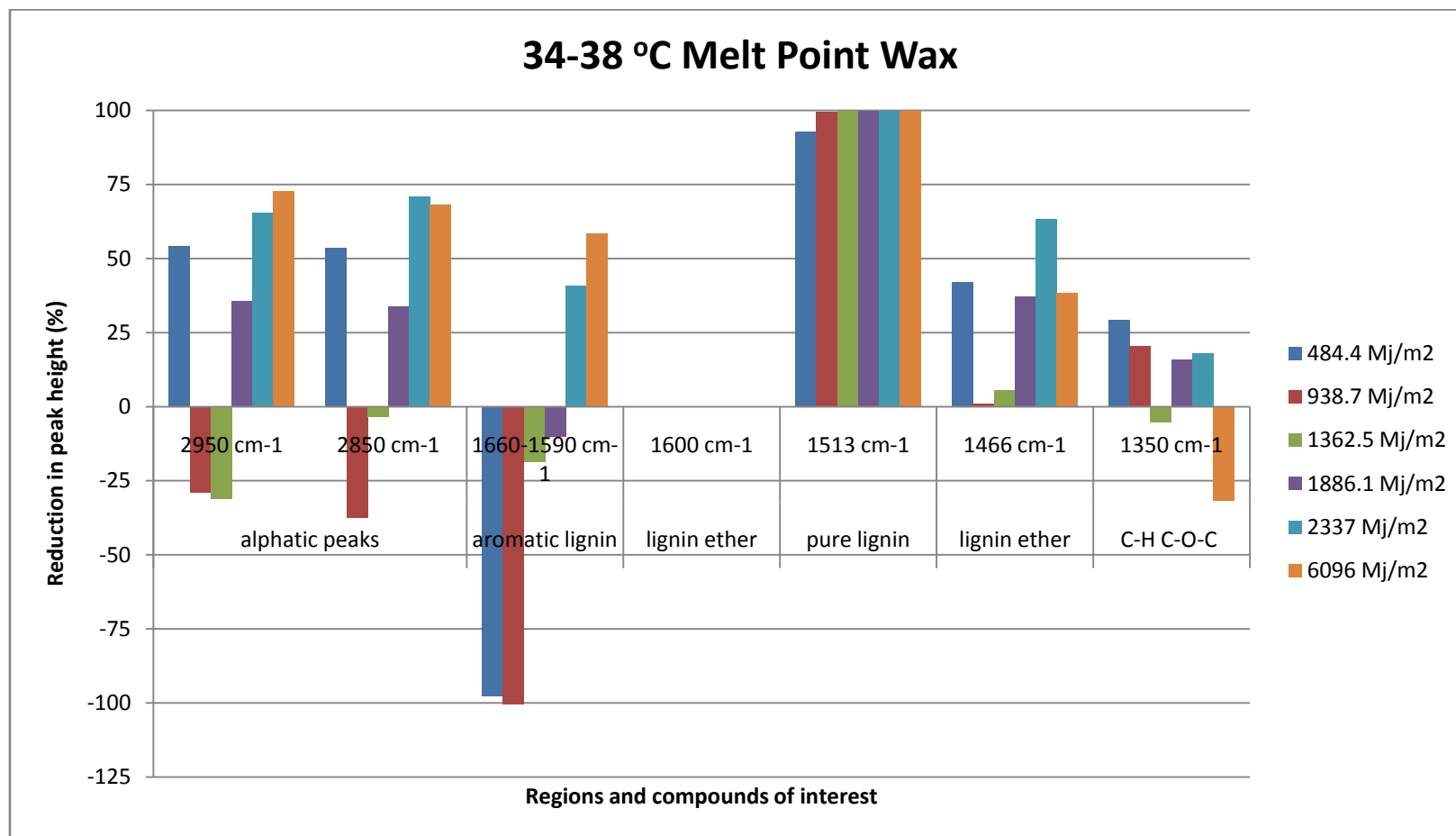


Figure 3.26. Reduction in FTIR peak intensity from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosage increments of 454 Mj/m².

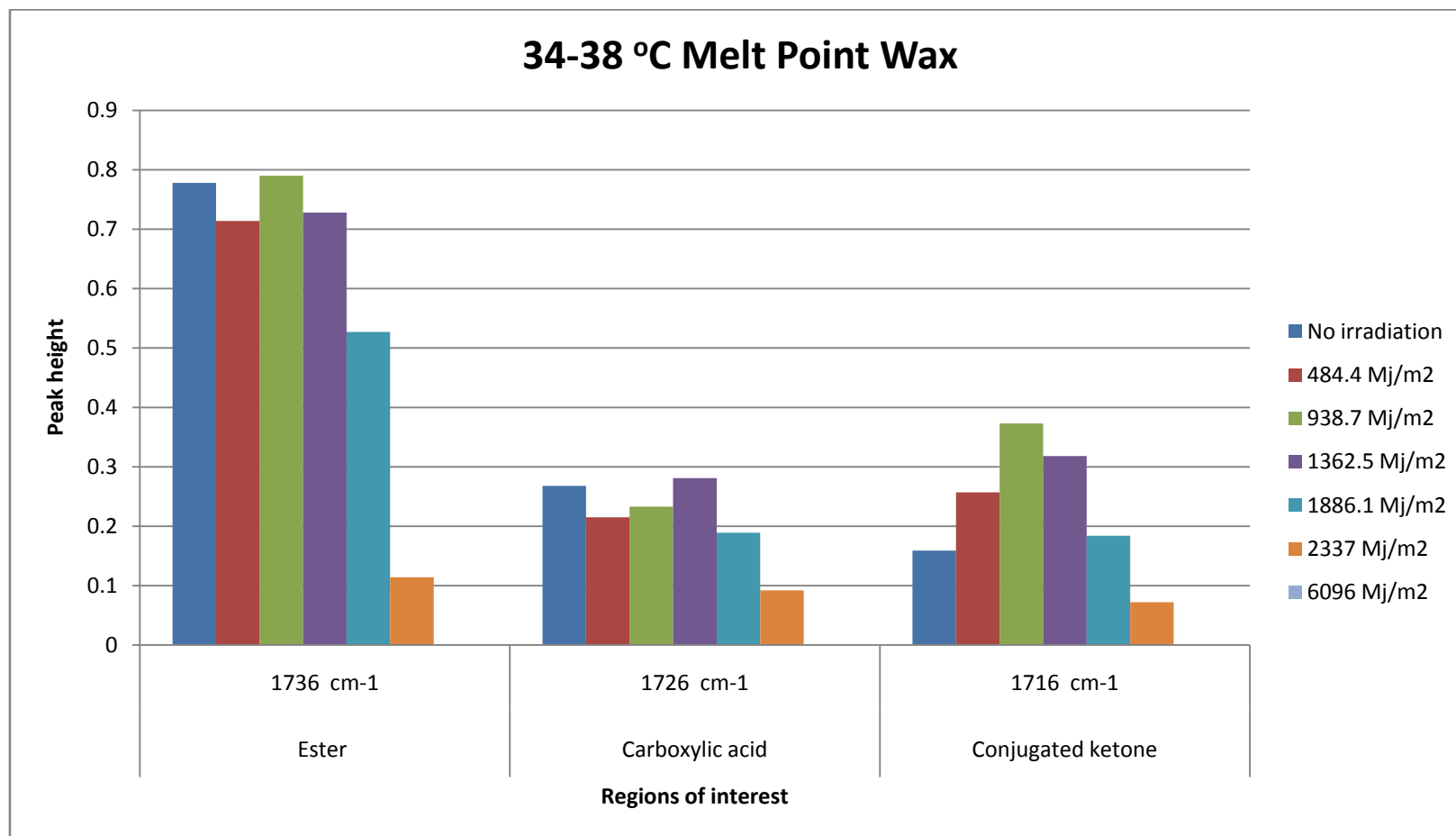


Figure 3.27. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

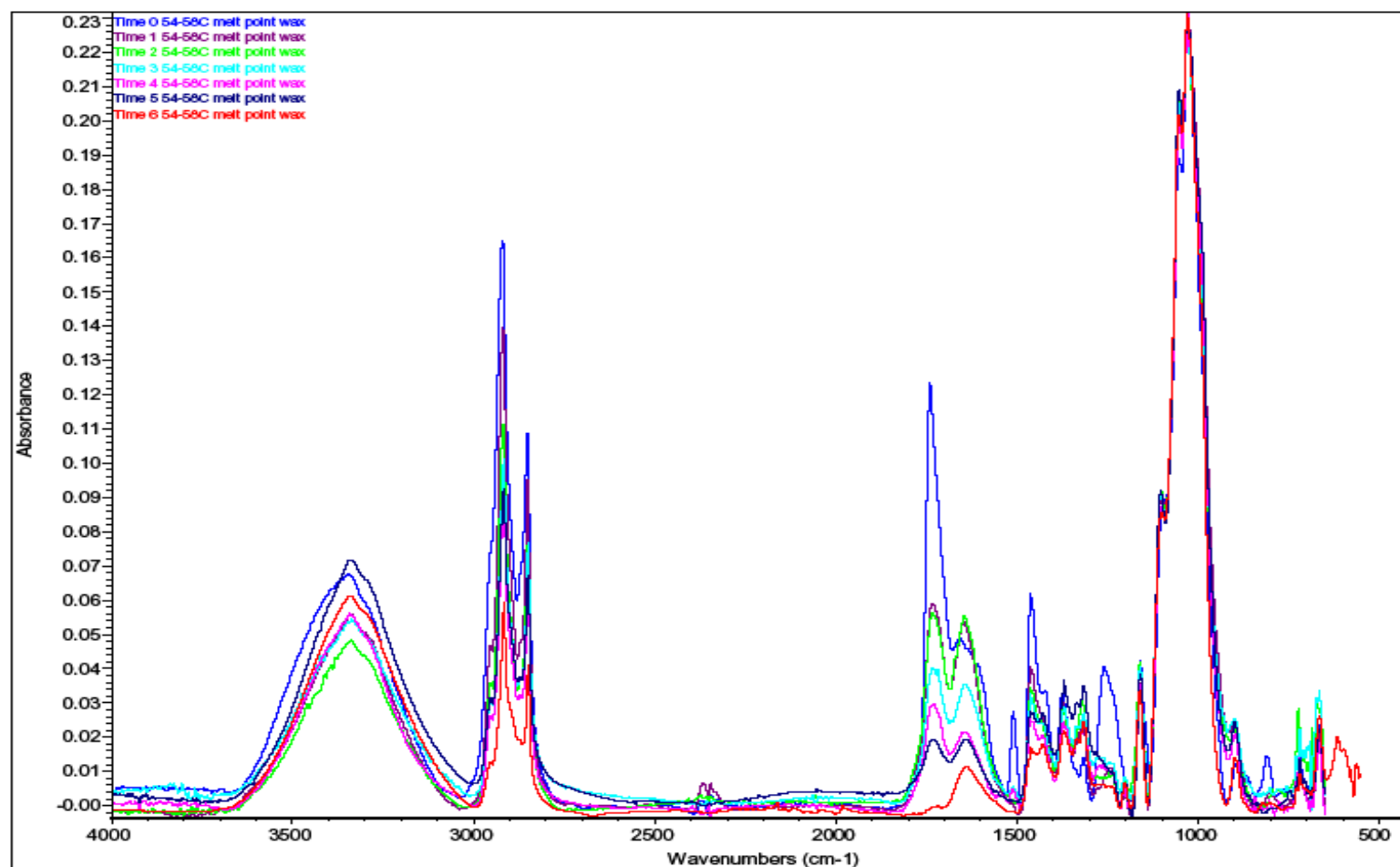


Figure 3.28. FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C. Spectra were collected after the samples had been exposed outdoors to 6 irradiation dosage increments of 454 MJ/m².

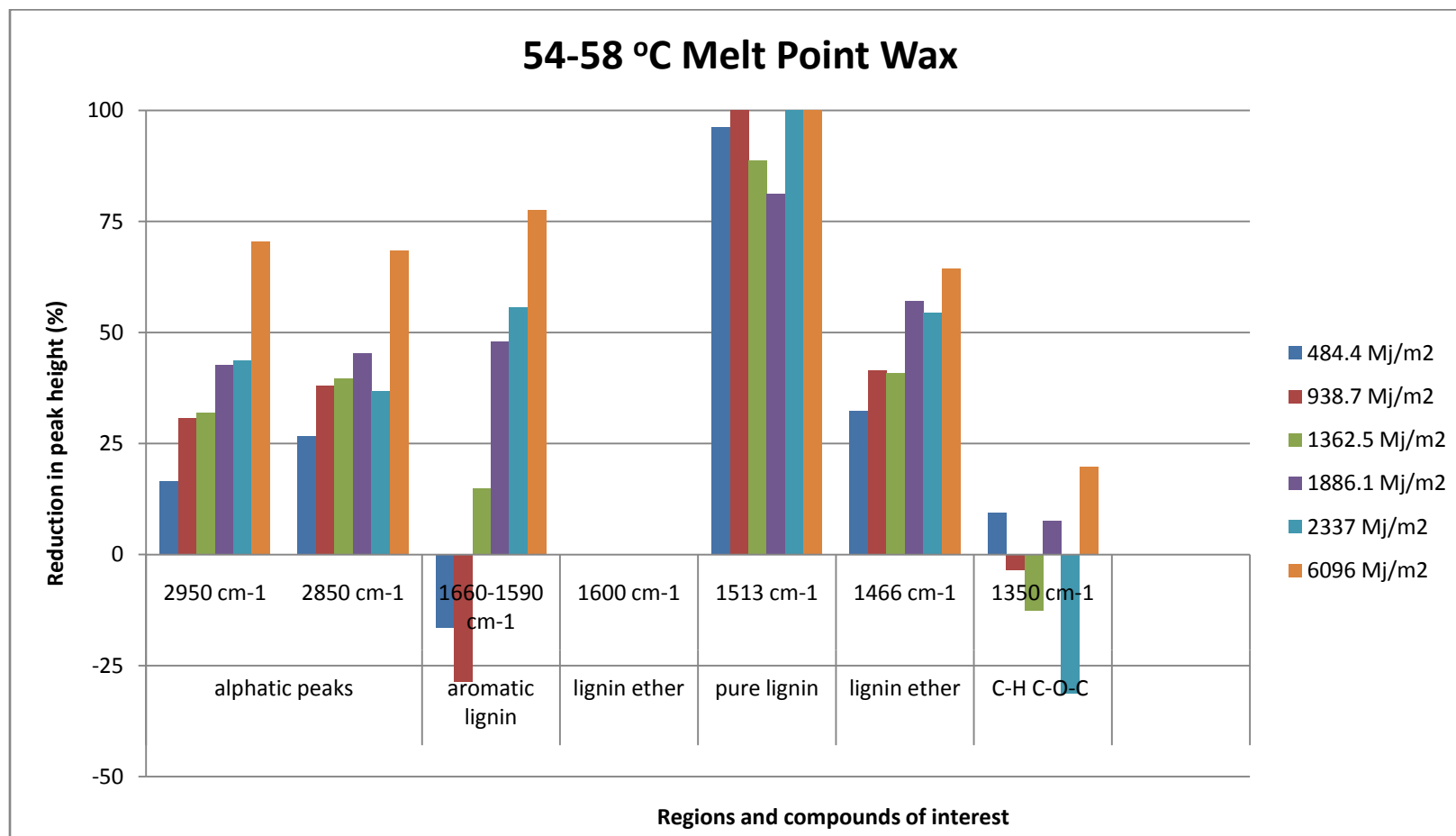


Figure 3.29. Reduction in FTIR peak intensity from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m².

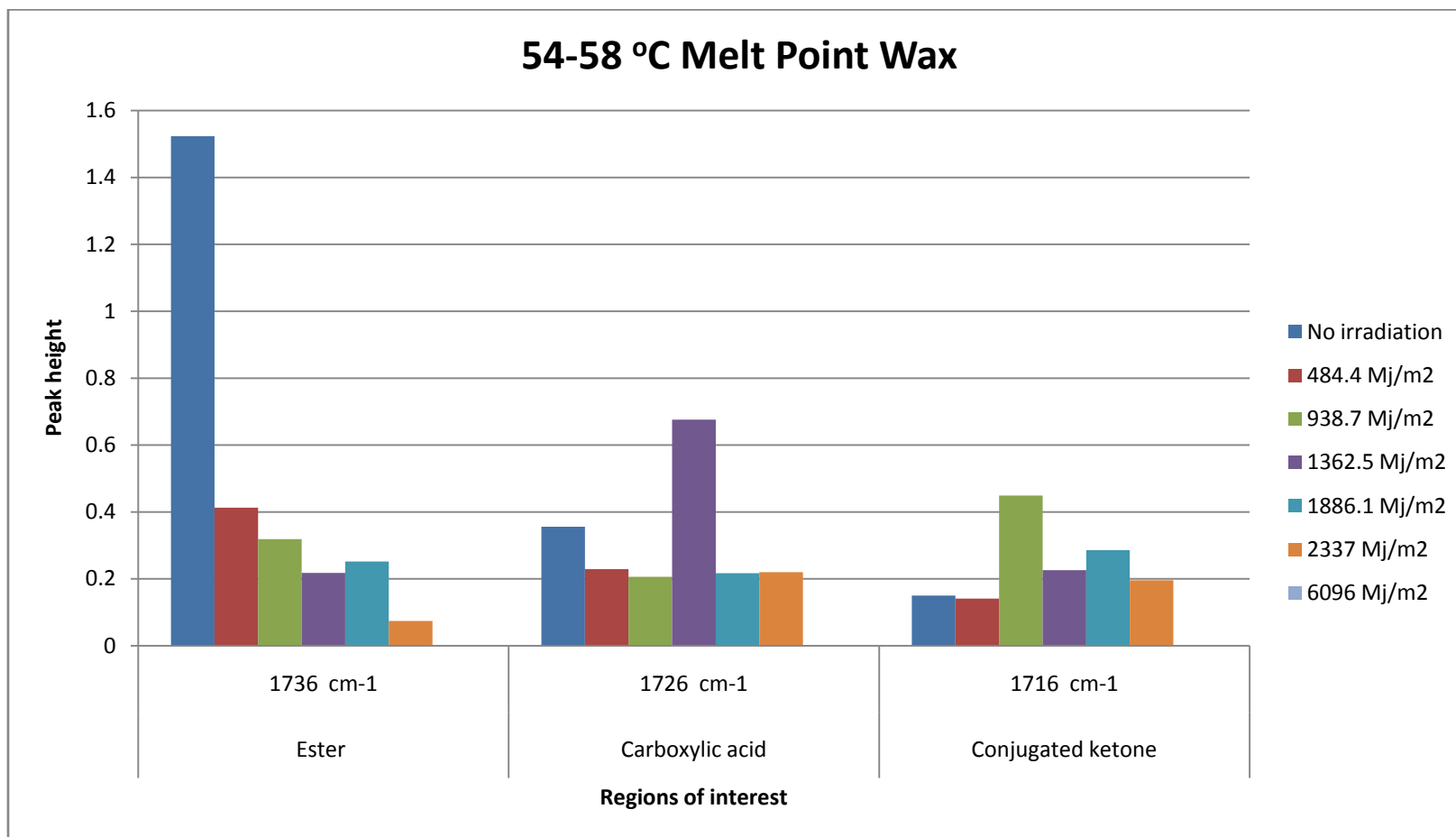


Figure 3.30. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

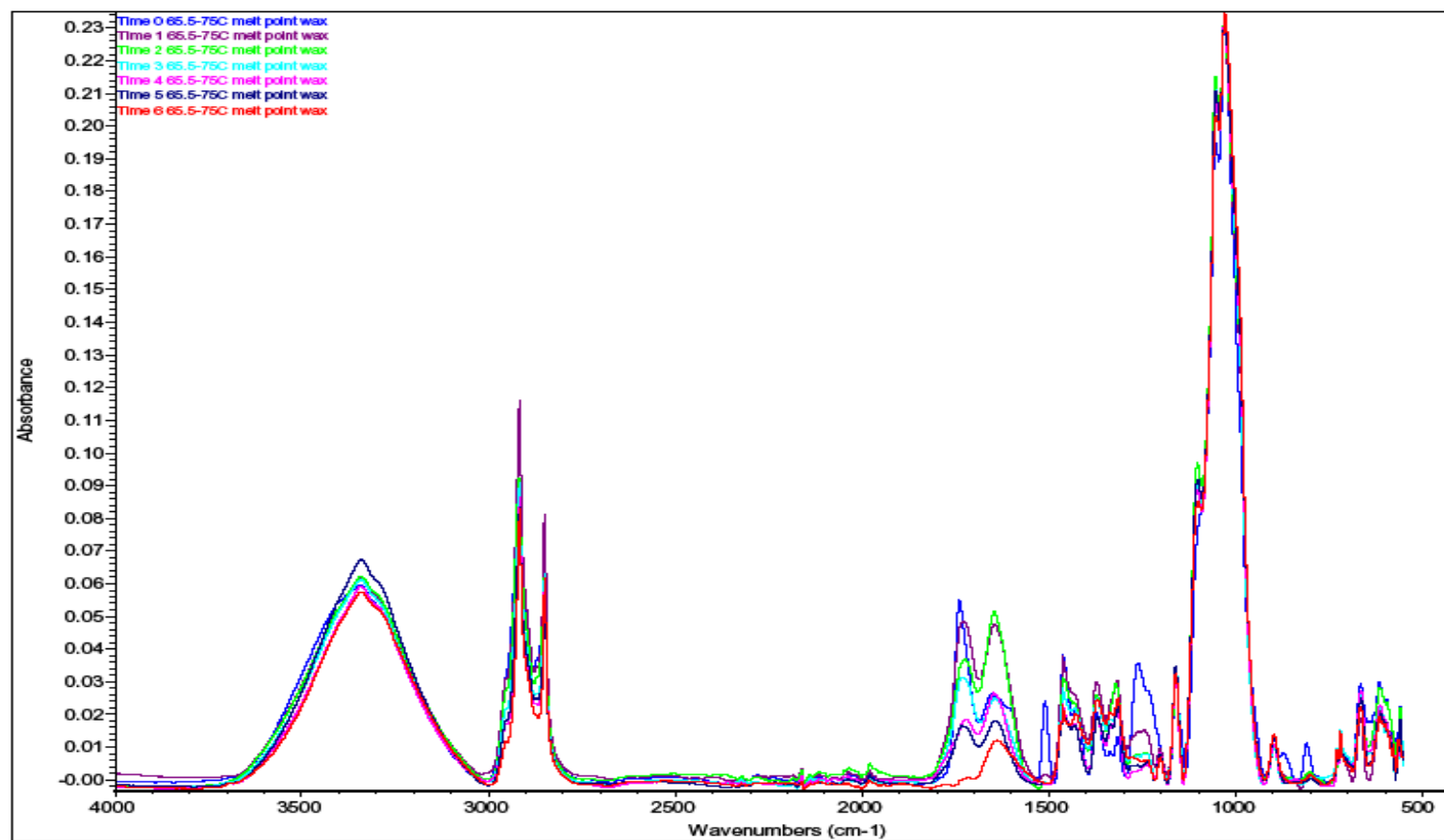


Figure 3.31. FTIR spectra collected from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 65.5-75 °C. Spectra were collected after the samples had been exposed outdoors to 6 irradiation dosage increments of 454 MJ/m².

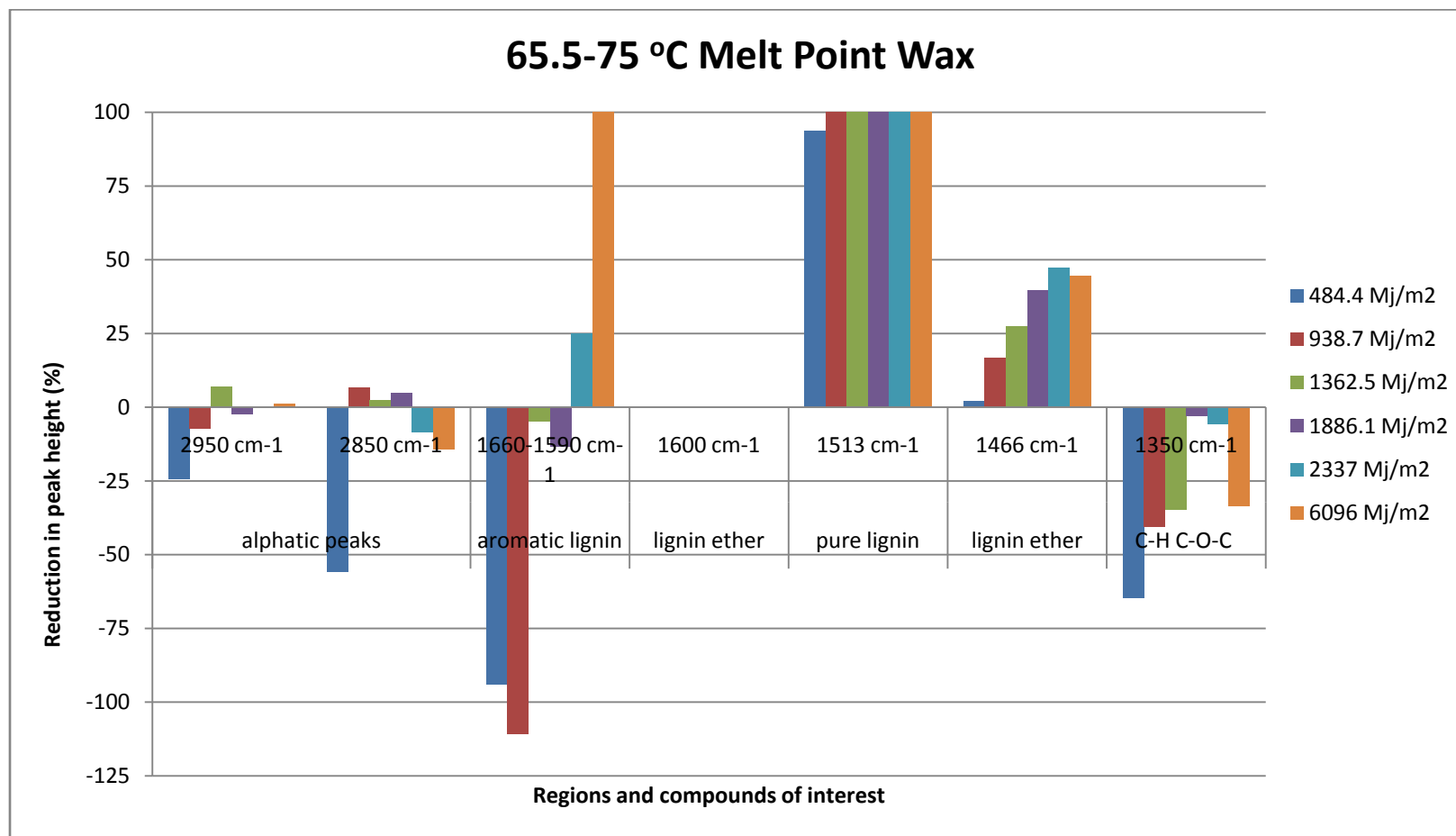


Figure 3.32. Reduction in FTIR peak intensity from southern pine samples treated with a 20,000 ppm wax in water emulsion with a melt point of 65.5-75 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m².

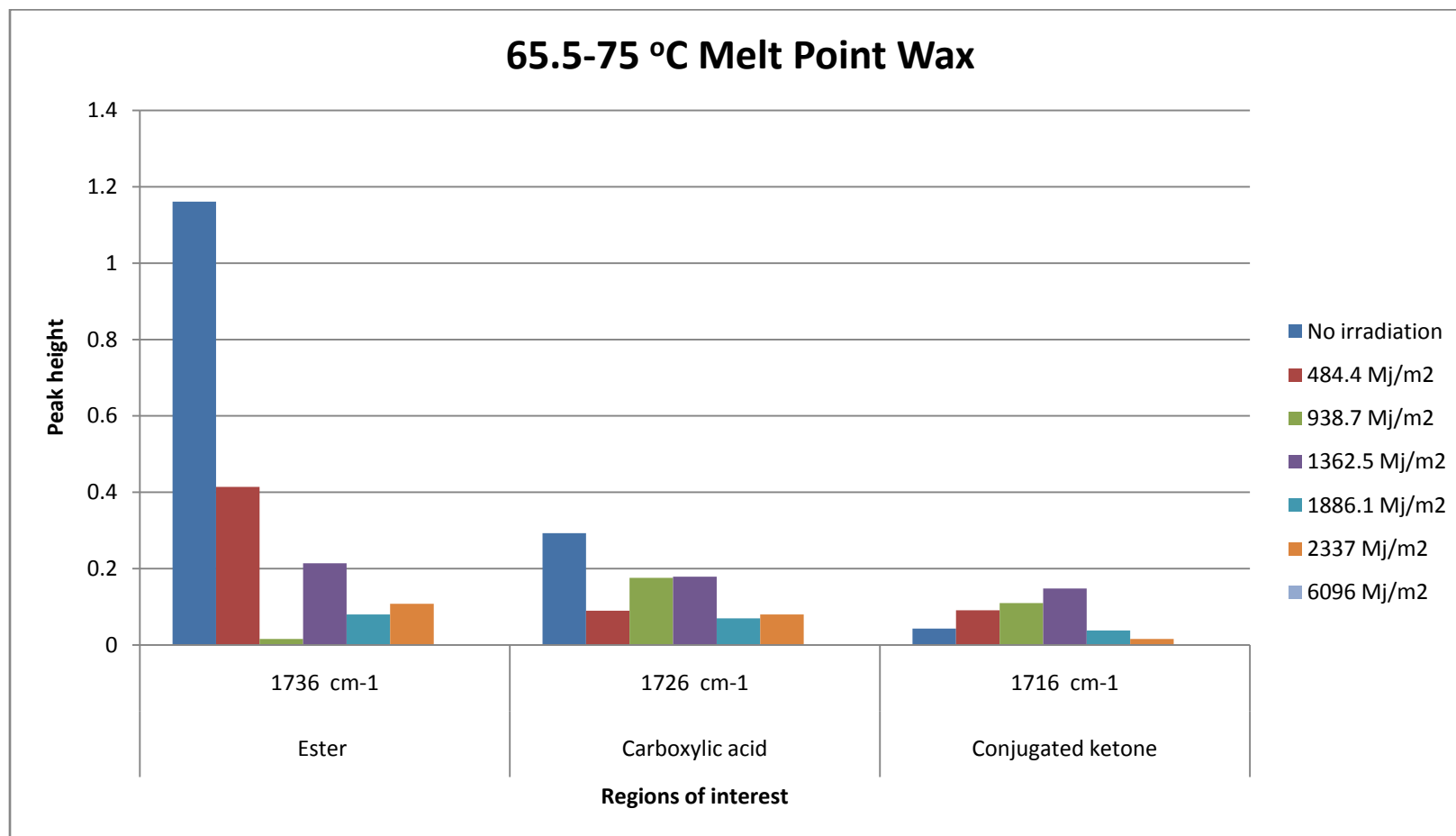


Figure 3.33. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 20,000 ppm wax in water emulsion with a melt point of 65.5-75 °C and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

FTIR spectra collected from samples treated with silicate were inconclusive since the silicates interfered with the collection of clean spectra (Figures 3.34 and 3.35); however, the spectra suggest that these treatments did not provide any protection to either the lignin or hemicellulose. The spectra suggested that silicate treatment resulted in loss of wood extractives as evidenced by the lack of well defined aliphatic peaks. Spectra collected from the acrylic polymer treated samples suggested that this treatment stabilized the aliphatic compounds found on the wood surface and may have slowed hemicelluloses loss, since a small peak in the unconjugated carbonyl region was still visible after one year of exposure (Figures 3.36 and 3.37). Further analysis of the carbonyl region suggested that the ester peak was stabilized after a large initial loss, while the carboxylic acid peak remained enriched for the entire exposure period (Figure 3.38). The treatment seemed to result in the steady loss of conjugated ketones, suggesting that the cellulose was being degraded. This compound, however, failed to provide any protection to the lignin.

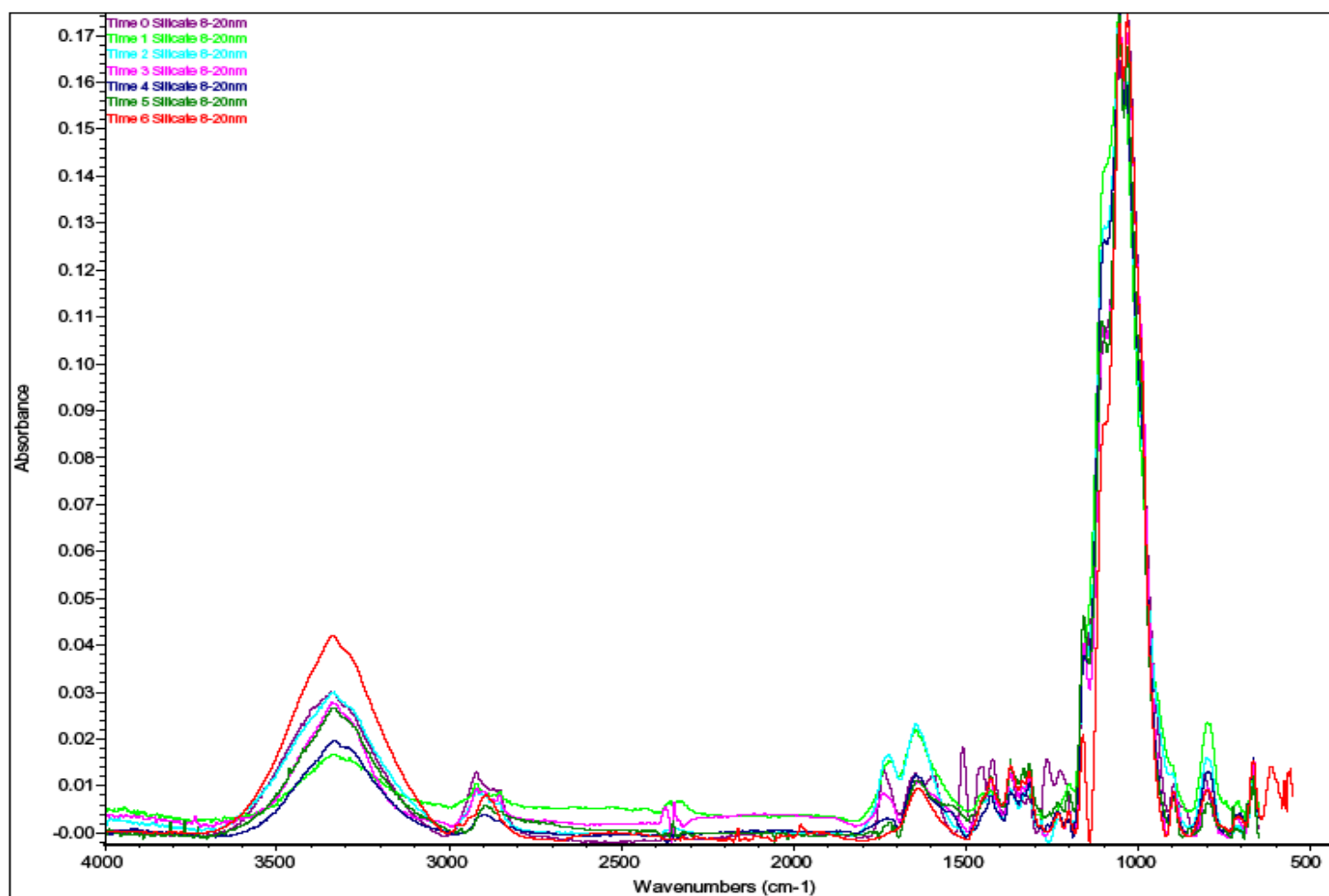


Figure 3.34. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 8-20 nm silicate particles and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m².

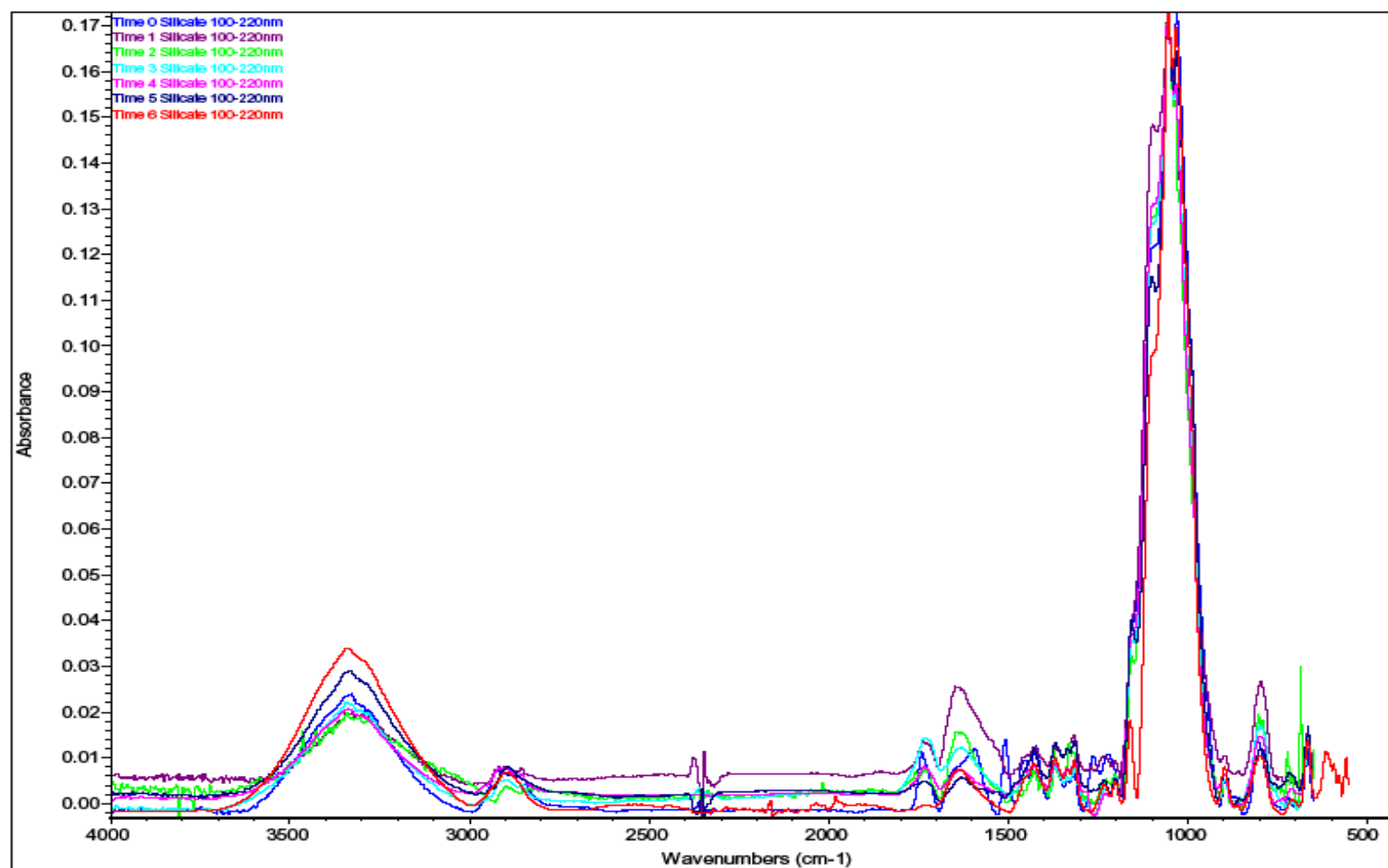


Figure 3.35. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 100-220 nm silicate particles and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m^2 .

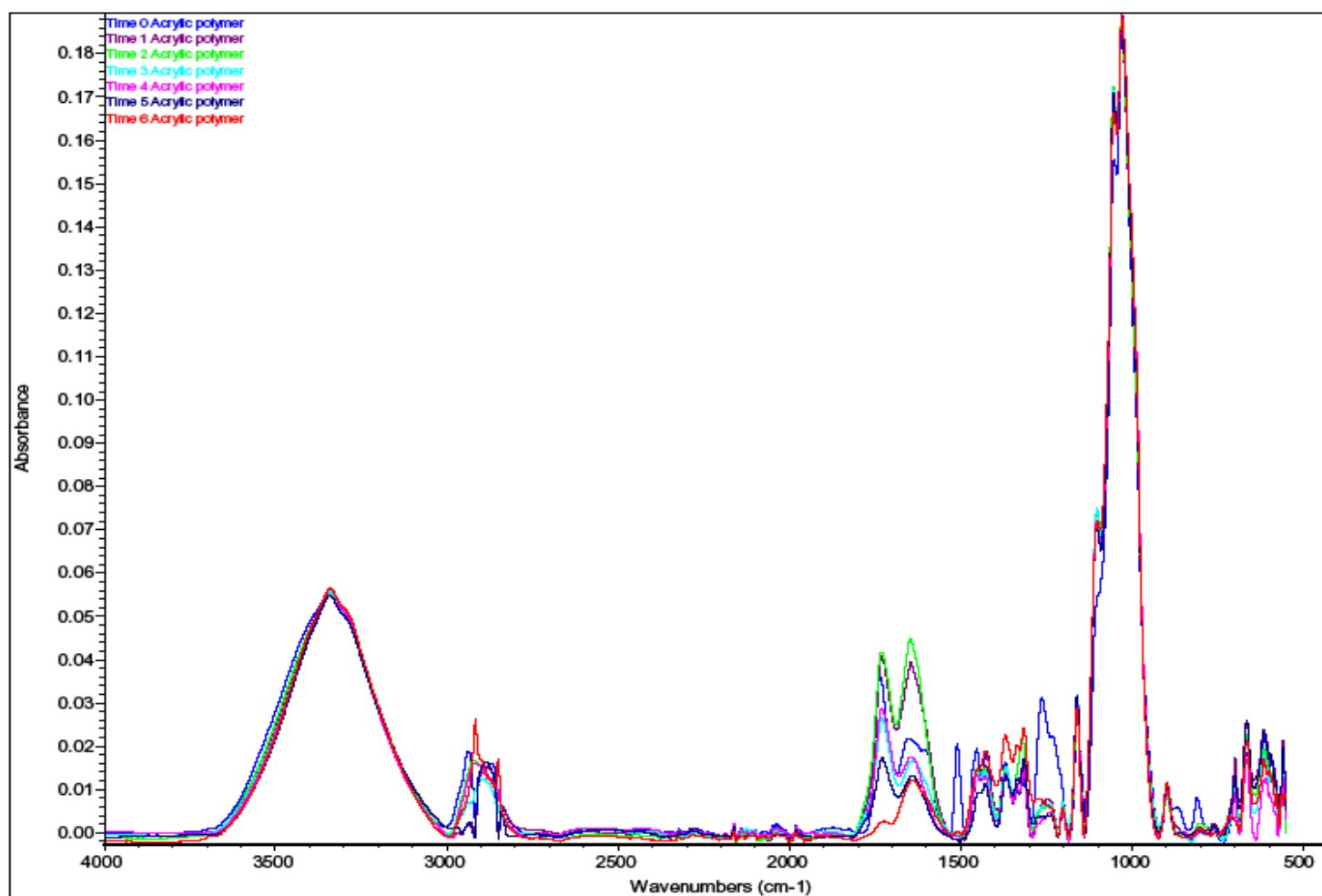


Figure 3.36. FTIR spectra collected from southern pine samples treated with a 4000 ppm solution of acrylic polymer and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m².

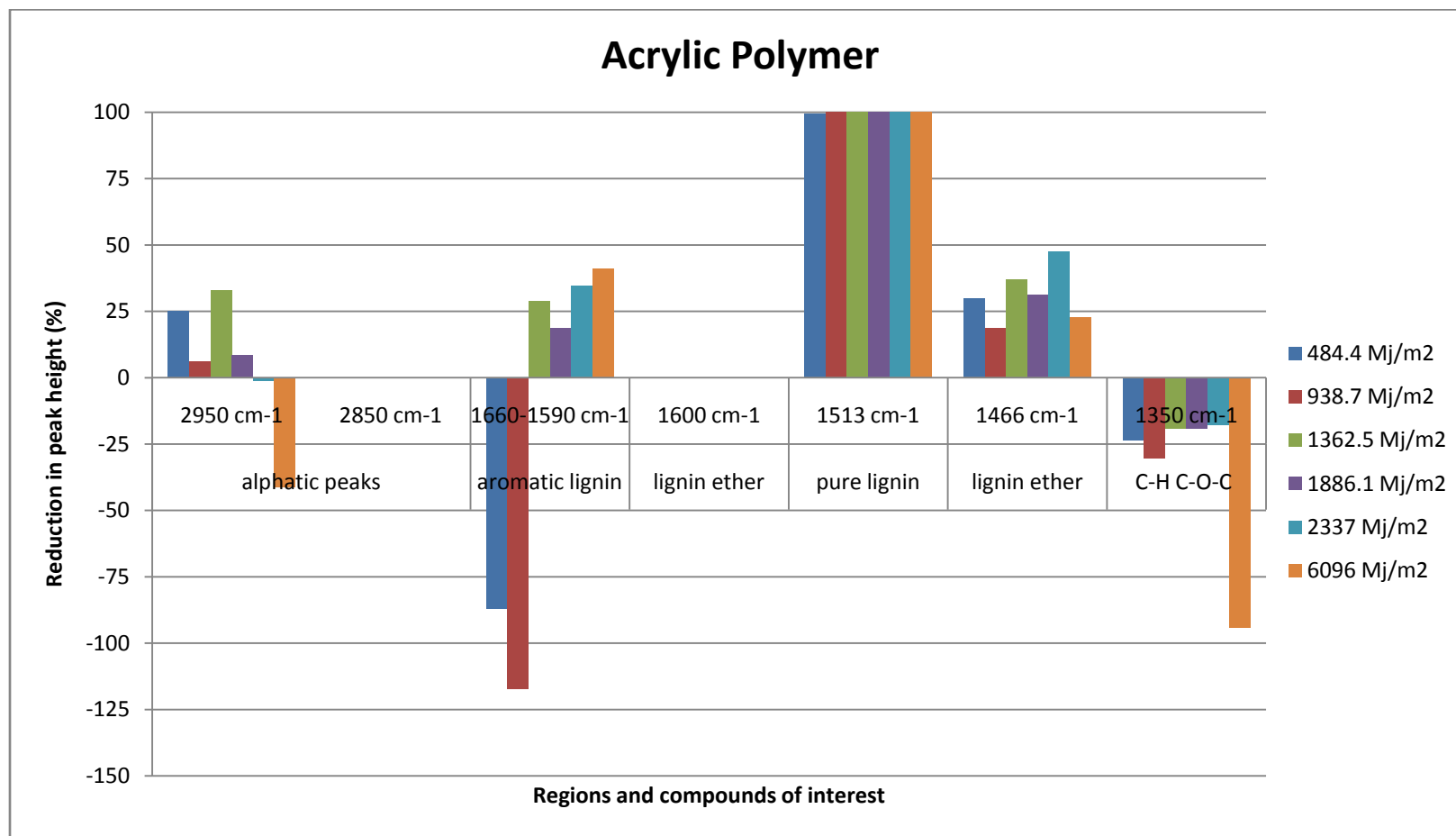


Figure 3.37. Reduction in peak intensity from southern pine samples treated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosage increments of 454 MJ/m².

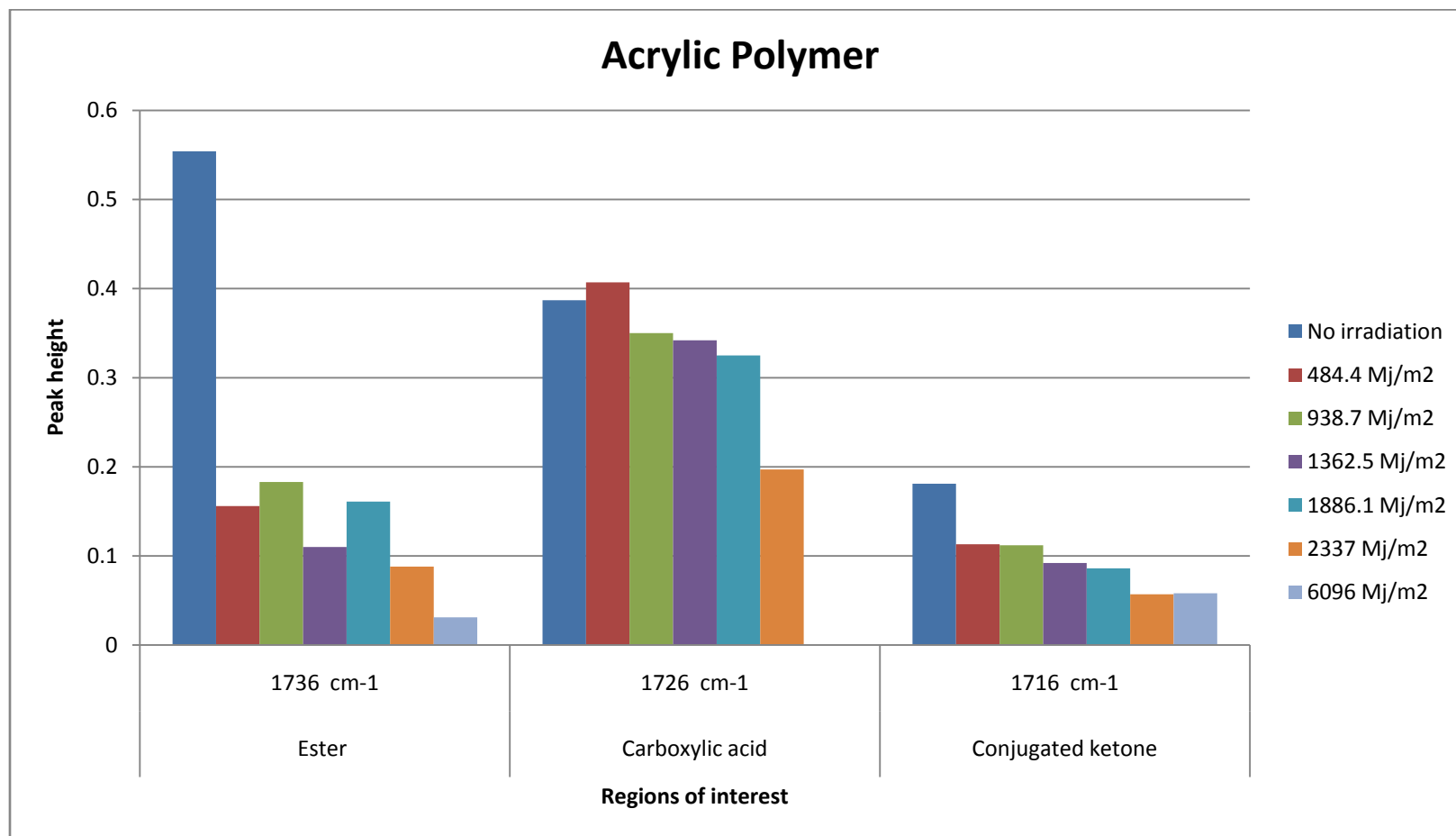


Figure 3.38. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

Spectra from samples treated with organic UV stabilizers indicated that preventing UV absorption in the polymers was a much more effective approach for preventing degradation than quenching the free radicals after they had formed (Figures 3.39-44). Hydroxyphenylbenzotriazole treatment slowed loss of aliphatic compounds compared to the untreated controls, while deconvolution of the carbonyl region indicated that this compound prevented hemicellulose degradation for the first 1886.12 Mj/m^2 of irradiation (Figures 3.39-41). This was the largest improvement in weathering performance achieved by any of the compounds investigated. This compound also slowed lignin loss as evidenced by the presence of the pure lignin peak at 1513 cm^{-1} . FTIR spectra of samples treated with the free radical quenching compound suggest that this treatment provided little protection to hemicellulose and lignin compounds at the concentration investigated (Figures 3.42-44). These observations suggest that it is very difficult to prevent the process from moving forward once the degradation mechanism has been activated through UV light absorption.

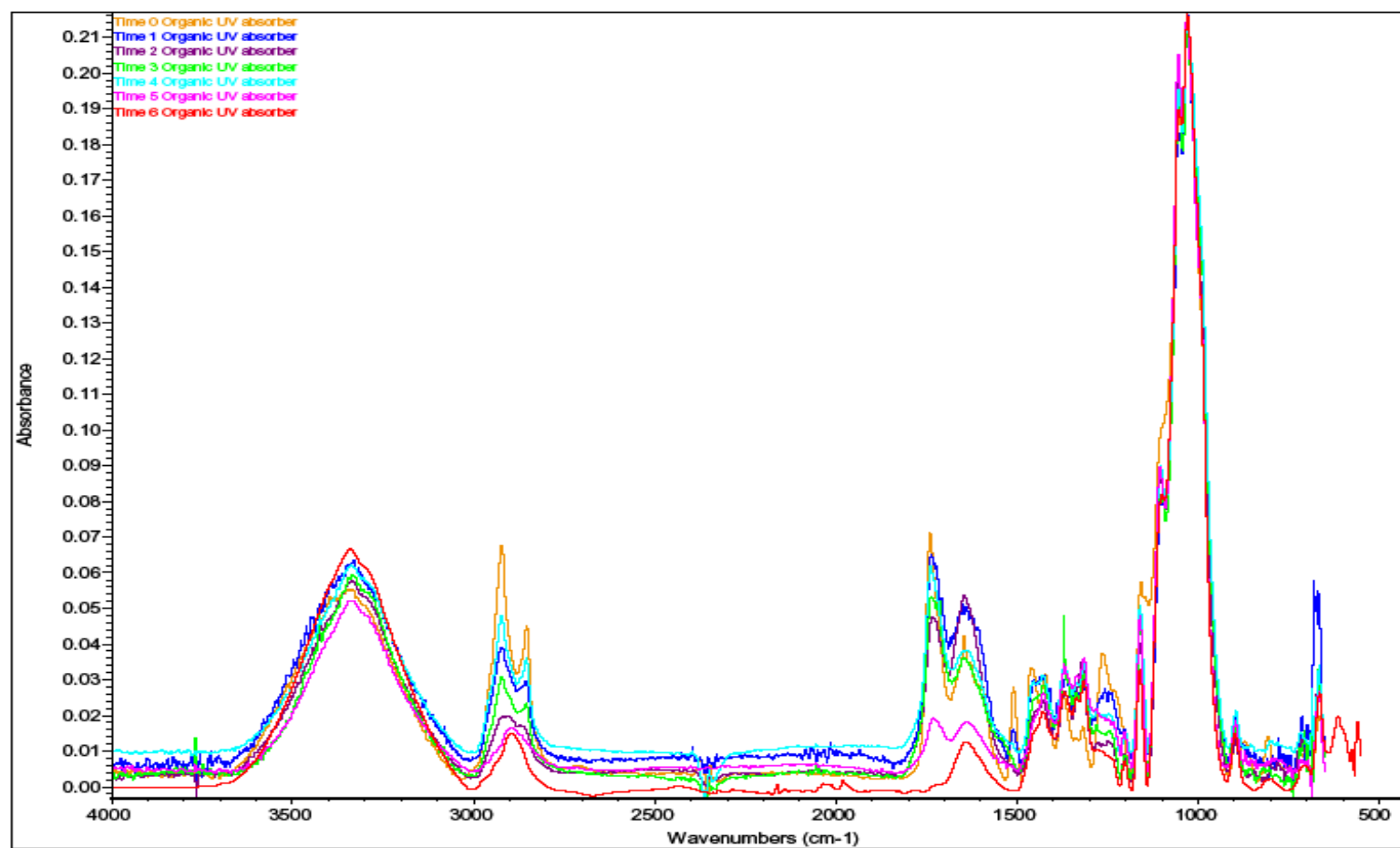


Figure 3.39. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed outdoors to irradiation dosage increments of 454 MJ/m².

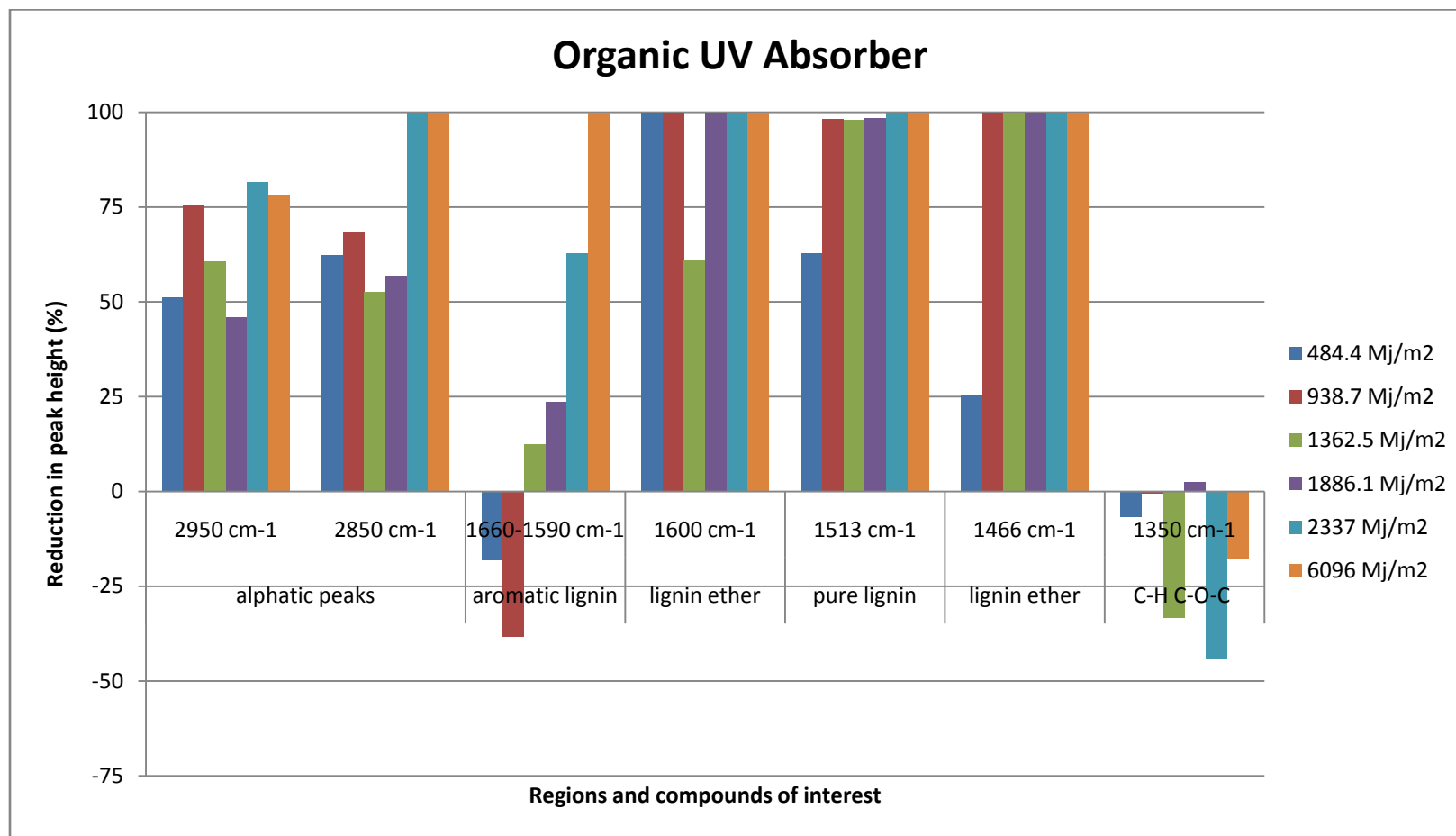


Figure 3.40. Reduction in peak intensity from southern pine samples treated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed outdoors to irradiation dosage increments of 454 MJ/m².

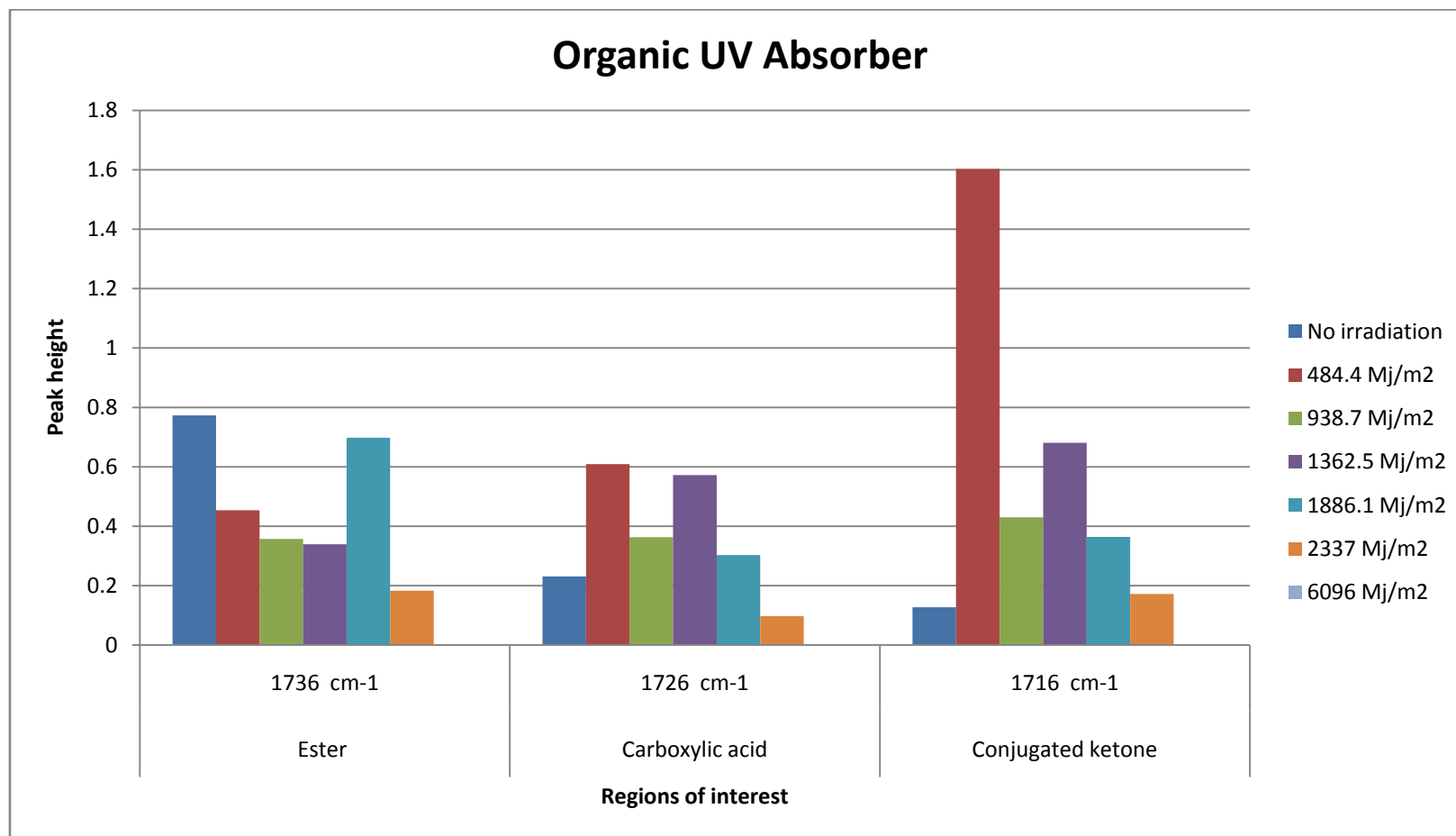


Figure 3.41. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed outdoors to irradiation dosage increments of 454 Mj/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

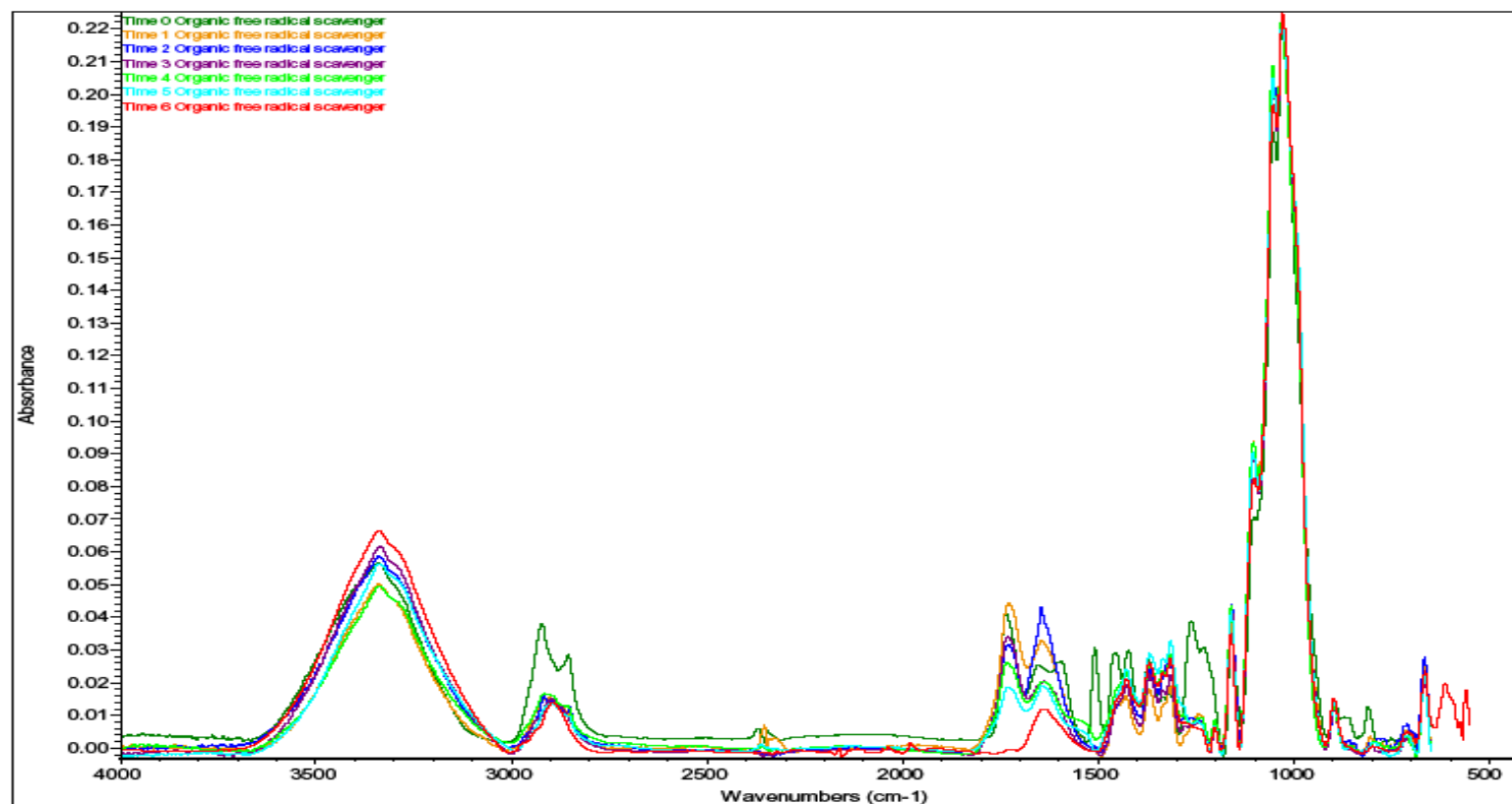


Figure 3.42. FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of an organic free radical scavenger of the hindered amine light stabilizer class and exposed outdoors to 6 irradiation dosage increments of 454 MJ/m².

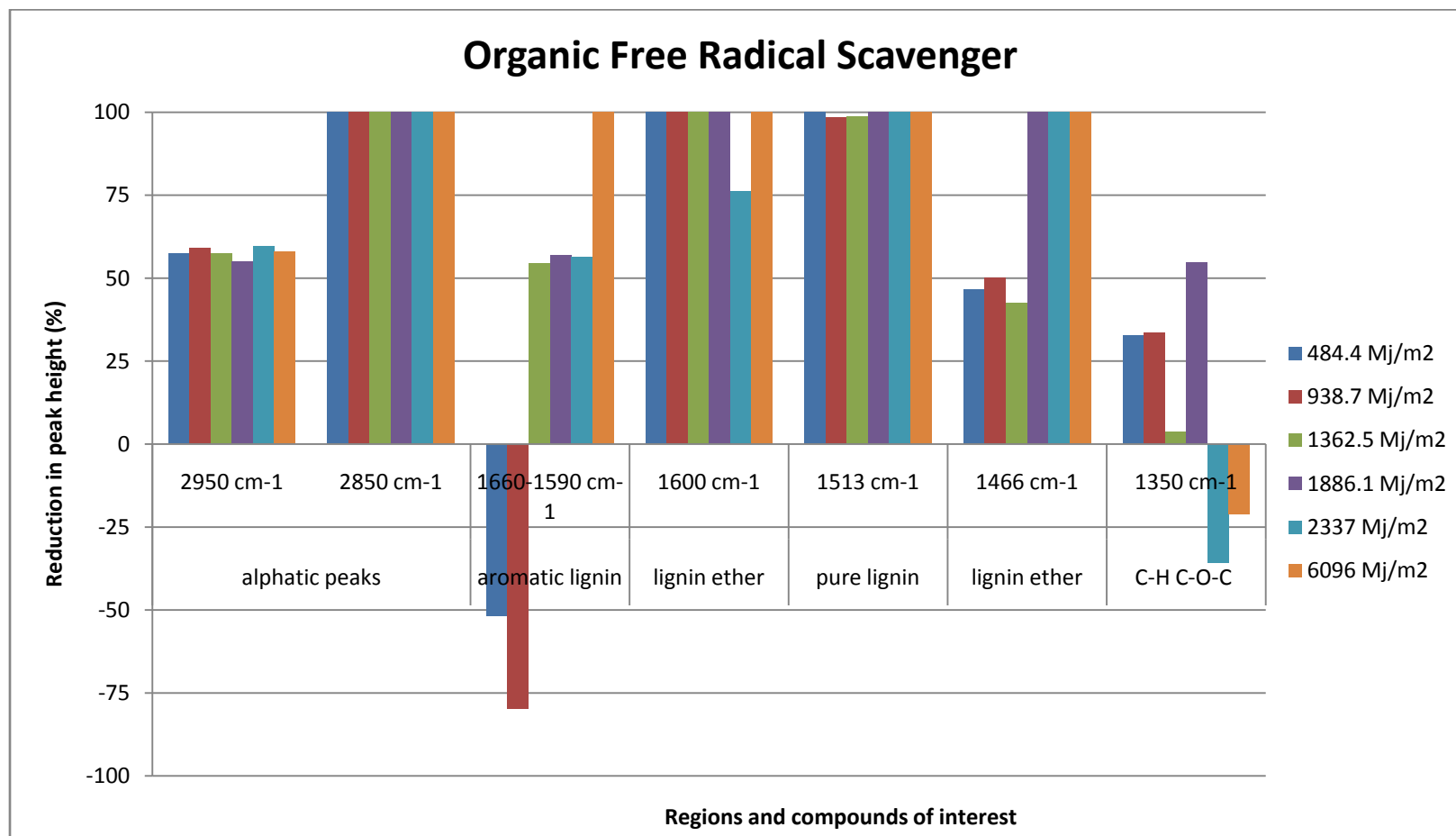


Figure 3.43. Reduction in FTIR peak intensity from southern pine samples treated with 1000 ppm of an organic free radical scavenger of the hindered amine light stabilizer class and exposed outdoors to irradiation dosage increments of 454 MJ/m².

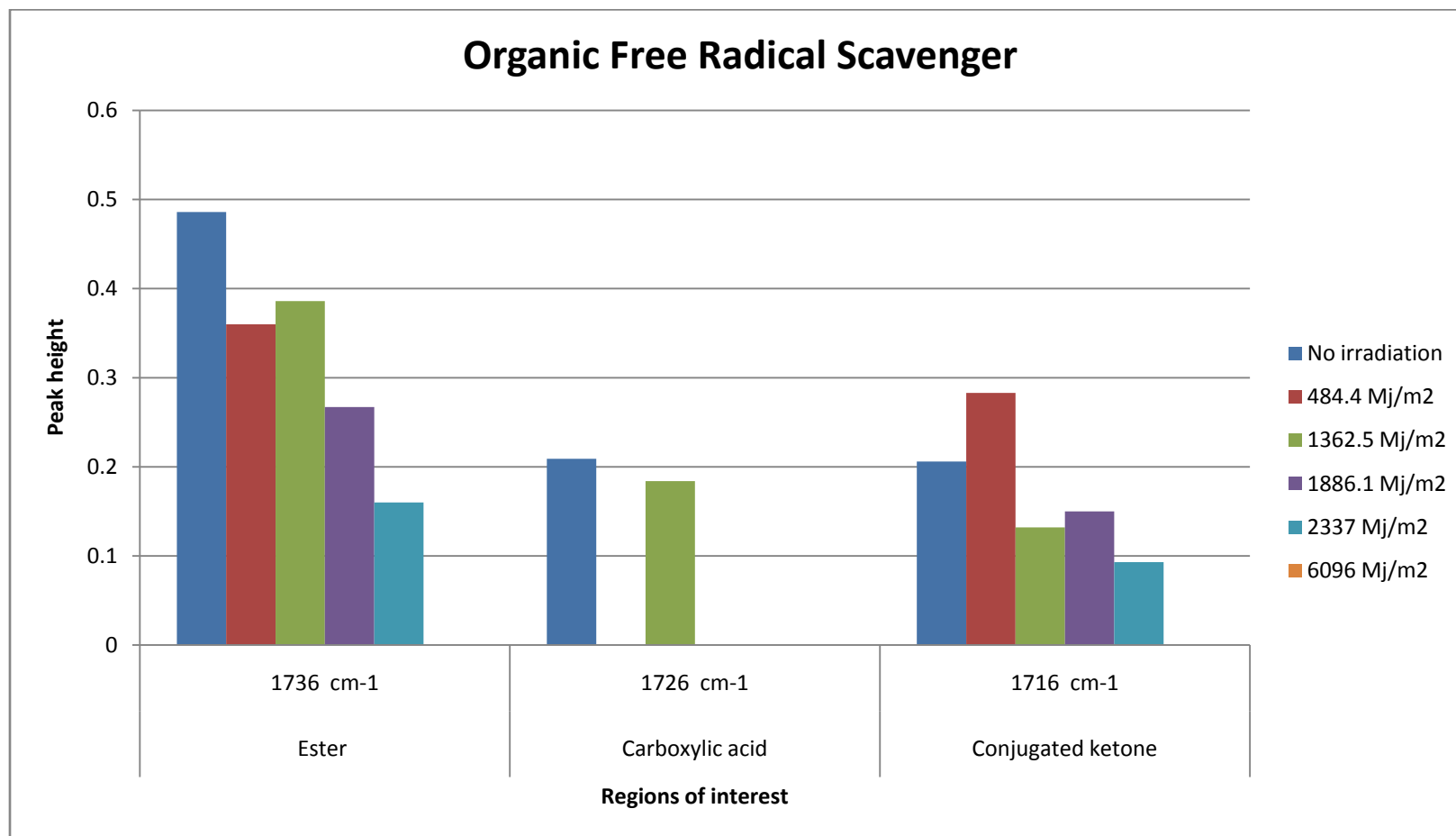


Figure 3.44. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with 1000 ppm solution of organic free radical scavenger of the hindered amine light stabilizer class and exposed outdoors to irradiation dosage increments of 454 Mj/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

The biocide 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) was investigated as part of this study since field observations suggested that this compound turns wood surfaces bright white after short exposures to sunlight and then prevents graying for an extended period of time. FTIR analysis of samples treated with this compound showed that a large aliphatic peak present after treatment was lost during the first 487 Mj/m^2 of irradiation (Figures 3.45 and 3.46). The remainder of the spectra collected from this treatment followed the same patterns observed with the untreated control samples. This treatment appeared to produce more rapid loss of the ester peak and a steady loss of the carboxylic acid and conjugated ketone peaks. These observations suggest that DCOIT prevented the growth of dark pigmented fungi on the surface of the samples, but did not alter the abiotic surface degradation process (Figure 3.47). The bright white appearance of these samples was most likely due to the presence of pure cellulose on the sample surface as a result of pulping reactions initiated by the chlorine found in DCOIT.

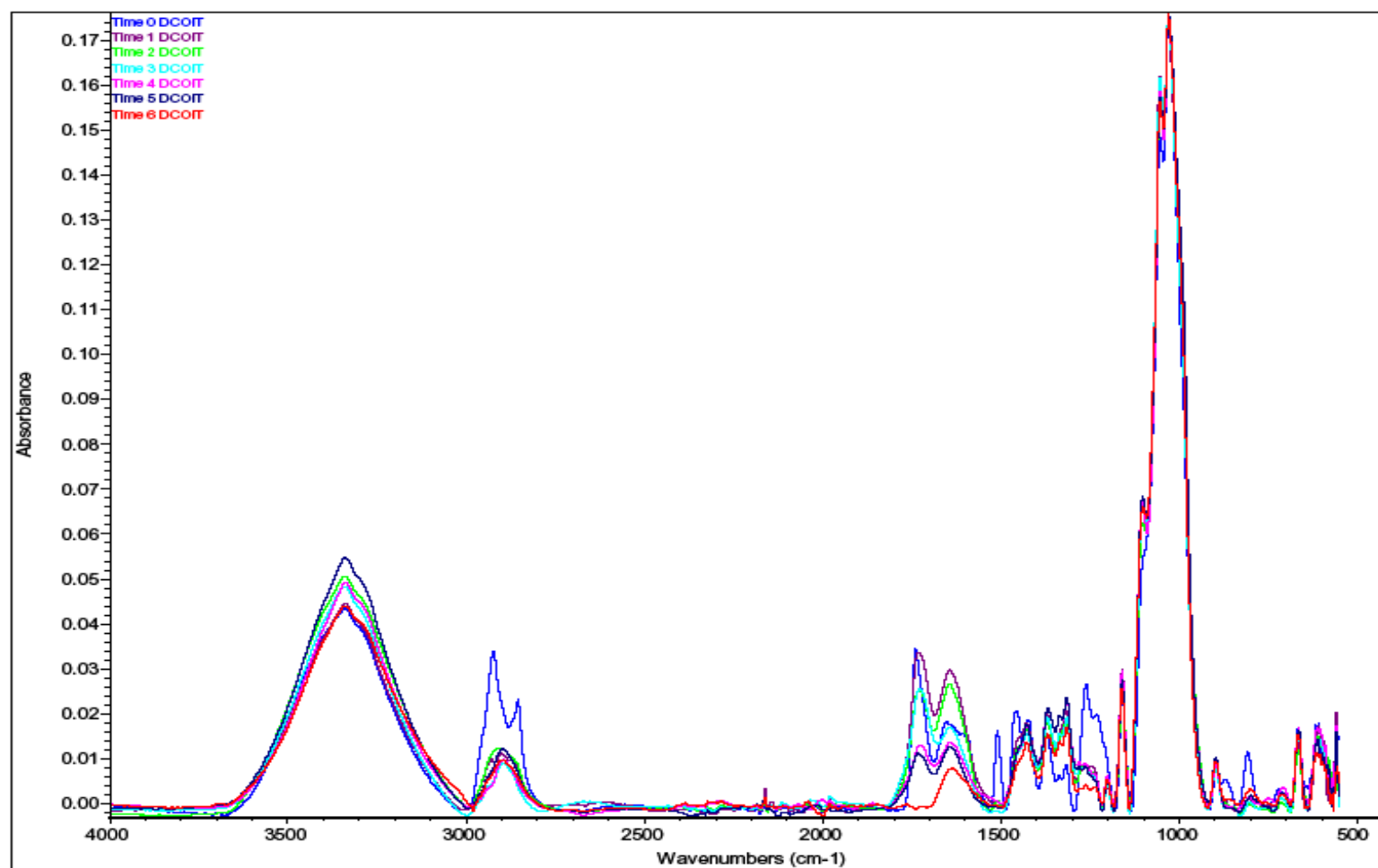


Figure 3.45. FTIR spectra collected from southern pine samples treated with a 1000ppm solution of 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed outdoors to irradiation dosage increments of 454 MJ/m².

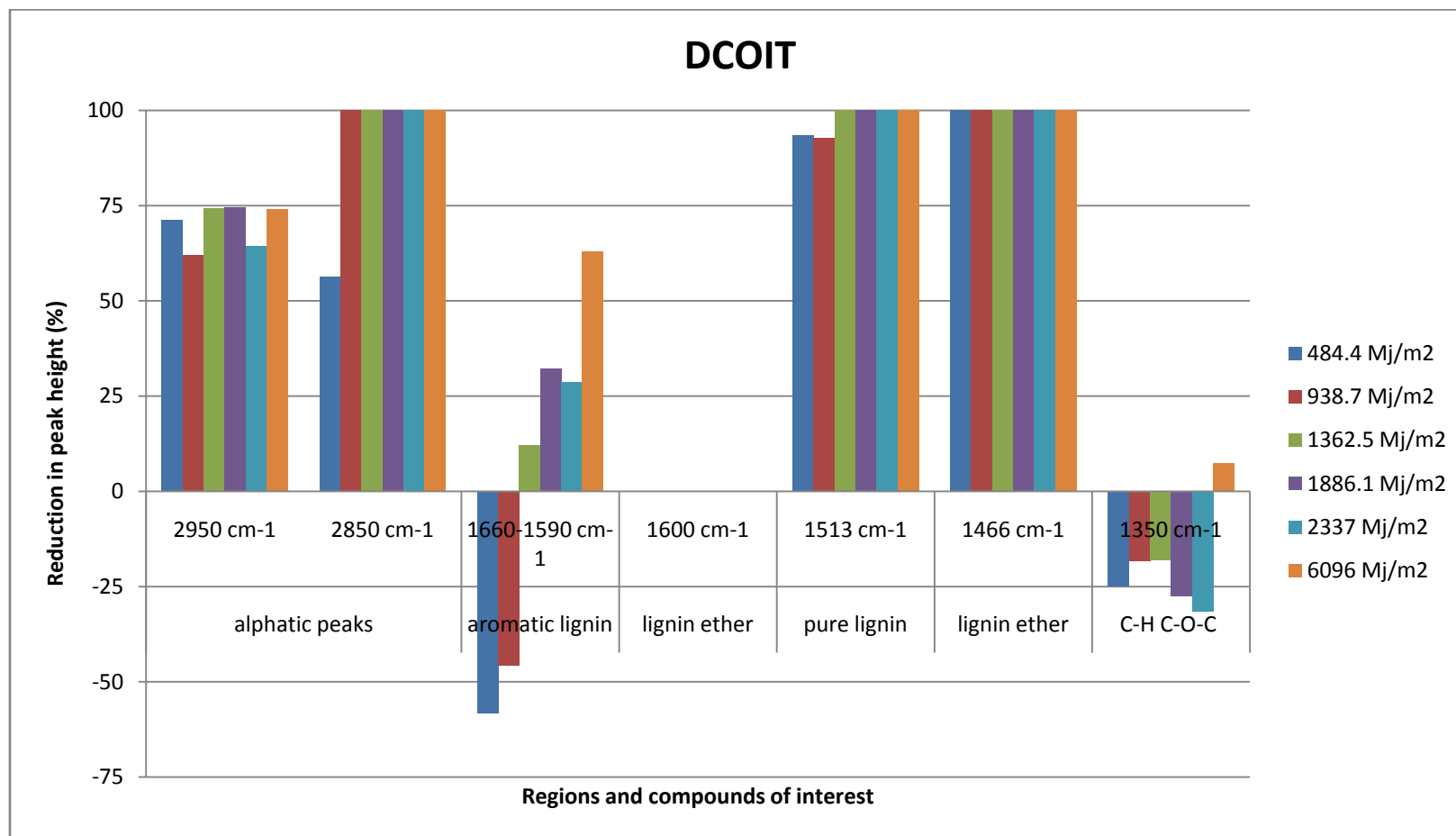


Figure 3.46. Reduction in FTIR peak intensity from southern pine samples treated with a 1000 ppm solution of 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed outdoors to irradiation dosage increments of 454 MJ/m².

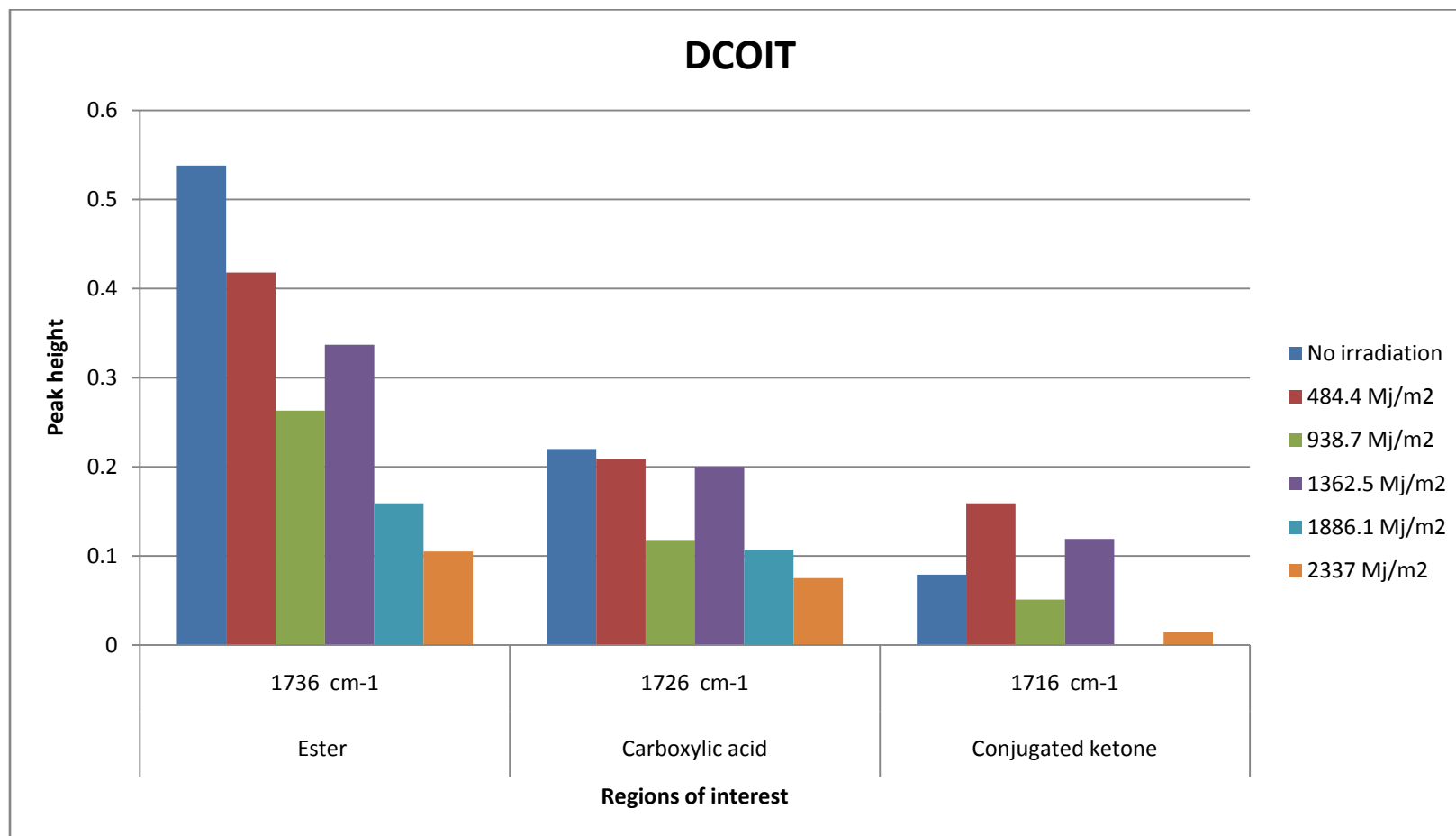


Figure 3.47. Changes in the carbonyl region of FTIR spectra collected from southern pine samples treated with a 1000 ppm solution of 4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed outdoors to irradiation dosage increments of 454 MJ/m². Peaks for individual compounds of interest were obtained through deconvolution of the carbonyl region.

3.5 Conclusion

Exposing samples treated with different surface protection systems to outdoor weathering in eastern Oregon indicated that preventing UV light from initiating the degradation process is more effective at preventing depolymerization of hemicelluloses and lignin than removing the free radicals once they have been generated. FTIR spectra of different pigment systems indicated that both iron oxide and titanium dioxide particles partially prevented lignin and hemicelluloses degradation. However, efficacy was highly dependent upon particle size and crystal shape, with smaller particles and those that imposed a red color being more effective at preventing lignin loss. Finally, spectra generated from the different water repellent systems suggest that these systems interact with the basic polymers that comprise the cell wall, providing some protection to the hemicellulose. The results suggest a need for future research focusing on the effects of iron oxide crystal shape and particle size on wood surfaces is needed. In addition a greater understanding of the interactions between petroleum based waxes and solar irradiation is desirable.

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Effects of geographical location on weathering of wood surfaces

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4. EFFECTS OF GEOGRAPHICAL LOCATION ON WEATHERING OF WOOD SURFACES

4.1 Abstract

Wood products have traditionally been tested in warm, humid climates to evaluate resistance against biotic deterioration, while other materials are often tested in the multiple extreme climates. This is important because materials may also be damaged by abiotic agents, particularly ultra violet light. Investigation of the weathering characteristics of wood products in different climates have produced inconclusive results. Some indicate that climate does not influence weathering characteristics of wood, while others contradict these findings. In order to determine if different potential surface protection compounds performed differently under different climate regimes, loblolly pine samples were impregnated with pigments, water repellents, organic UV inhibitors or an organic biocide. Samples were exposed on 45° racks oriented due south under tropical conditions near Hilo, Hawaii and to desert conditions in Eastern Oregon. Samples were harvested after set solar radiation doses from the Eastern Oregon location and after six months of exposure in Hilo, Hawaii. The surfaces of the samples were investigated for discoloration, checking and chemical changes. None of the compounds provided complete protection; however, some performed better than others. The results also suggested that weathering was affected by climate. Samples exposed to tropical conditions turned very dark, suggesting interactions between biotic and abiotic deterioration, while samples exposed in the desert checked more, suggesting that moisture cycling was more important at this site. FTIR analysis also suggested that biological activity on the surface of the samples exposed in the tropics enhanced removal of degradation products. The results suggested the need for multiple test sites when evaluating surface coatings of wood.

4.2 Introduction

Weathering characteristics of materials are influenced by the interaction of solar radiation, moisture, temperature and other climatic factors, such as surface ozone

concentrations. Combinations of these factors can result in embrittlement, cracking, fading and, eventually, complete degradation of a material. Outdoor testing has traditionally been conducted in subtropical and desert climates to rapidly assess the resistance of a particular material or product to different combinations of these factors. Devices have also been developed to simulate and accelerate environmental effects to develop service life predictions for a given substance (Wypych 2008). Traditionally, wood products testing has differed from that of other materials since biotic degradation has been the primary interest. Thus, wood based material testing has been chiefly conducted in warm humid climates such as Australia, Japan and Hawaii to take advantage of accelerated biological activity. Additional test sites have also been established to study the behavior of the material in a particular area such as the Nordic region.

Wood finishing research in the United States traces its roots to 1922 with the initiation of the Wood Finishing Research Project at the USDA Forest Products Laboratory (Gorman and Feist 1989). Since then, numerous studies have been conducted to understand and prevent the effects of weathering on wood surfaces for reviews see (Fiest and Hon, 1984; Williams, 1995). While progress has been made to understand and reduce the effects of weathering on wood surfaces, it remains difficult to effectively protect wood without using a pigmented film-forming coating.

Although evaluations at multiple locations are invaluable for accurate service life predictions, there are few comparative studies of wood surface weathering across multiple exposure locations for other materials (Wypych 2008). Initially, the Forest Products Laboratory established a number of test fences across the country in cooperation with university and industry partners, primarily evaluating the performance of different lead and zinc based coatings. Test sites in Madison, Wisconsin, Saucier, Mississippi, and Olympia, Washington remain active and data from these studies shows that coating service life is primarily a result of proper surface adhesion and preventing water ingress over time (Gorman

and Feist 1989). A study comparing transparent, semitransparent and opaque coatings on different wood and wood composite materials found that the coatings behaved similarly in Madison, Wisconsin and Dübendorf, Switzerland (Kropf, Sell and Feist 1994). Similarly, Evans et al (2000) evaluated checking in chromate copper arsenate (CCA) treated timbers at four locations across Australia and found that climate did not significantly affect checking. Other studies found that the results of weathering studies cannot be transferred from one region to another. A study comparing the performance of coatings on wood samples exposed in Germany and New Zealand found that the type of coating used and the exposure location significantly affected service life (Dawson, Göttgens and Hora 2005). Similar results were obtained when a round robin test was conducted at nine test sites in Europe to develop a regional weathering index. The results indicated that weathering was location dependent and that global irradiation, total precipitation and days with more than 0.1 mm of precipitation were poor predictors of weathering. Thus, weathering results could not be transferred from one location to another (Creemers et al 2002). These studies suggested that locations at similar latitude and elevation are comparable and, the effects of climate on surface durability are small, but climate may have a significant effect when samples are exposed in distinctly different regions. One important aspect of an exposure site is the interaction between biological and physical degradation. Very few studies compare sites with varying biological activities under comparable weathering conditions. This type of study could help segregate the roles of each component on finish performance. In this study, we compare finish performance at two sites with strong UV exposure but different biological risks.

4.3 Methods

Loblolly pine (*Pinus taeda* L) samples were produced and exposed as described in Schauwecker et al (2009). Briefly, sapwood samples (10 mm thick, 85 mm wide, and 155 mm long) were pressure impregnated with various compounds selected for their potential to reduce the effects of weathering (Table 4.1). After treatment, gauge retentions were

calculated based upon weight gain. Baseline color measurements were collected using a color-ometer and a centering jig. Samples were exposed on 45 degree racks in the high desert of Oregon or near Hilo, Hawaii. Each treatment was replicated on two samples at each site. The Oregon site receives less than 350 mm of precipitation per year; however, natural precipitation was augmented by spraying the samples with non-chlorinated irrigation water at dawn each day between May and October. Temperatures ranged from an average low of 1 °C (range -7 to 10 °C) to an average high of 16 °C (range 3 to 29 °C). Solar radiation was monitored at the Oregon location and two matched samples were removed after each 454 MJ/m² irradiation interval (U.S. Department of the Interior 2008-2009). The Hilo, Hawaii test site averages, 1900 mm of precipitation during the fall and winter months with average daily low and high temperatures of 20 °C and 28 °C, respectively (National Oceanic and Atmospheric Administration 2010). Equipment to monitor solar radiation was not available in Hilo. Thus, the samples were removed after six months of exposure. Studies conducted by the Hawaii statewide GIS project indicate that the Hilo site typically received 2665 MJ/m² of irradiation during the time frame used for this study (Marion and Wilcox 1994).

Samples removed from the exposure sites were subject to colorimetry readings to assess color change and reconditioned at 25 °C and 65% relative humidity. The number of checks along with their characteristics was evaluated using a dedicated software package (Schauwecker et al 2009). Chemical changes that occurred during exposure were evaluated using FTIR as described in Schauwecker et al (2011). In brief, six small specimens (~2 mm x 10 mm x 20 mm) were removed from the surface of one sample from each treatment. Spectra were collected using a single bounce attenuated total reflection (ATR) probe. After collection, the spectra were baseline corrected and the six spectra per sample averaged using Omic 7.4 software to produce a composite spectrum representing the entire sample (Thermo Fisher inc. Waltham MA). Regions of the spectra relevant to photodegradation of wood were quantified using the Omic 7.4 Software package. Individual peak heights were measured and normalized

using the large cellulose and hemicelluloses C-O stretching peak located at 1033 cm^{-1} . Changes in peak height were expressed as a percent, using the unexposed reading as a baseline. The carbonyl region was treated differently due to overlapping peaks in this portion of the spectra. The region between 1750 and 1700 cm^{-1} was normalized within a treatment and Fourier self deconvolution applied to resolve overlapping peaks, allowing for the analysis of esters (1736 cm^{-1}), carboxylic acid (1726 cm^{-1}) and conjugated ketones (1716 cm^{-1}).

Table 4.1. Compounds assessed for their ability to reduce weathering of loblolly pine sapwood.

Category	Compound	Purpose	Application Concentration (ppm)
Pigment	Red iron oxide suspension (particle size of 190 nm)	Assess particle size effect on surface discoloration	1000
Pigment	Yellow iron oxide suspension (particle size of 190 nm)	Effect of crystal shape on surface discoloration	1000
Pigment	Red iron oxide suspension (particle size of 700 nm)	Baseline for particle size and crystal shape comparison	1000
Pigment	Titanium dioxide suspension (particle size of 195 nm)	Compound and particle size on discoloration	1000
UV stabilizer	Hydroxyphenylbenzotriazole Class	UV absorber	1000
UV stabilizer	Hindered amine light stabilizer (HAL)	Free radical scavenger	1000
Water repellent	Oil in water emulsion (wax melt point of $34\text{--}38\text{ }^{\circ}\text{C}$)	Effect of melt point and wax on water repellency	20,000
Water repellent	Oil in water emulsion (wax melt point of $54\text{--}58\text{ }^{\circ}\text{C}$)	Effect of melt point and wax on water repellency	20000
Water repellent	Oil in water emulsion (wax melt point of $65.5\text{--}75\text{ }^{\circ}\text{C}$)	Effect of melt point and wax on water repellency	20,000

Table 4.1 (Continued).

Category	Compound	Purpose	Application Concentration (ppm)
Water repellent	Silicate (particle size of 8–20 nm)	Effect of particle size and silicates on water repellency	20,000
Water repellent	Silicate (particle size of 20–100 nm)	Effect of particle size and silicates on water repellency	20,000
Water repellent	Water dispersed acrylic polymer	Control water ingress by binding to the surface of the wood	4000
Biocide	4,5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT)	Known to control mold and prevent biological discoloration	1000
Positive control	Chromic acid	Known to control surface discoloration	30000
Negative controls	Untreated	Baseline for checking and discoloration	NA

4.4 Results

Gauge retentions within the pigment and UV stabilizer classes were not statistically different ($\alpha = 0.05$) as determined using a Tukey's multiple comparison test conducted using SAS version 4.1 (SAS Institute Cary NC 2006). Retentions of the low melt point wax were statistically different from some of the other treatments in the water repellent group; however, since the average retention was within two kg/m^3 of the others it was included in the comparisons. The results also indicated that gauge retentions were below the target retentions for all treatments. This systematic error suggests that the parent boards may have

originated from trees that were less permeable than the average loblolly pine specimen (Table 4.2).

Table 4.2. Target and average gauge retentions of potential anti-weathering compounds in loblolly pine sapwood.

Class	Compound	Target retention (kg/m³)	Gauge retention (kg/m³)*
Pigment	Red iron oxide suspension with a particle size of 190 nm	0.75	0.56 (0.54-0.58)
Pigment	Yellow iron oxide suspension with a particle size of 190 nm	0.75	0.56 (0.54-0.58)
Pigment	Red iron oxide suspension with a particle size of 700 nm	0.75	0.55 (0.53-0.57)
Pigment	Titanium dioxide suspension with a particle size of 195 nm	0.75	0.52 (0.51-0.53)
UV stabilizer	Hydroxyphenylbenzotriazole Class	0.75	0.56 (0.53-0.59)
UV stabilizer	Hindered amine light stabilizer (HAL)	0.75	0.55 (0.52-0.59)
Water repellent	Oil in water emulsion with a wax melt point of 34–38 °C	15.00	9.77 (8.74 – 10.80)
Water repellent	Oil in water emulsion with a wax melt point of 54–58 °C	15.00	11.13 (10.59-11.66)
Water repellent	Oil in water emulsion with a wax melt point of 65.5–75 °C	15.00	11.30 (10.27-12.32)
Water repellent	Silicate with a particle size of 8–20 nm	15.00	11.52 (11.25-11.80)
Water repellent	Silicate with a particle size of 20–100 nm	15.00	11.41 (11.04-11.77)
Water repellent	Water dispersed acrylic polymer	3.00	2.11 (1.97 – 2.25)
Biocide	DCOIT	0.75	0.50 (0.38-0.54)
Positive control	Chromic acid	3% solution brushed on surface	NA
Negative control	Untreated	NA	NA

(*) values in parentheses represent upper and lower confidence interval limits using an alpha value of 0.05.

Samples were installed at the Hilo, Hawaii test on July 24th, 2008 and removed on January 23rd 2009. They were exposed to approximately 2678 MJ/m² of irradiation. Samples

installed in Eastern Oregon were installed on August 20th 2008 and removed incrementally over the next year after exposure to 1890, 2340 or 6096 Mj/m^2 of solar radiation.

4.4.1 Effects of weathering on positive and negative controls

Physical property data collected from the surface of chromic acid treated (positive control) and untreated samples indicated that samples exposed in a tropical climate experienced greater surface color changes than samples exposed in the high desert of Oregon (Figure 4.1). While differences in UV radiation accounted for some of the color differences, the majority of discoloration could be attributed to microbial colonization. Moderate temperatures and large amounts of rainfall at the tropical site promoted extensive microbial activity, while conditions were less suitable for attack in the high desert (Figure 4.2). Chromic acid reduced the amount of fading in dry climates, yet it did not protect against fungal colonization.

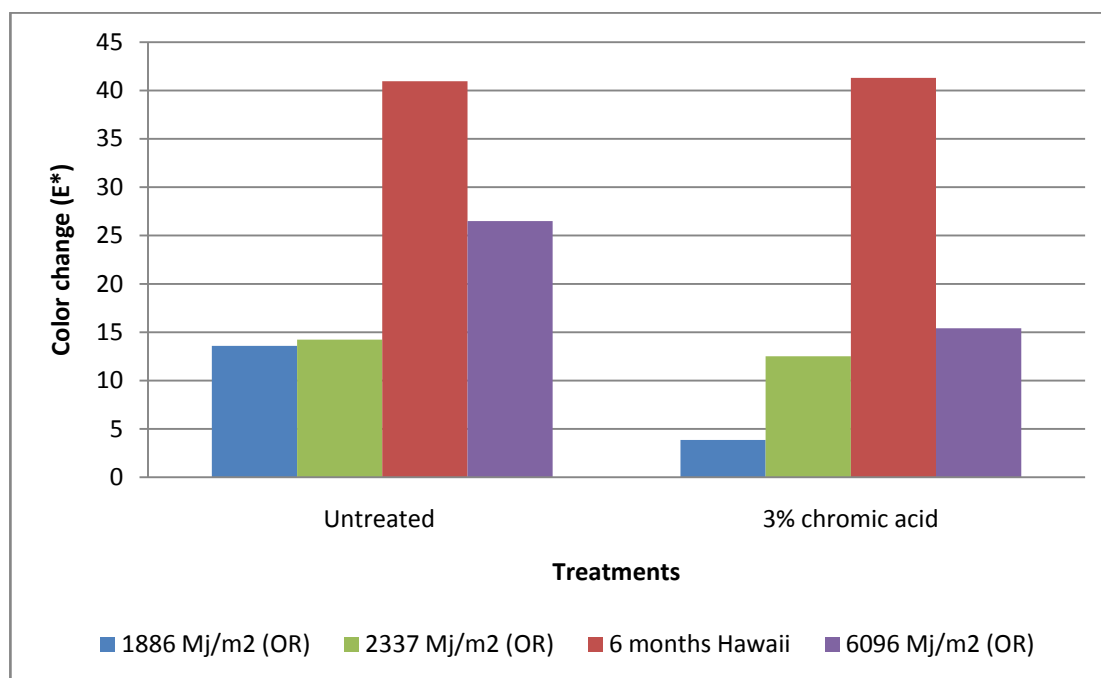


Figure 4.1. Degree of color change (discoloration) on the surfaces of untreated and chromic acid treated samples exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.



Figure 4.2. Surface appearance of untreated samples exposed to A) 2337 Mj/m^2 of solar radiation in Eastern Oregon or (B) six months on the leeward side of Hawaii.

While chromic acid protected wood surfaces from weathering, it had little effect on the number of checks that developed on the surface. This suggests that chromic acid slows degradation of wood polymers, but cannot dimensionally stabilize the wood to prevent checking when applied as a brush on treatment.

The poor performance of wood in exterior exposures reflects its dimensional instability coupled with its susceptibility to degradation. Protective treatments must address both issues. Fewer checks tended to develop in samples exposed to tropical conditions with more stable moisture regimes, indicating that moisture cycling dominates check development during the early stages of weathering. While sample surfaces exposed in the tropics experienced many moisture cycles, the cycles were relatively short with smaller moisture fluctuations that reduced drying stresses. In contrast, samples exposed in Eastern Oregon experienced infrequent, yet extreme moisture cycles due to the low average relative humidity between wetting events. This resulted in steeper moisture gradients and larger drying stresses within the wood, leading to more surface checks. The differences highlight the difficulties in using environmentally extreme test sites.

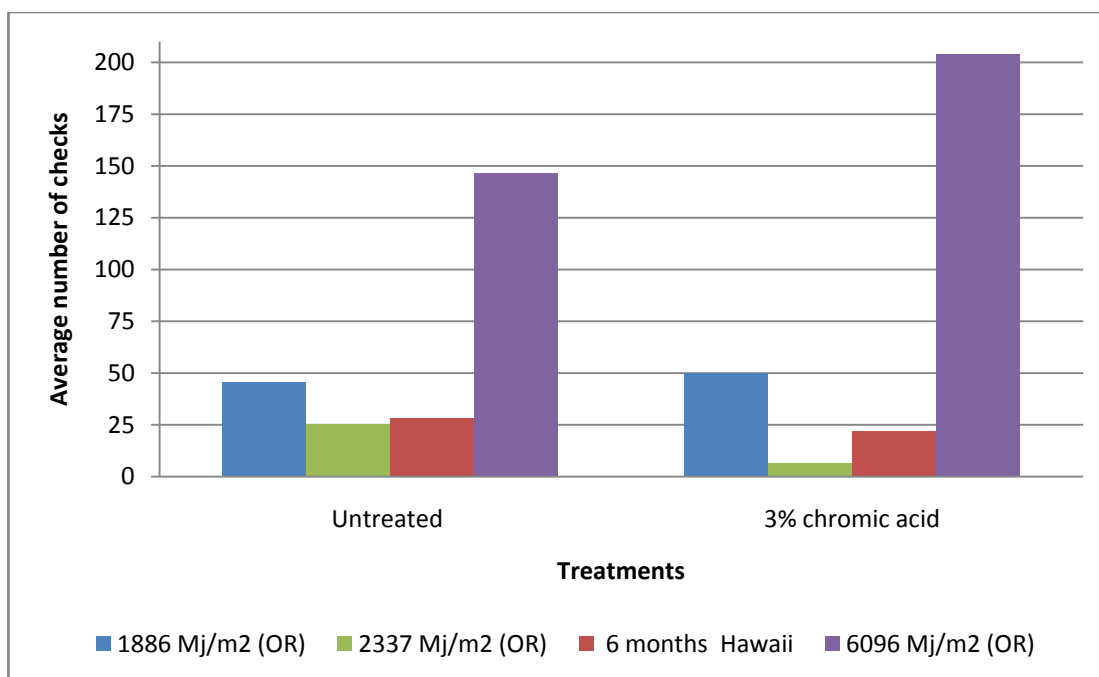


Figure 4.3. Number of surface checks on untreated and chromic acid treated samples after exposure to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

FTIR spectra collected from the untreated samples suggested that lignin was completely removed from the surface of the samples regardless of exposure location (Figure 4.4). The spectra also suggested that removal of extractives differed slightly between the two exposure locations with more of the aliphatic signal remaining for the samples exposed in Hawaii than for samples exposed in Eastern Oregon. This was surprising since the elevated rainfall in Hawaii should have accelerated extractive loss. However, the stronger aliphatic signal may also represent fungal metabolic products on the sample surface. Examination of the carbonyl region indicated that these compounds were lost more rapidly from sample surfaces exposed in the tropics than from those exposed in the desert (Figure 5). This suggests that hemicelluloses may be degraded more efficiently under tropical conditions or that these compounds are being consumed by microorganisms. Carboxylic acid, a byproduct of degraded lignin, was present at lower levels on samples exposed in Hawaii. The losses in lignin and hemicelluloses indicated that byproducts and degraded polymers were removed

from the surface of the samples more efficiently when exposed under tropical conditions than when exposed in the desert.

Differences in surface chemical composition were also detected when samples were brushed with chromic acid and exposed at the two different test sites. Hemicelluloses and cellulose were lost at a greater rate when exposed in Hawaii, while lignin degradation was less pronounced. Increased hemicellulose loss was supported by the complete loss of the ester peak after exposure in Hawaii, while cellulose degradation was supported by the loss of the conjugated ketone peak (Figure 4.6). Meanwhile, preservation of lignin in the samples exposed in Hawaii was supported by the stronger aromatic, pure and the ether lignin peak located at 1466 cm^{-1} (Figure 4.7). Changes in the polysaccharide fractions may reflect biological rather than physical degradation leaving behind a lignin rich matrix. These differences suggest that while chromic acid did not prevent discoloration or checking in tropical climates it helped protect the underlying wood polymer and may increase service life because it maintained the wood appearance.

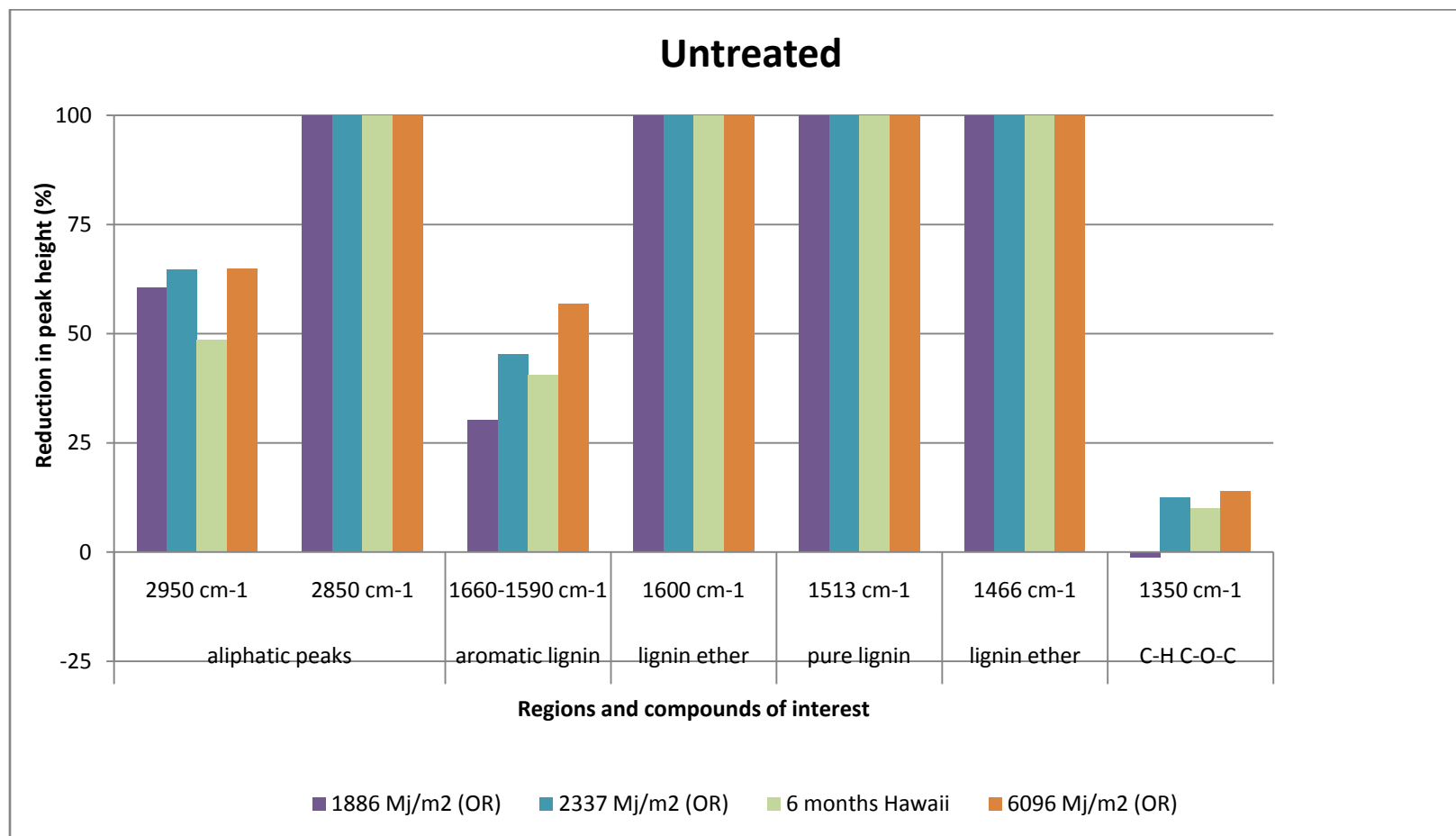


Figure 4.4. Reduction in FTIR peak height on untreated loblolly pine samples exposed to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

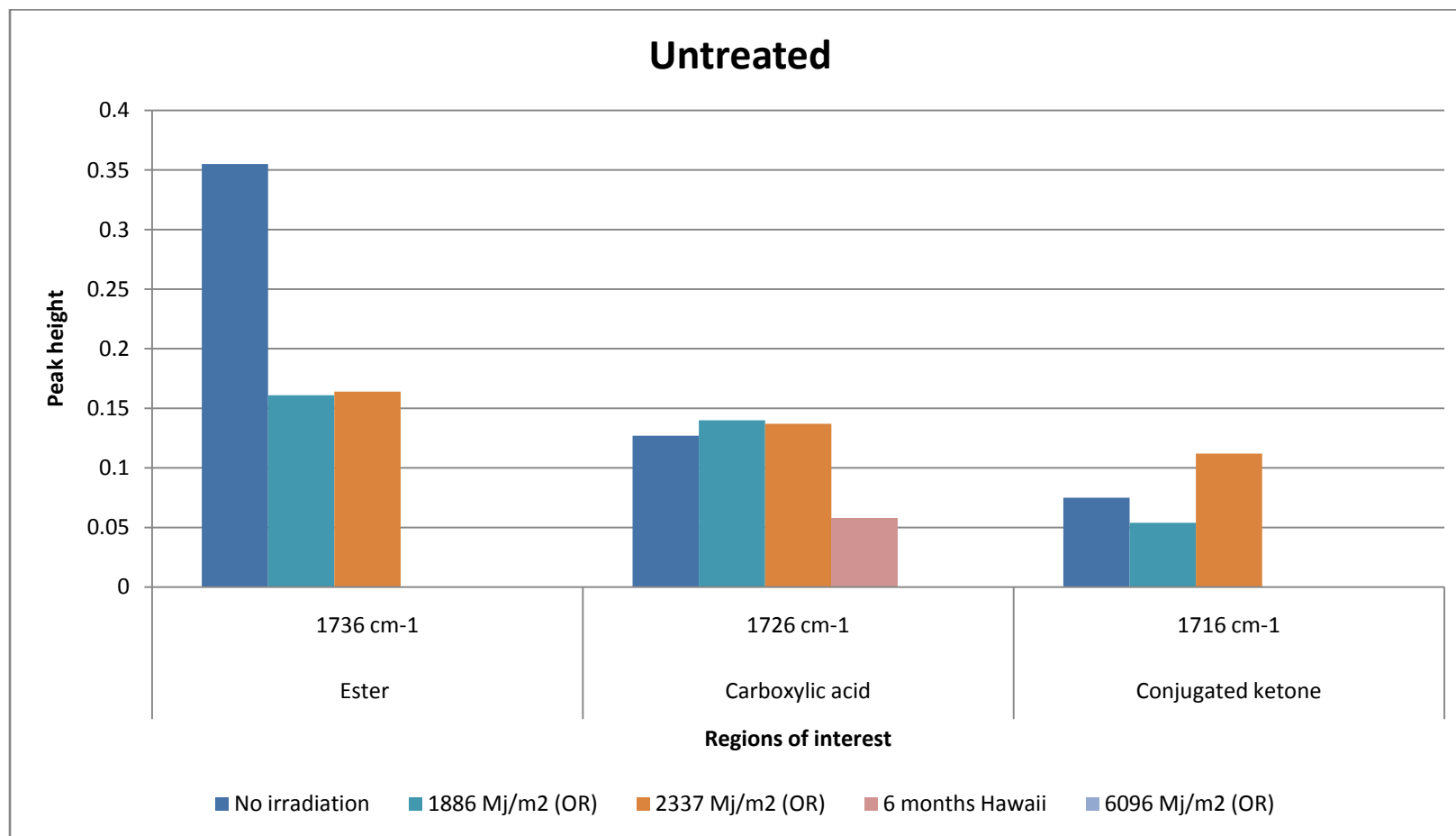


Figure 4.5. FTIR peak heights for the carbonyl region on unexposed loblolly pine samples exposed to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

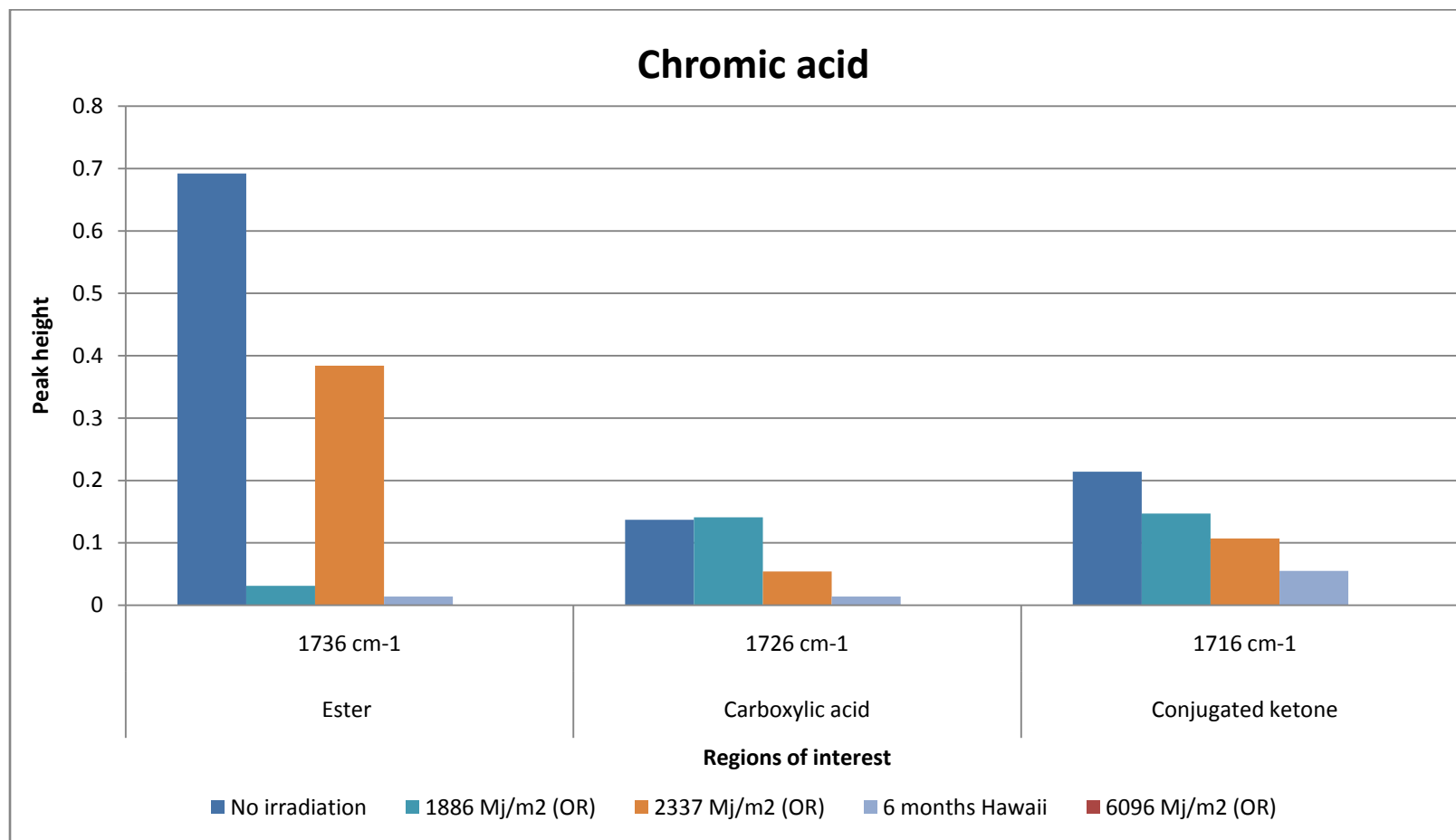


Figure 4.6. FTIR peak heights for the carbonyl region on loblolly pine samples brushed with a 3% chromic acid solution and exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

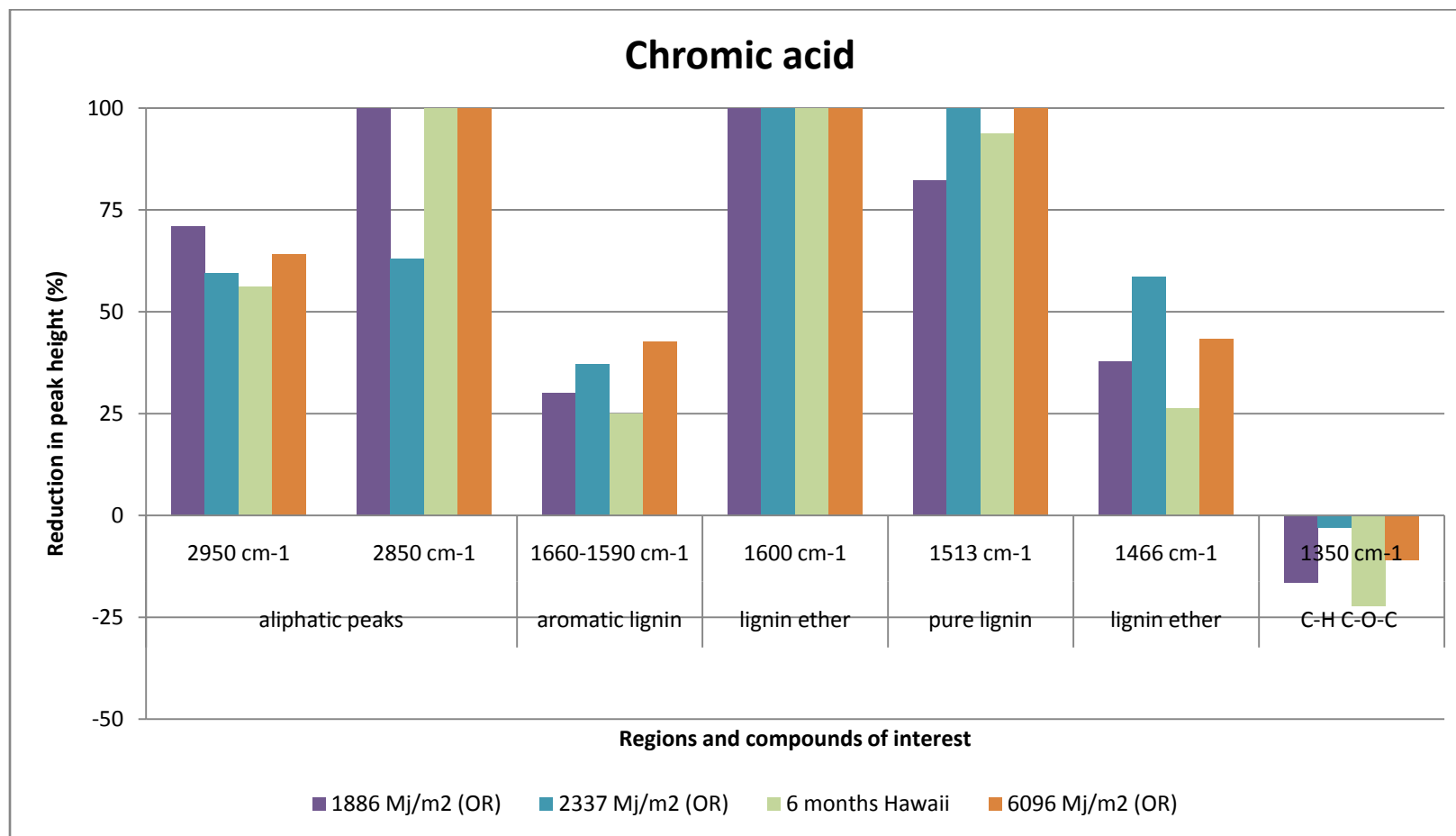


Figure 4.7. Reduction in FTIR peak height on loblolly pine samples brushed with a 3% solution of chromic acid and exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

4.4.2 Effects of weathering on loblolly pine samples treated with pigments

Loblolly pine samples that were impregnated with iron oxide pigments had a red or yellow hue on the surface, similar to the effects of transparent and semi-transparent deck stains. Titanium dioxide treatments did not impart a color to the surface of the samples. As with the untreated and chromic acid treated samples, all pigmented samples experienced significant fungal discoloration when exposed in Hawaii. Despite the microbial damage, pigment treated samples experienced lower color losses than either untreated and chromic acid treated controls (Figure 4.8). This was most evident for iron oxides exposed in Hawaii. The greatest color fastness was achieved with the large particle size iron oxide treatment; however, this may be due to the strong red hue initially imparted by this treatment. These improvements in color fastness suggest that these compounds interacted and protected the pigmented organics and wood polymers from solar radiation.

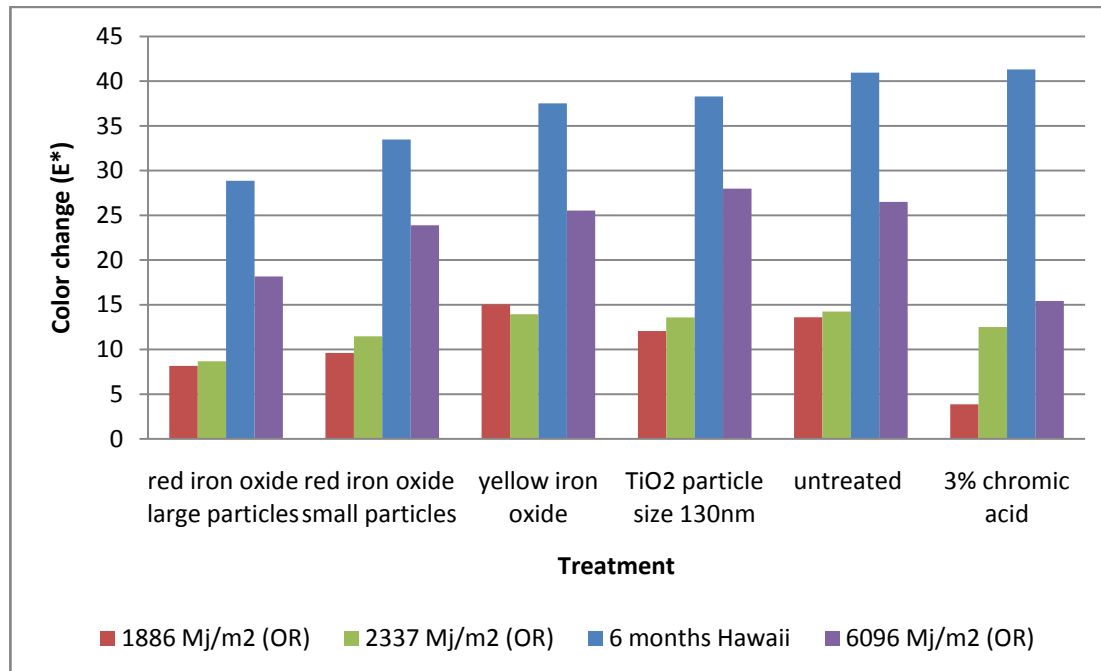


Figure 4.8. Effects of pigments on color change of loblolly pine samples exposed to 1886 to 6096 Mj/m² of irradiation in Eastern Oregon or for six months in Hawaii. Untreated and samples treated with 3% chromic acid are included as negative and positive controls respectively.

No consistent pigment effect on checking was observed at either Hawaii or Eastern Oregon (Figure 4.9). As with the controls, the number of checks that developed on samples in Hawaii was greatly reduced compared to Eastern Oregon. Checking increased in samples treated with the large particle red and yellow iron oxide when compared to the untreated control samples. This was especially evident after 6096 Mj/m^2 of solar irradiation at the Eastern Oregon location. This suggests the surfactant package used to suspend these materials may have contained compounds that facilitated moisture absorption and checking.

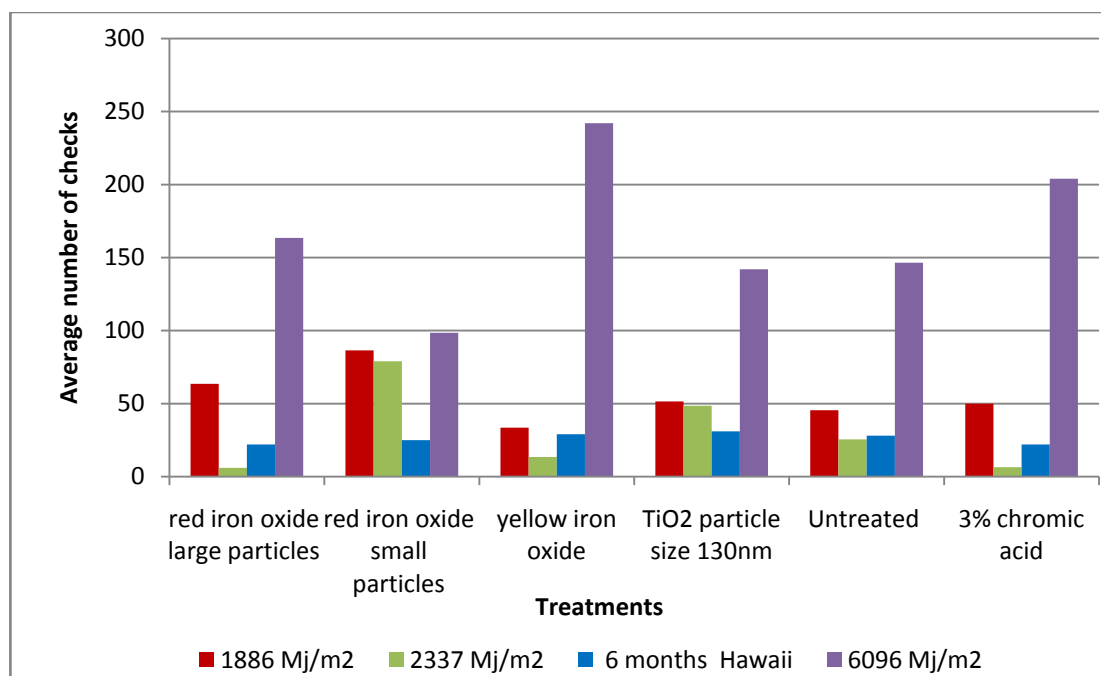


Figure 4.9. Number of surface checks present on samples treated with different inorganic pigment formulations and then exposed to 1886 to 6096 Mj/m^2 of solar radiation in Eastern Oregon or for six months in Hawaii.

FTIR analysis of exposed samples indicated that pigment treated samples from either location experienced similar changes in chemical composition that was dominated by lignin loss from the surface (Figures 4.10-13). FTIR analysis suggested that the aliphatic regions were not as severely degraded in Hawaii as in Eastern Oregon. This suggests that some extractives remained on the surface of the Hawaiian samples. In addition, further analysis of the lignin peaks showed that samples exposed in Hawaii lost less of the aromatic component

as demonstrated by the stronger peak at $1660\text{-}1590\text{ cm}^{-1}$ for all of the treatments. The lignin difference between the sites may be caused by the rapid removal of degraded materials from the surface of the samples exposed to frequent rain events in Hawaii or because microbial growth on the surface consumed the decomposition products. Deconvolution of the carbonyl region also suggested that exposing samples in different climates had little outcome on the chemical degradation of the wood (Figures 4.14-17). No differences in this portion of the spectra were noted for samples treated with titanium dioxide, yellow iron oxide or the large particle size red iron oxide. Conversely, the carbonyl region on samples treated with the small particle size red iron oxide pigment indicated that hemicelluloses and cellulose were preserved on the surface of the samples exposed in Hawaii (as indicated by peaks located at 1736 and 1716 cm^{-1} respectively). Given the higher microbial activity in Hawaii, these results suggest that small particle iron oxide protected lignin to a greater extent than other systems.

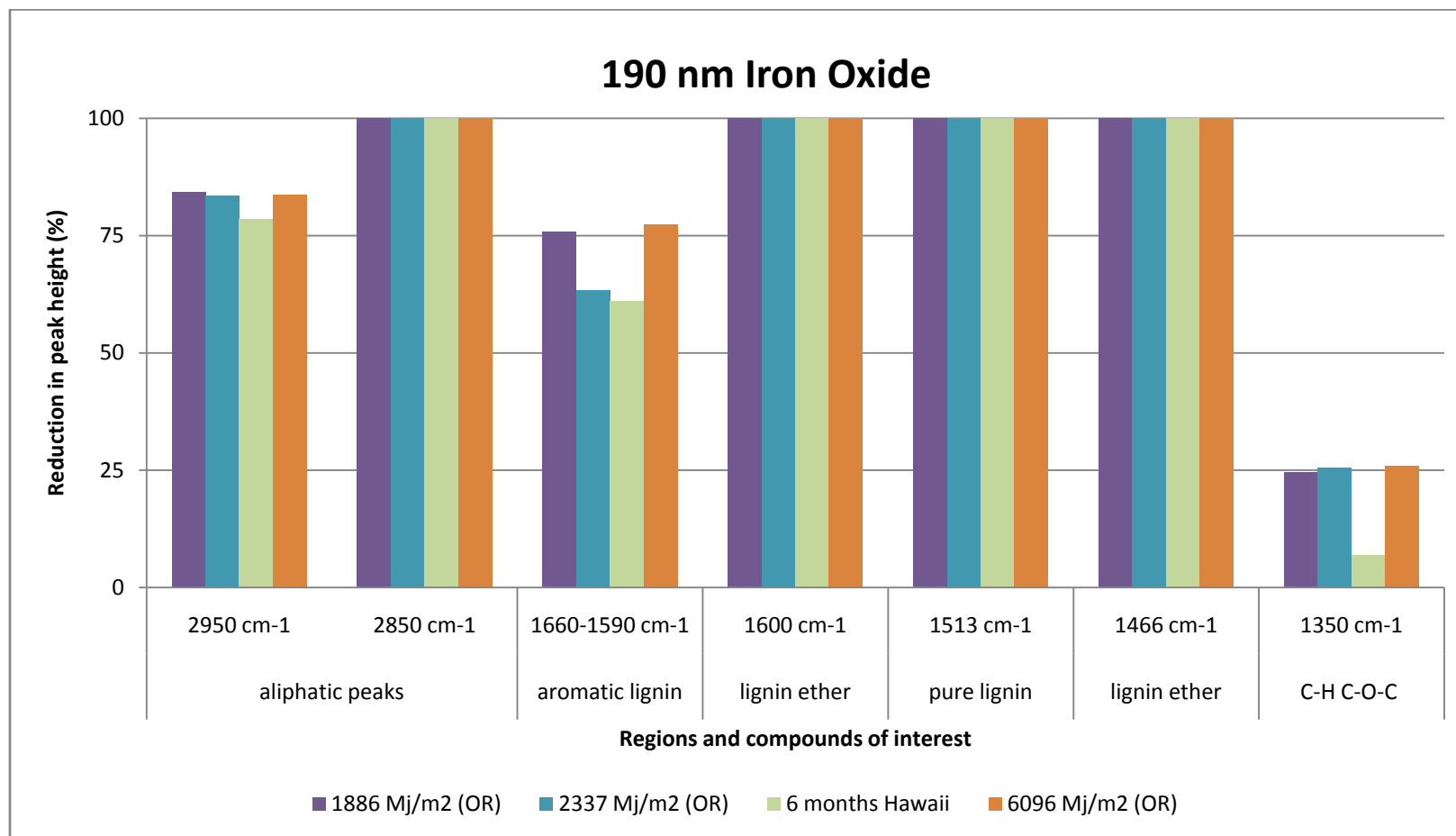


Figure 4.10. Reduction in FTIR peak height on loblolly pine samples impregnated with a 1000 ppm suspension of 190 nm red iron oxide particles and then exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

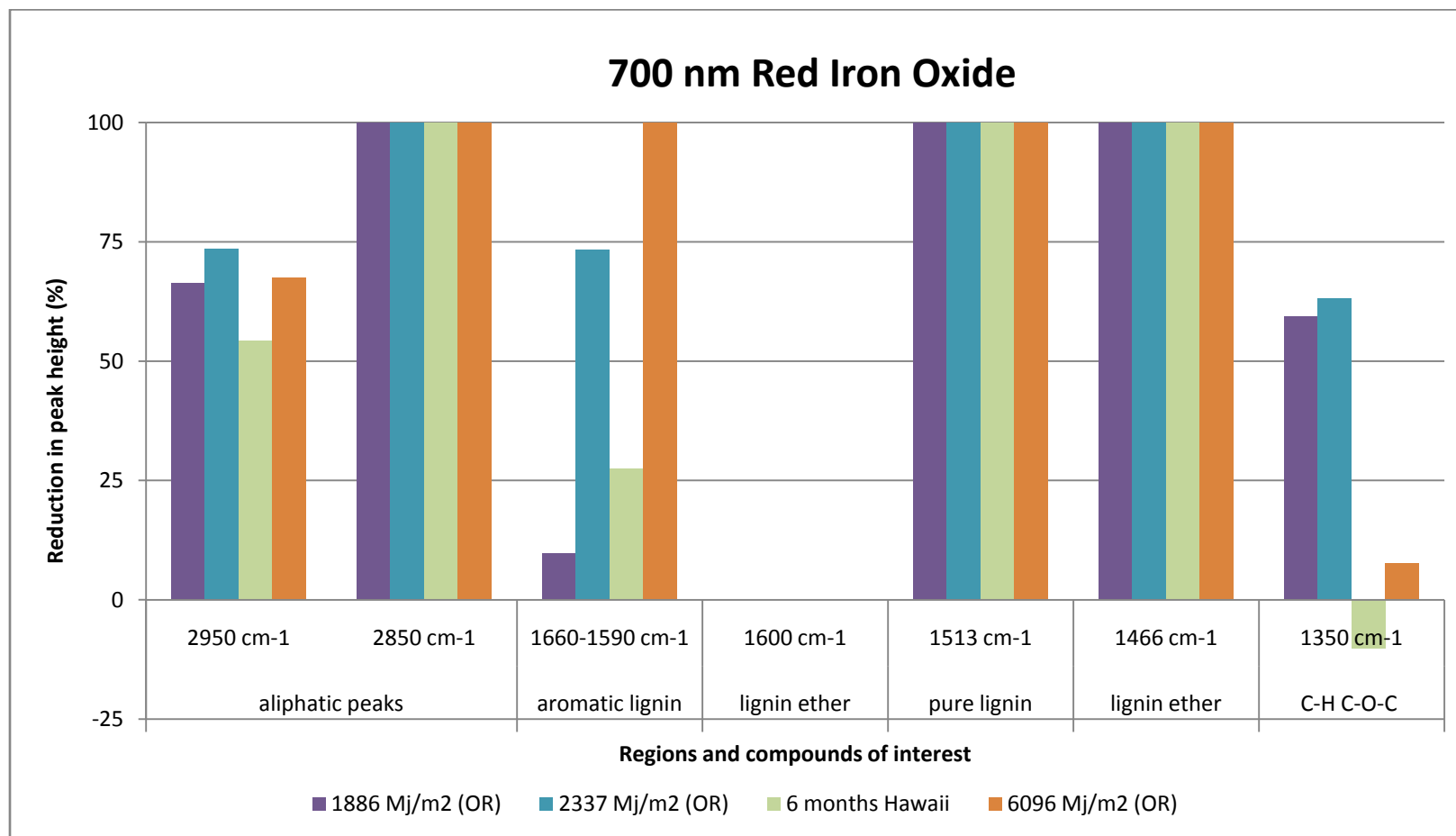


Figure 4.11. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm suspension of 700 nm red iron oxide and exposed outdoors to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

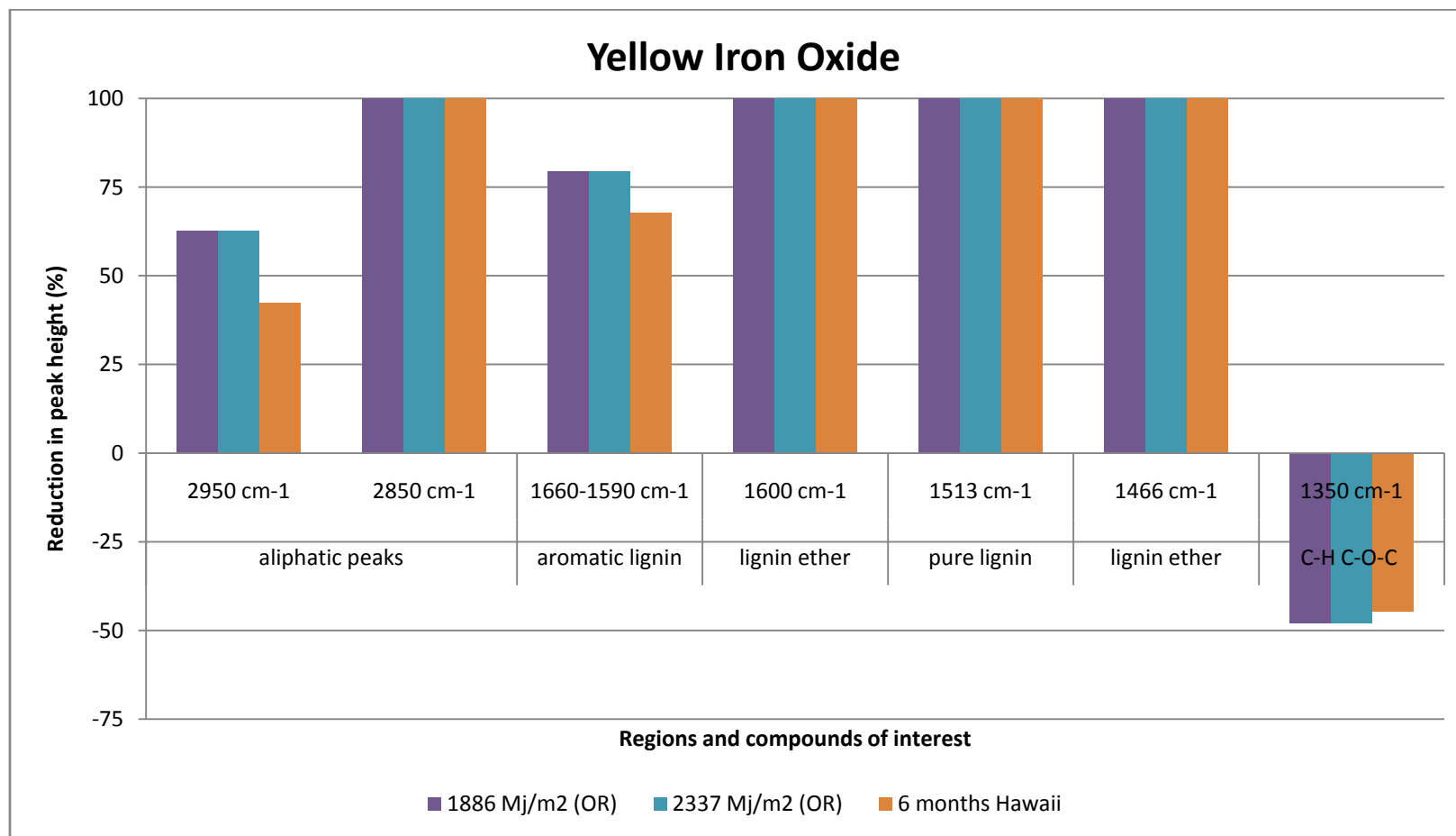


Figure 4.12. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm suspension of yellow iron oxide and exposed outdoors to irradiation dosages ranging from 1886 to 2337 Mj/m² in Eastern Oregon or for six months in Hawaii.

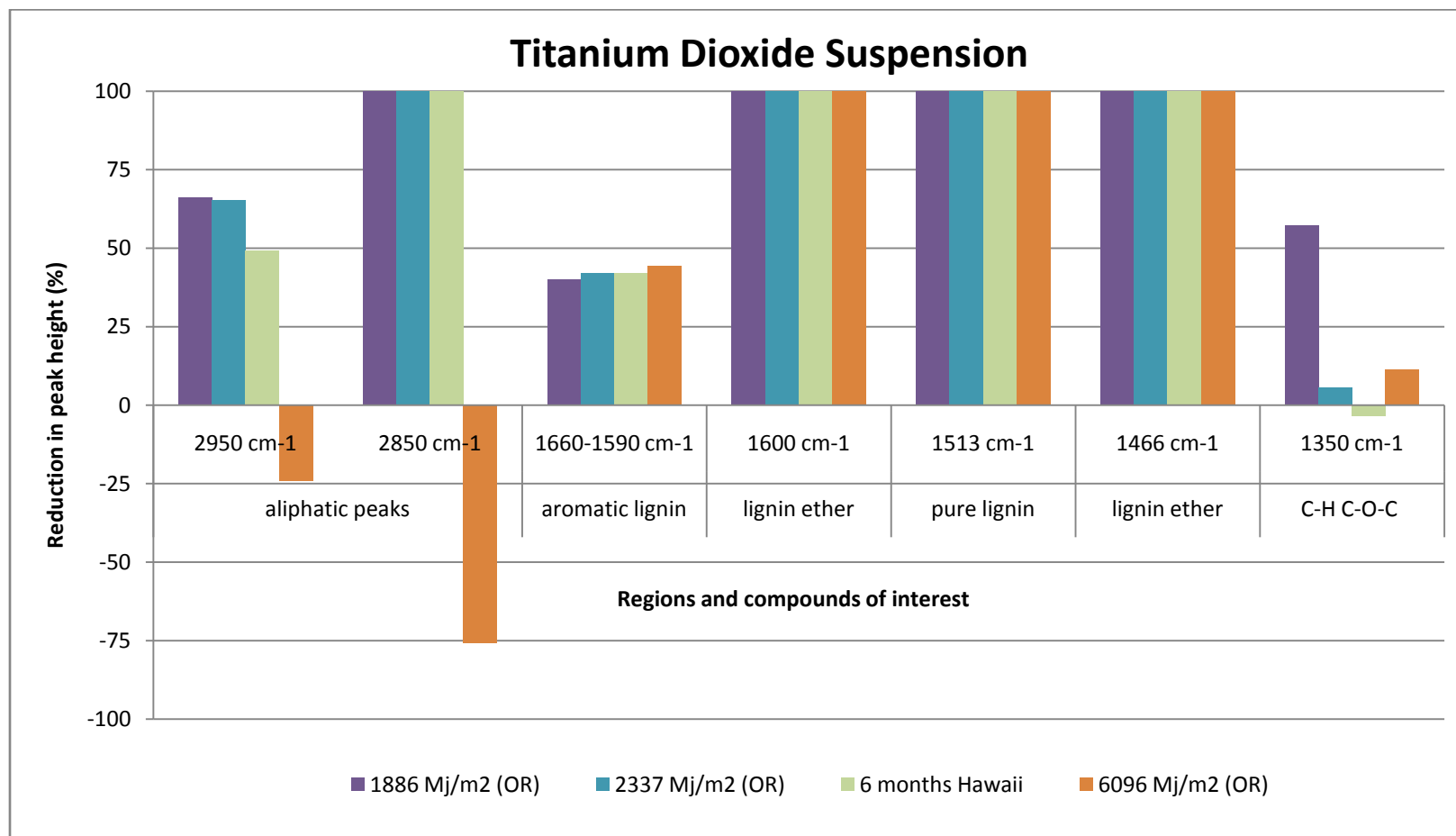


Figure 4.13. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm suspension of titanium dioxide and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

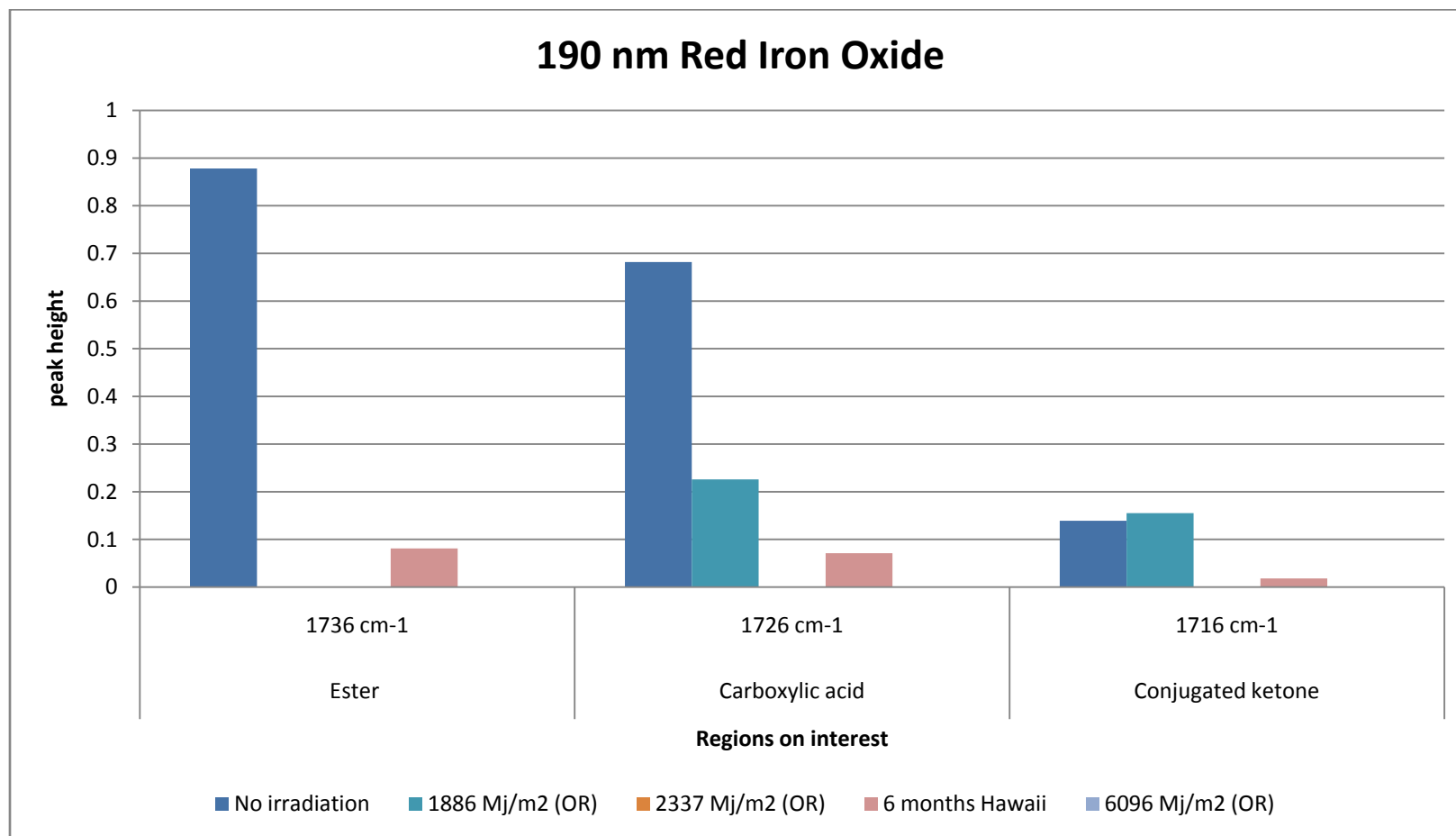


Figure 4.14. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of red iron oxide particles and exposed to irradiation doses ranging from 1886 to 6096 Mj/m² in Eastern Oregon or to six months in Hawaii.

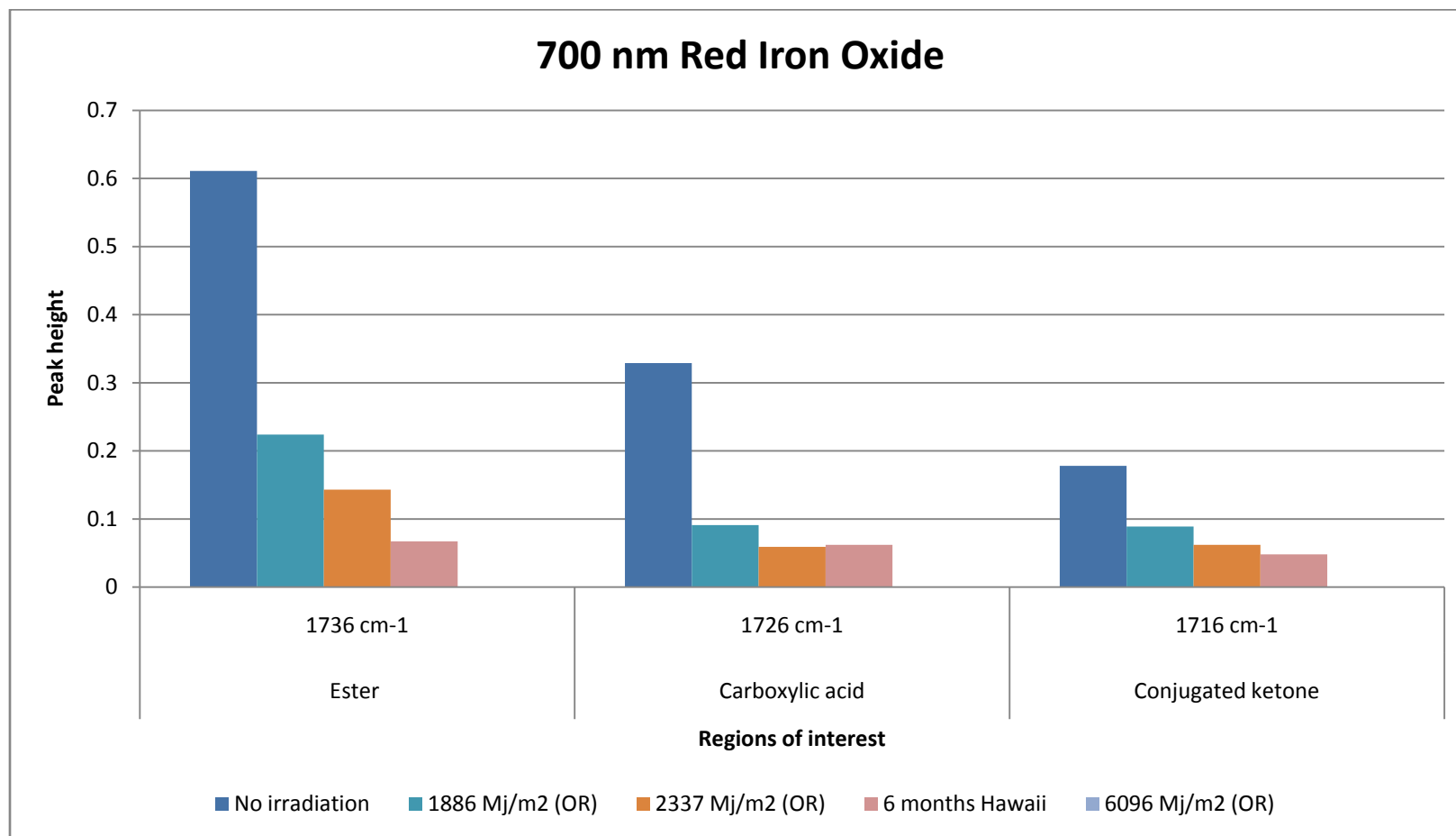


Figure 4.15. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of 700 nm red iron oxide and exposed to irradiation doses ranging from 1886 to 6096 Mj/m² in Eastern Oregon or to six months in Hawaii.

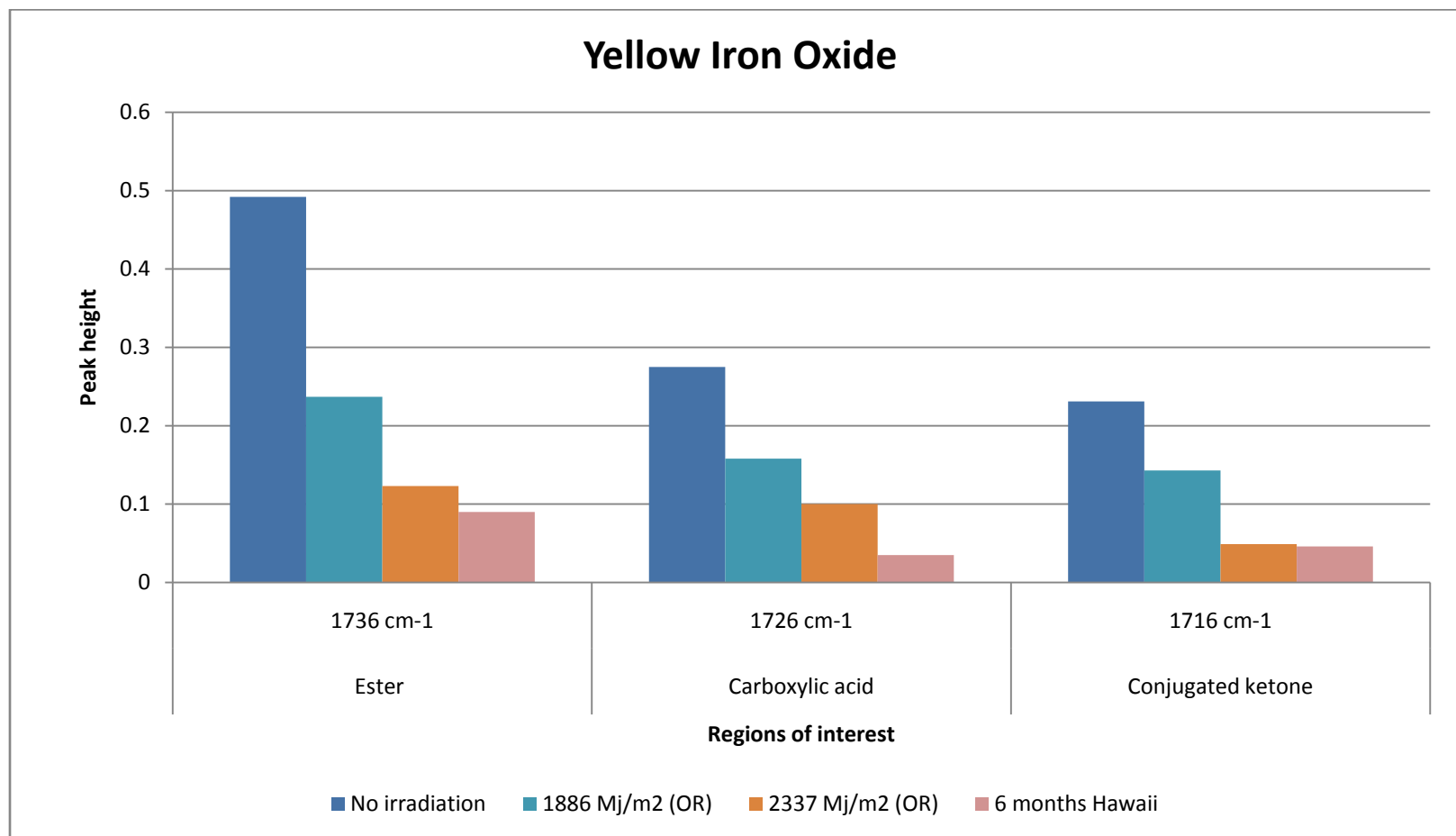


Figure 4.16. Peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of yellow iron oxide particles and exposed to irradiation doses ranging from 1886 to 6096 Mj/m² in Eastern Oregon or to six months on Hawaii.

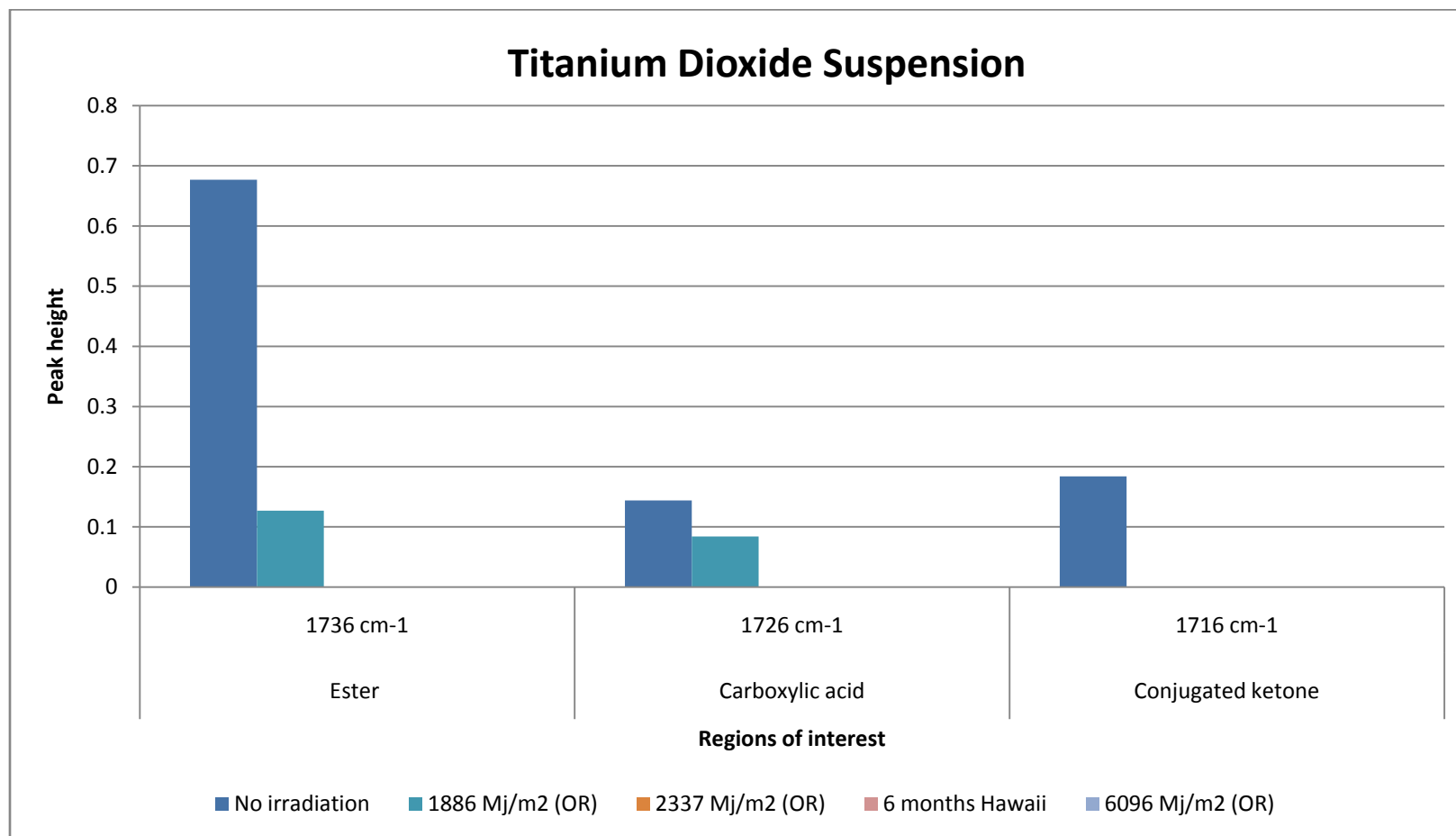


Figure 4.17. Peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm suspension of titanium dioxide particles and exposed to irradiation doses ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

4.4.3 Effects of weathering on loblolly pine samples treated with water repellents

Water repellents were included in the study to evaluate their effect on checking behavior on exterior exposures. Surprisingly, petroleum wax and silicate-based compounds had positive effects on color fastness (Figure 4.18). While discoloration at both locations was still severe, water repellents were associated with slight reductions in discoloration under tropical conditions, compared to untreated control samples cut from the same parent board. The benefit was greatest when samples were treated with long chain petroleum waxes. These same compounds have also been shown to reduce lignin degradation at the Eastern Oregon location, yet the reason for this improvement is unknown (Schauwecker et al 2011).

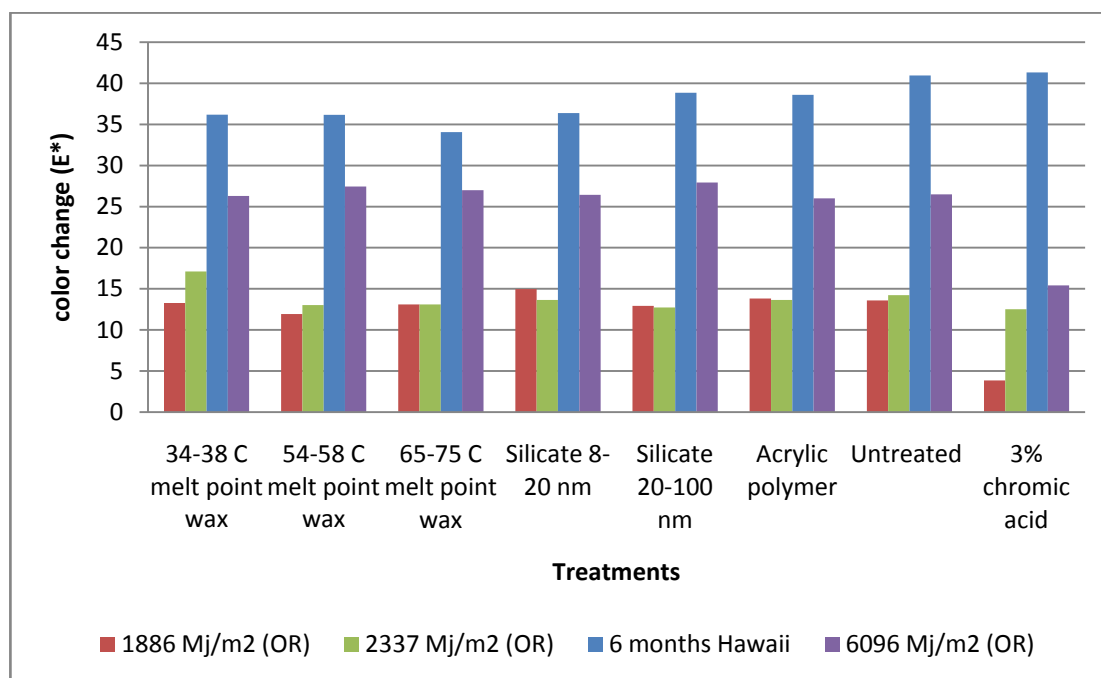


Figure 4.18. Effects of water repellents on color fastness of loblolly pine samples exposed to 1886 to 6096 Mj/m² of irradiation in Eastern Oregon or for six months in Hawaii. Untreated and samples treated with 3% chromic acid are included as negative and positive controls.

High melt point waxes reduced the number of checks that developed on the samples, especially when exposed in the desert, yet water repellents did not significantly reduce the amount of checking that occurred under wet tropical conditions (Figure 4.19). The lack of effect may reflect the susceptibility of these waxes to microbial degradation, which would be

greater in Hawaii. In addition, silicates, regardless of their particle size, provided little protection from checking. This was unexpected since these compounds are commonly used to waterproof concrete and other masonry building material (Aitken and Litvan 1989).

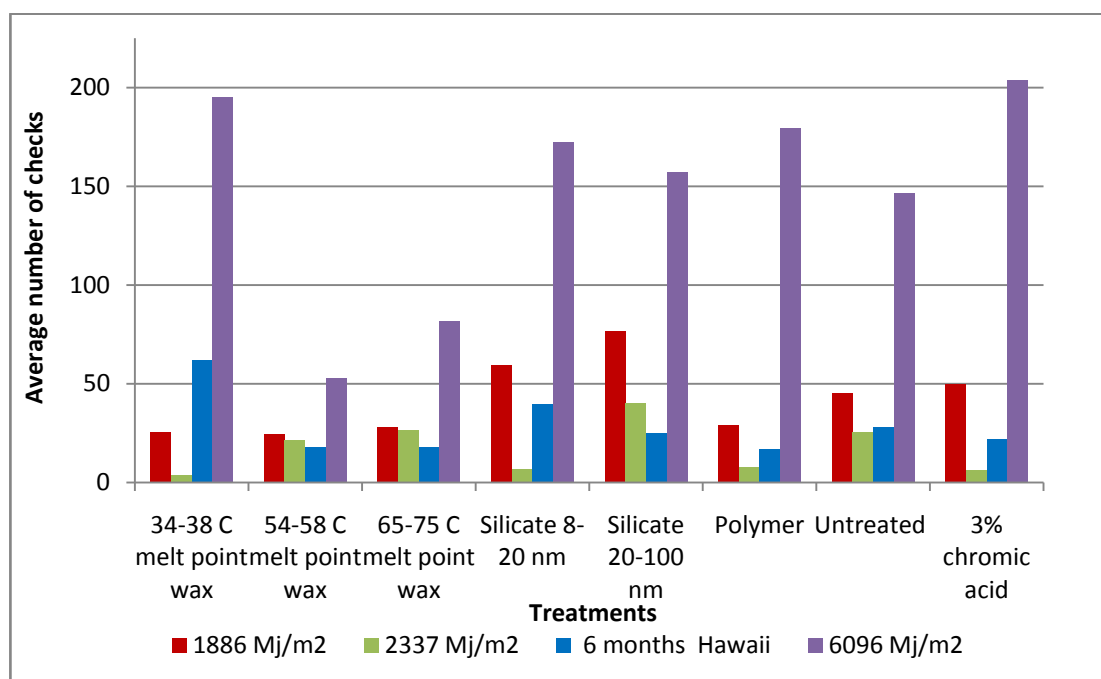


Figure 4.19. Number of surface checks on samples treated with different water repellents and exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

FTIR analyses of the wax silicate based systems could not be conducted, due to interferences between the ATR crystal and the silicates.

FTIR analysis showed that aliphatic peaks were significantly reduced over time in samples treated with an emulsion containing a 34-38 °C melt point wax (Figure 4.20). These losses were less severe when samples were exposed to tropical conditions. The pure lignin peak was completely absent after weathering regardless of location, although the spectra indicated that concentrations of the aromatic components of lignin were higher after exposure in Hawaii than in Eastern Oregon. Deconvolution of the carbonyl region indicated that esters, carboxylic acids and conjugated ketones were completely degraded after one year (6096 MJ/m²) in Eastern Oregon (Figure 4.21).

Loblolly pine samples treated with a water repellent formulated with a 54-58 °C melt point wax also experienced significant peak height losses in the aliphatic, aromatic and pure lignin regions of the FTIR spectra (Figure 4.22). Losses in the aliphatic and aromatic lignin regions exceeded those observed in the samples treated with the shorter chain wax. Losses were lower in samples exposed under tropical conditions. Changes in the carbonyl region of samples treated with the 54-58 °C melt point wax were similar to those seen in the samples treated with the short chain waxes (Figure 4.23). However, the data indicated that larger peak height reductions occurred for the carboxylic acid and conjugated ketone components of these samples when exposed in Hawaii. This suggests that cellulose degradation accelerated and more of the lignin degradation products were lost from the surface under tropical conditions. This may reflect concurrent physical and biological degradation under the tropical conditions.

Degradation in samples treated with a long chain length wax differed from the other treatment in that the aliphatic region experienced little loss in intensity, regardless of location or exposure duration. These results indicate that the wax was not lost from the surface over time (Figure 4.24). In addition, FTIR spectra of these samples indicated that lignin loss was more significant for the samples exposed in Hawaii and generally increased with exposure. This trend was also evident in the carbonyl region of the spectra (Figure 4.25), suggesting that this treatment had no influence on cellulose degradation.

FTIR analysis of samples treated with a 4000 ppm emulsion of acrylic polymer suggested that this compound may have stabilized the aliphatic compounds. In addition, FTIR analysis of samples exposed in Hawaii suggested that this compound may also provide some lignin protection (Figure 4.26). However, this effect was not observed in samples exposed in Eastern Oregon. The difference suggests that this may be a site specific effect. Investigation of the carbonyl region indicated that the conjugated ketone peak was stabilized after an initial reduction, suggesting that, while a substantial amount of the cellulose was initially degraded, a steady state was reached after 2337 MJ/m² of radiation (Figure 4.27).

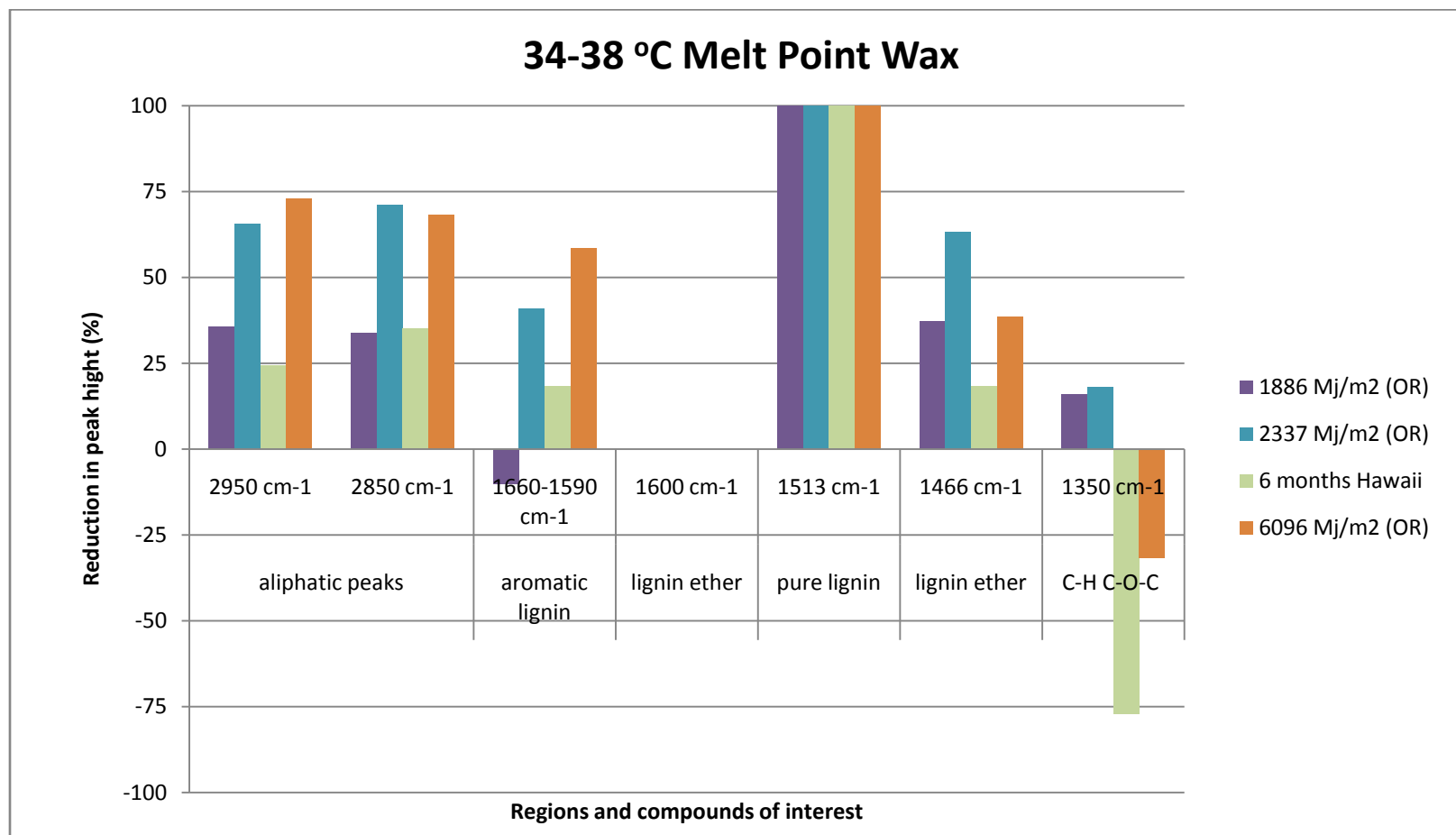


Figure 4.20. Reduction in FTIR peak height for loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 34-38 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

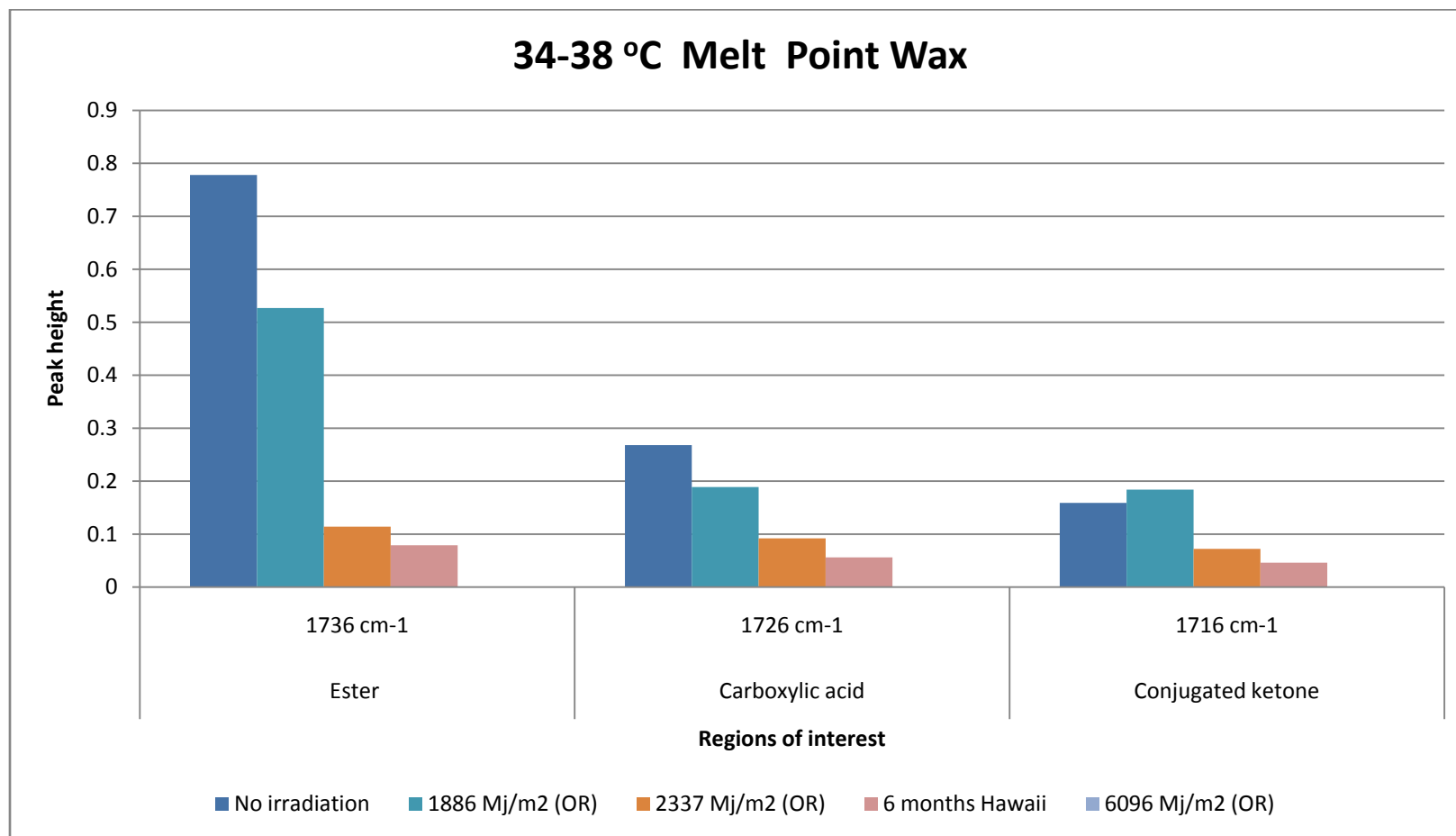


Figure 4.21. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 34-38°C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

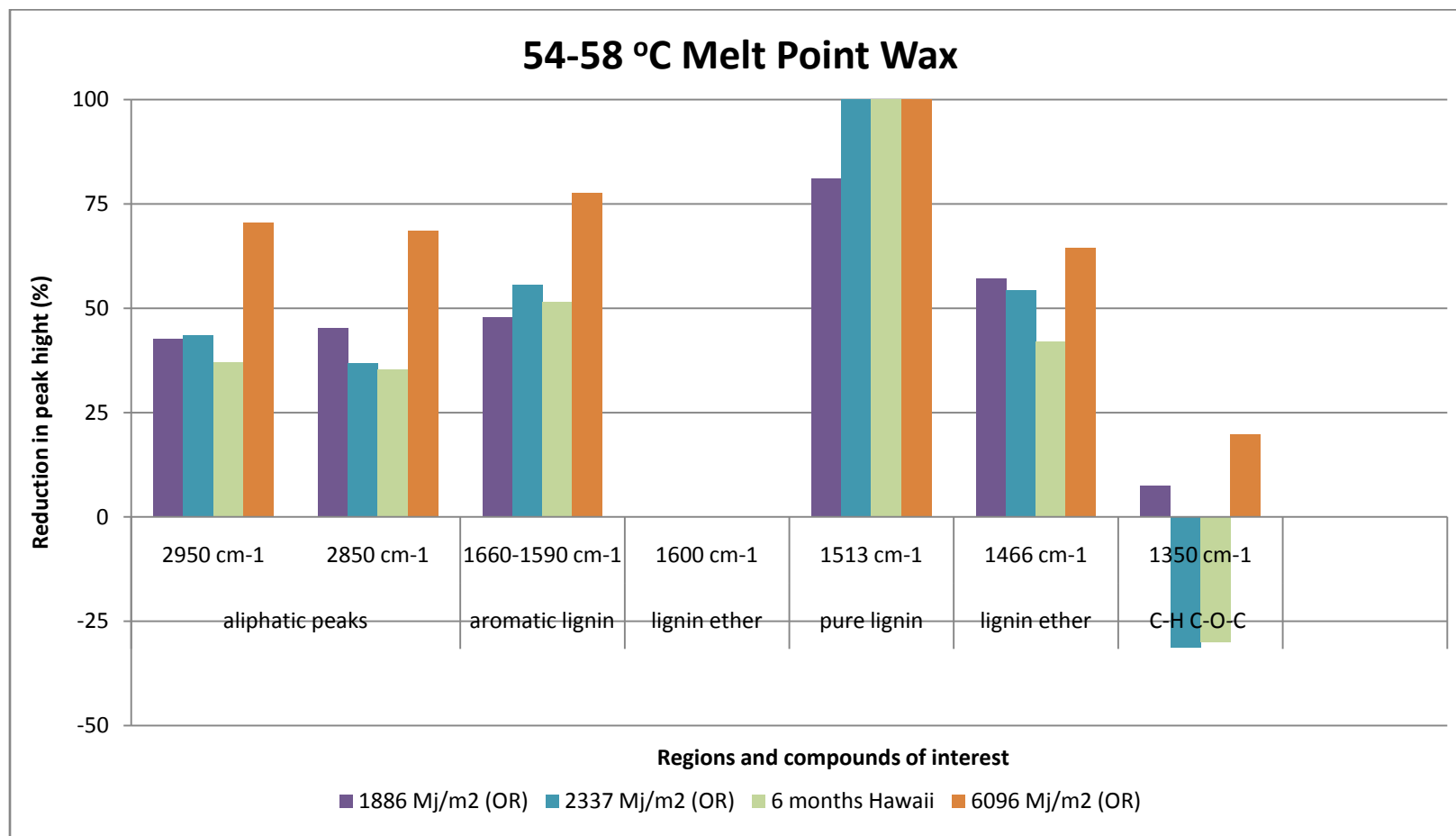


Figure 4.22. Reductions in FTIR peak height for loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

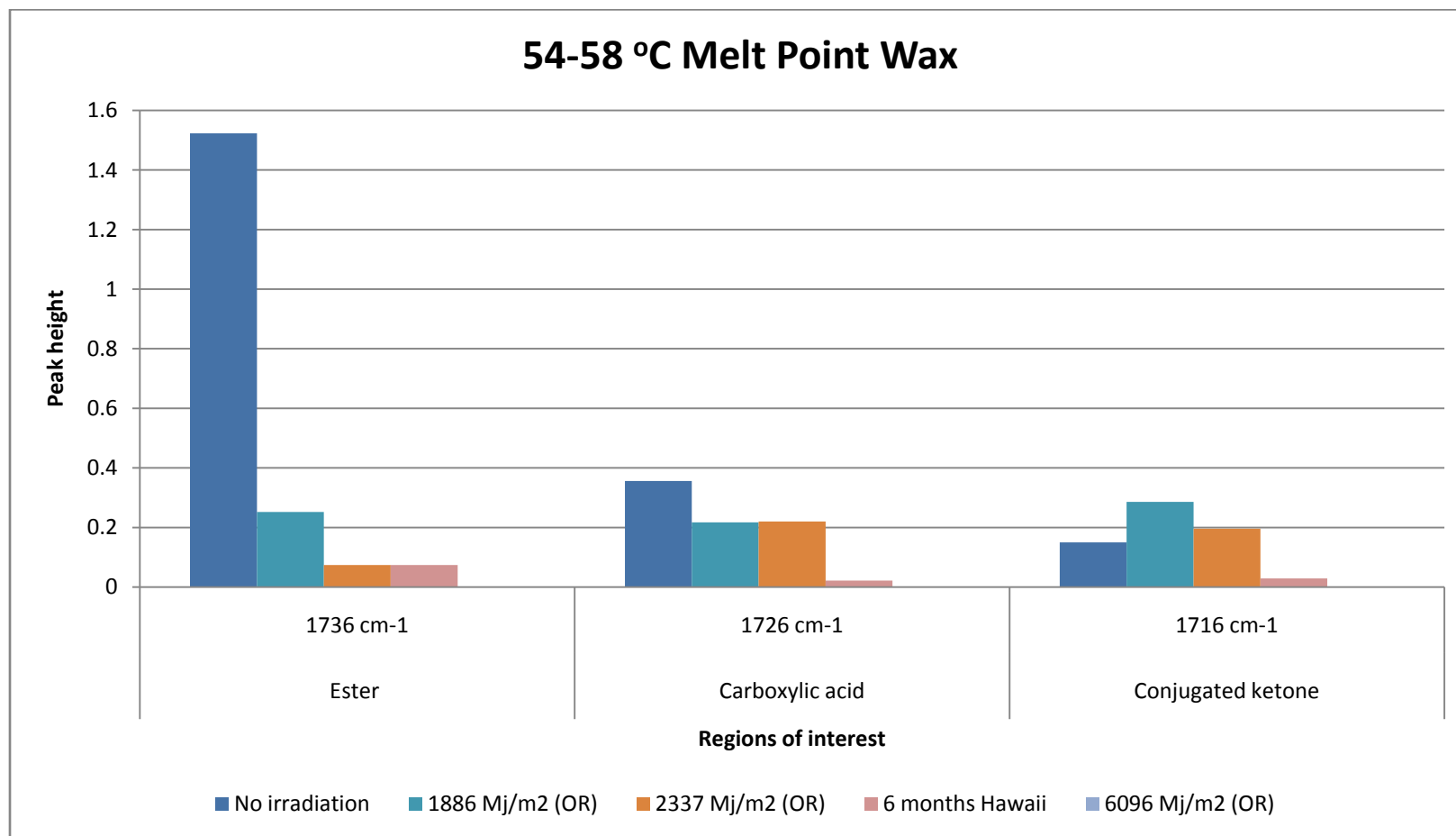


Figure 4.23. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 54-58 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

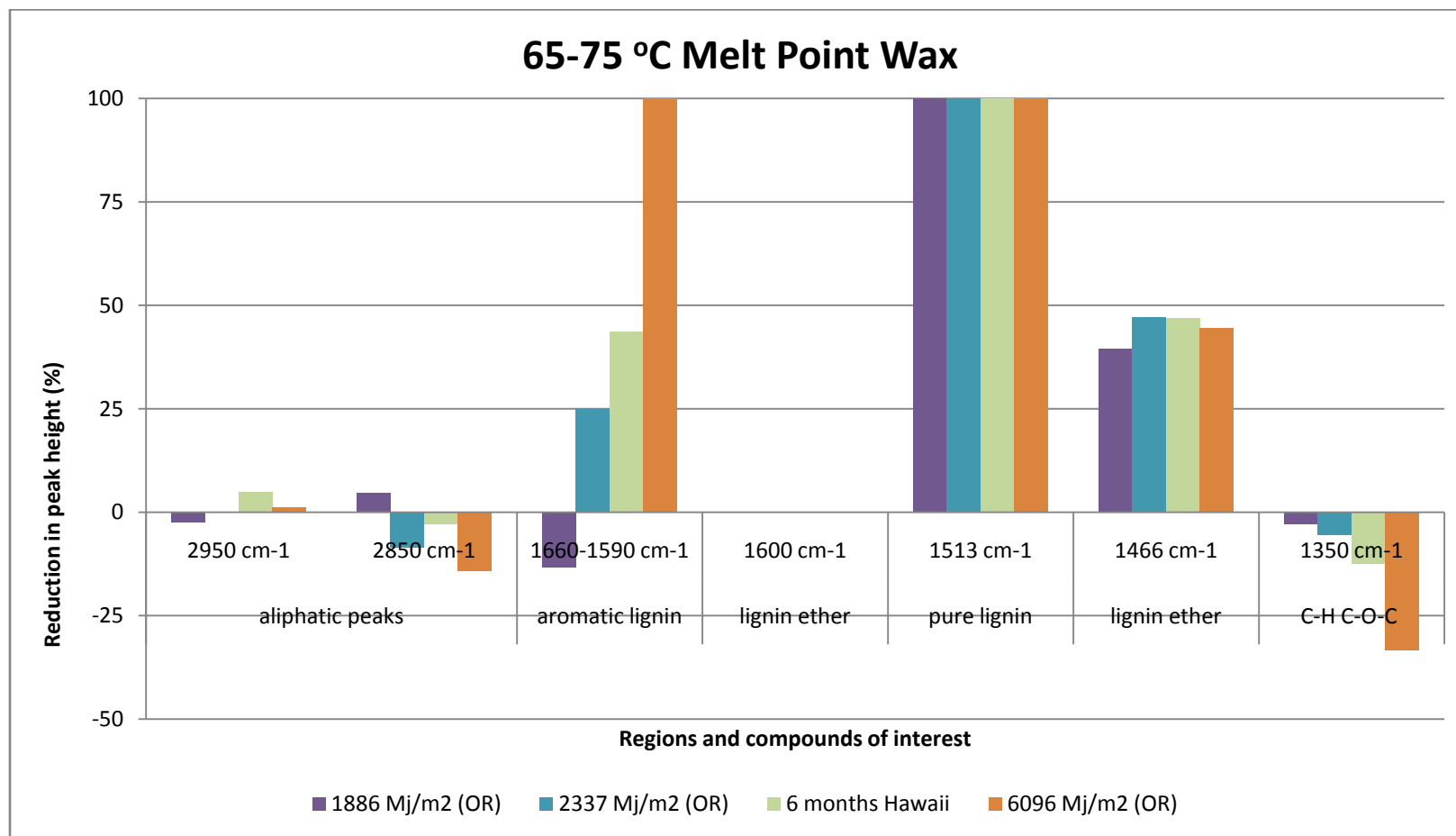


Figure 4.24. Reductions in FTIR peak height for loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 65-75 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

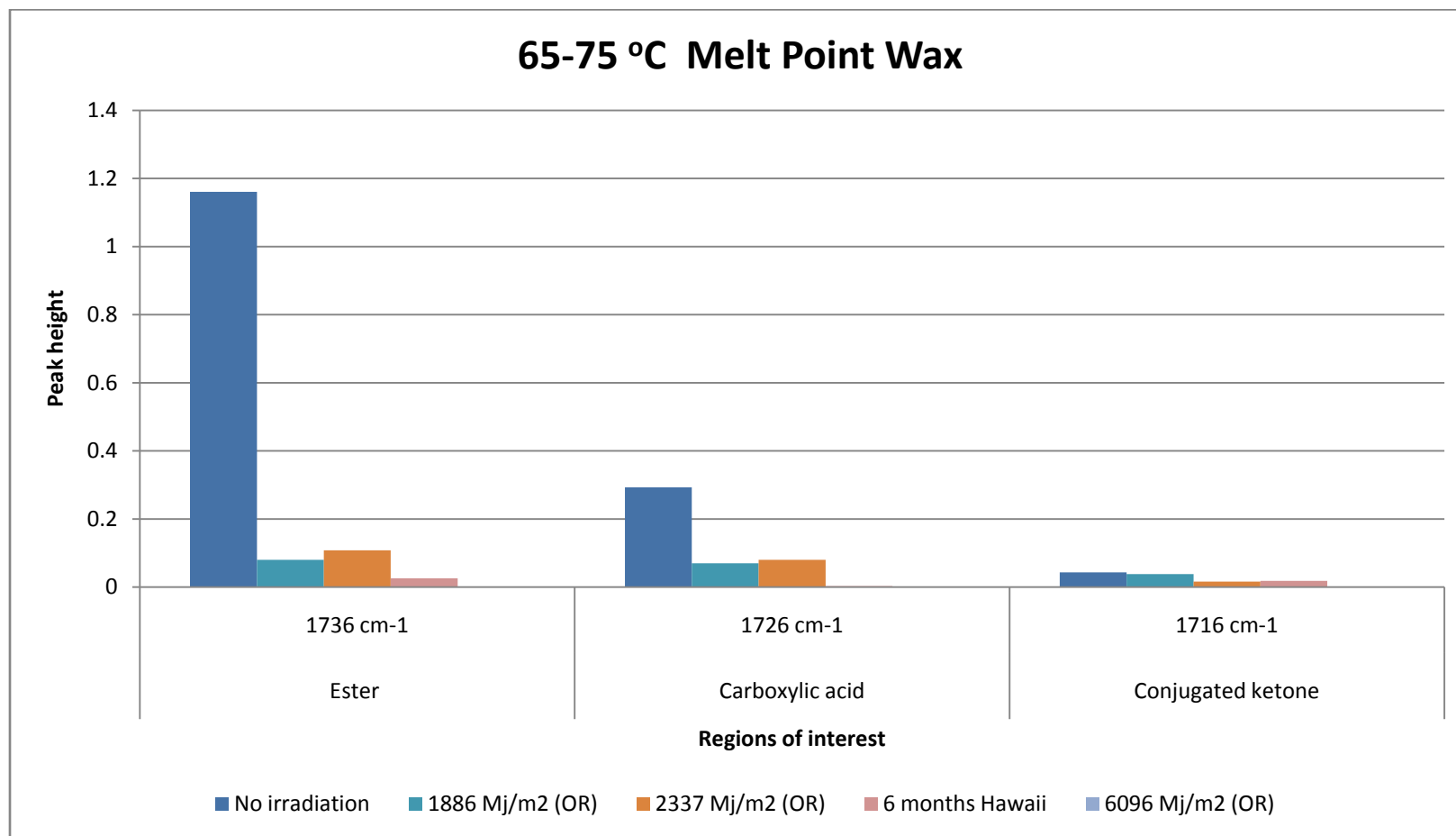


Figure 4.25. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 20,000 ppm wax in water emulsion with a melt point of 65-75 °C and exposed outdoors to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

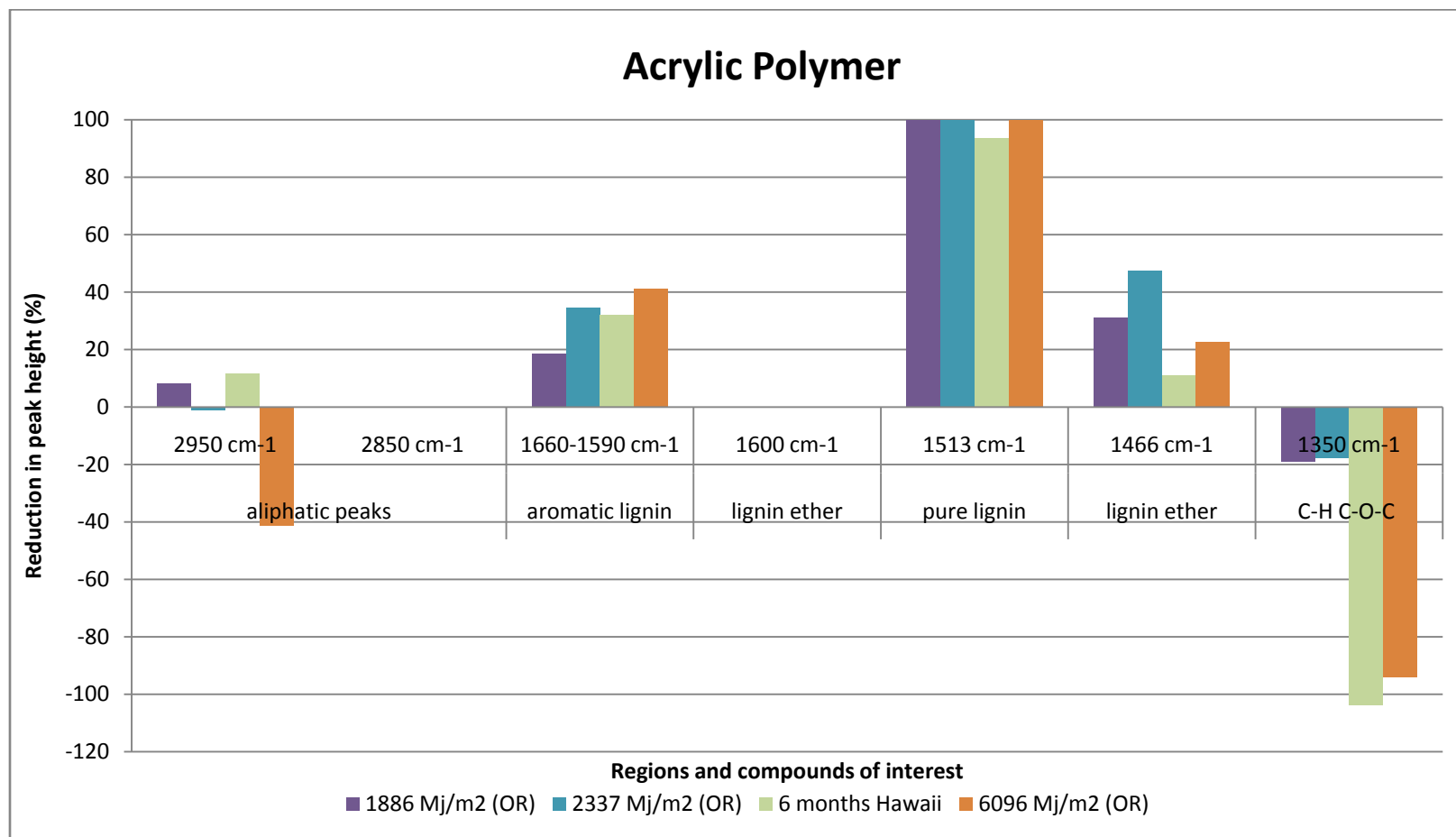


Figure 4.26. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

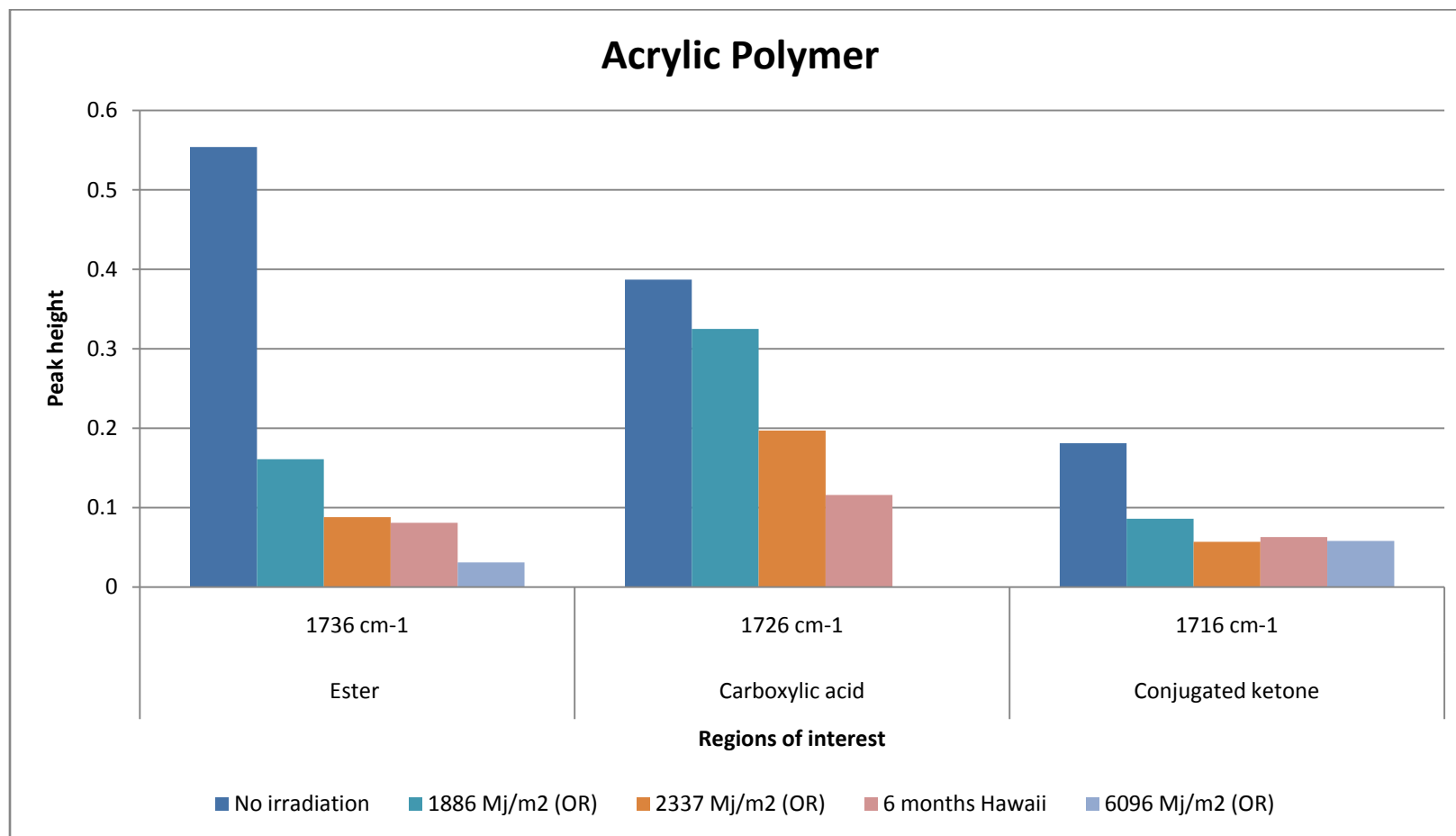


Figure 4.27. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 4000 ppm solution of acrylic polymer and exposed outdoors to irradiation dosages of ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

4.4.4 Effects of organic UV inhibitors on weathering on loblolly pine samples

Organic UV inhibitors provided some protection against color fading to loblolly pine at both exposure locations (Figure 4.28). However, protection at the levels tested was less than that provided by the chromic acid treatment. The protection was limited to less than one year of exposure in the high desert of Oregon, suggesting that the compounds either degraded over time or were removed from the surface. Organic UV inhibitors had little effect on the number of checks that developed over time (Figure 4.29). The greatest protection was provided by the hydroxyphenylbenzol UV absorber, especially at the early stages of exposure in the Oregon high desert. While FTIR analysis of these samples suggested reduced wood polymer degradation, the oilborne nature of this compound may also have improved performance by reduced wetting.

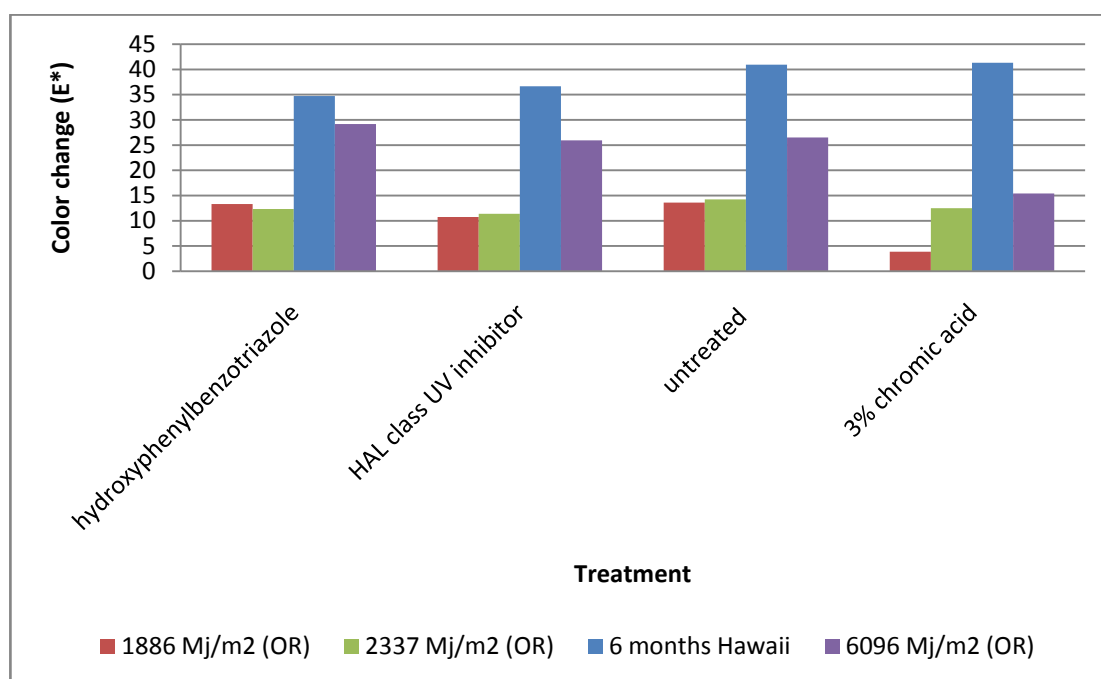


Figure 4.28. Effects of organic UV stabilizers on color fastness for loblolly pine samples exposed to outdoor conditions in Eastern Oregon or Hawaii. Untreated and 3% chromic acid treated samples are included as negative and positive controls.

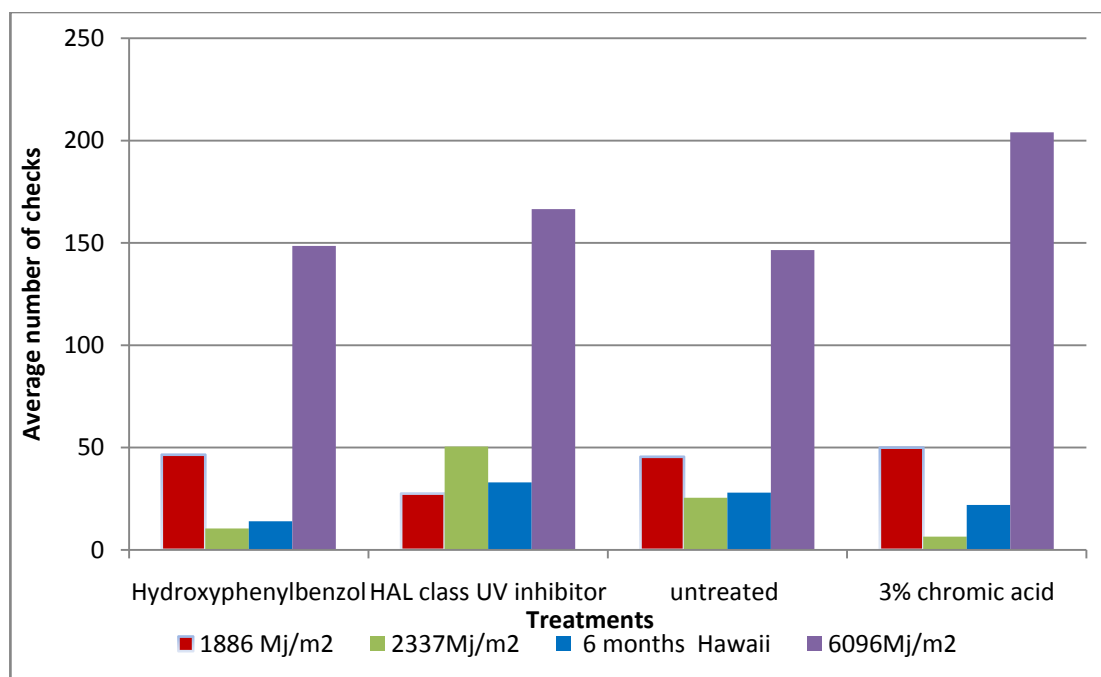


Figure 4.29. Number of surface checks present in samples treated with different organic UV stabilizers and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

Hydroxyphenylbenzol UV light absorbers provided the most protection of all of the treatments against polymer degradation when samples were exposed under desert conditions (Schauwecker et al 2011). This compound also provided greater protection compared to the free radical scavenger (HAL) when exposed under tropical conditions. This treatment functions by absorbing the energy contained in the UV spectrum, and preventing free radical production that initiates the degradation process. This protects both the aliphatic region and aromatic components of lignin, as evidenced by the FTIR peaks at 1660-1590 cm⁻¹ (Figure 4.30). Carboxylic acid was still present on the surface of the samples after six months of exposure under tropical conditions, indicating that lignin was still present on the surface although it was still being degraded by the weathering process. Examination of the carbonyl region indicated that hemicelluloses and cellulose were degraded further when exposed in Hawaii, compared to analysis of the samples exposed to 2337 Mj/m² in Eastern Oregon (Figure 4.31). The organic free radical scavenger was still associated with substantial losses in the aliphatic region, but the samples exposed in Hawaii experienced lower losses of the

compounds than similar samples exposed in Oregon (Figure 4.32). The peak found at 1660-1590 cm^{-1} remained strong for the samples exposed under tropical conditions suggesting that more aromatic lignin components remained on the wood surface after weathering. However, the pure lignin peak had been completely degraded, suggesting that the lignin was present as fragments. Furthermore, the data indicates that carboxylic acid was still present on the surface of the samples exposed in the tropics, suggesting that some lignin components were still being degraded. Deconvolution of the carbonyl region indicated that the degradation was further advanced in Hawaii. This was expected, given that combination of higher solar radiation and microbial activity compared to the Oregon samples harvested after 2337 Mj/m^2 of exposure (Figure 4.33).

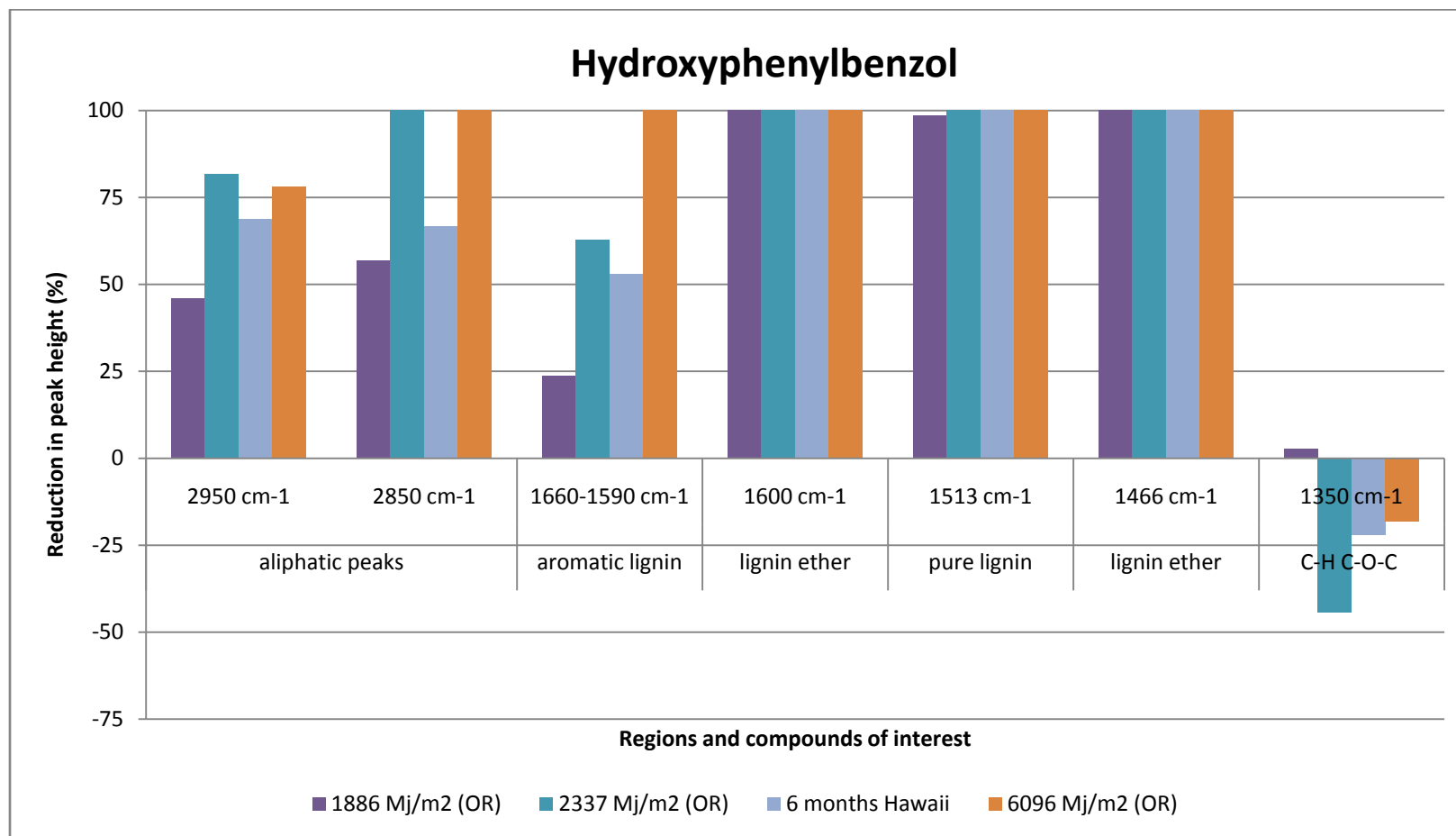


Figure 4.30. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

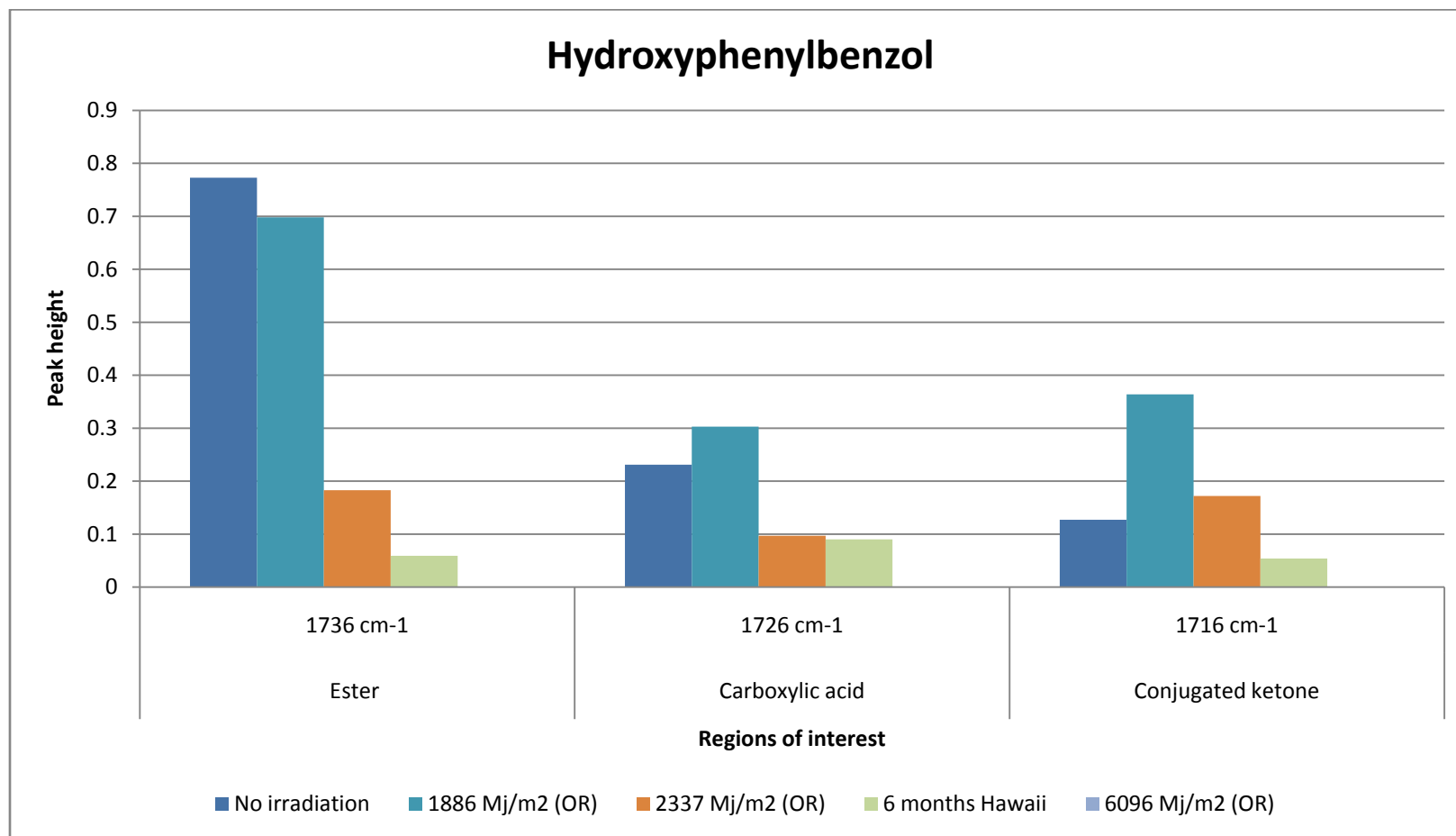


Figure 4.31. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm solution of hydroxyphenylbenzotriazole class UV absorber and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

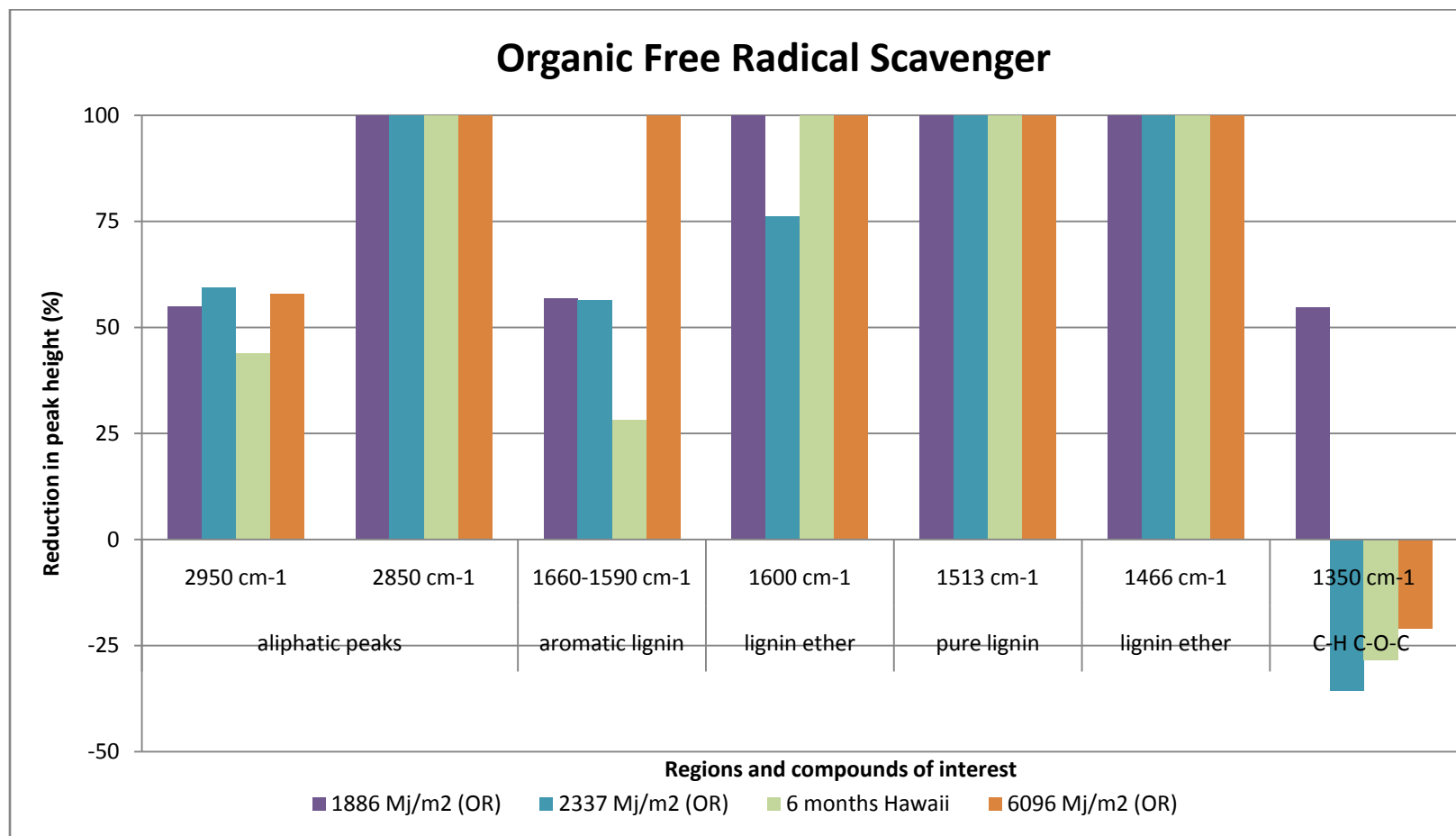


Figure 4.32. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 1000 ppm solution of an organic free radical scavenger and exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

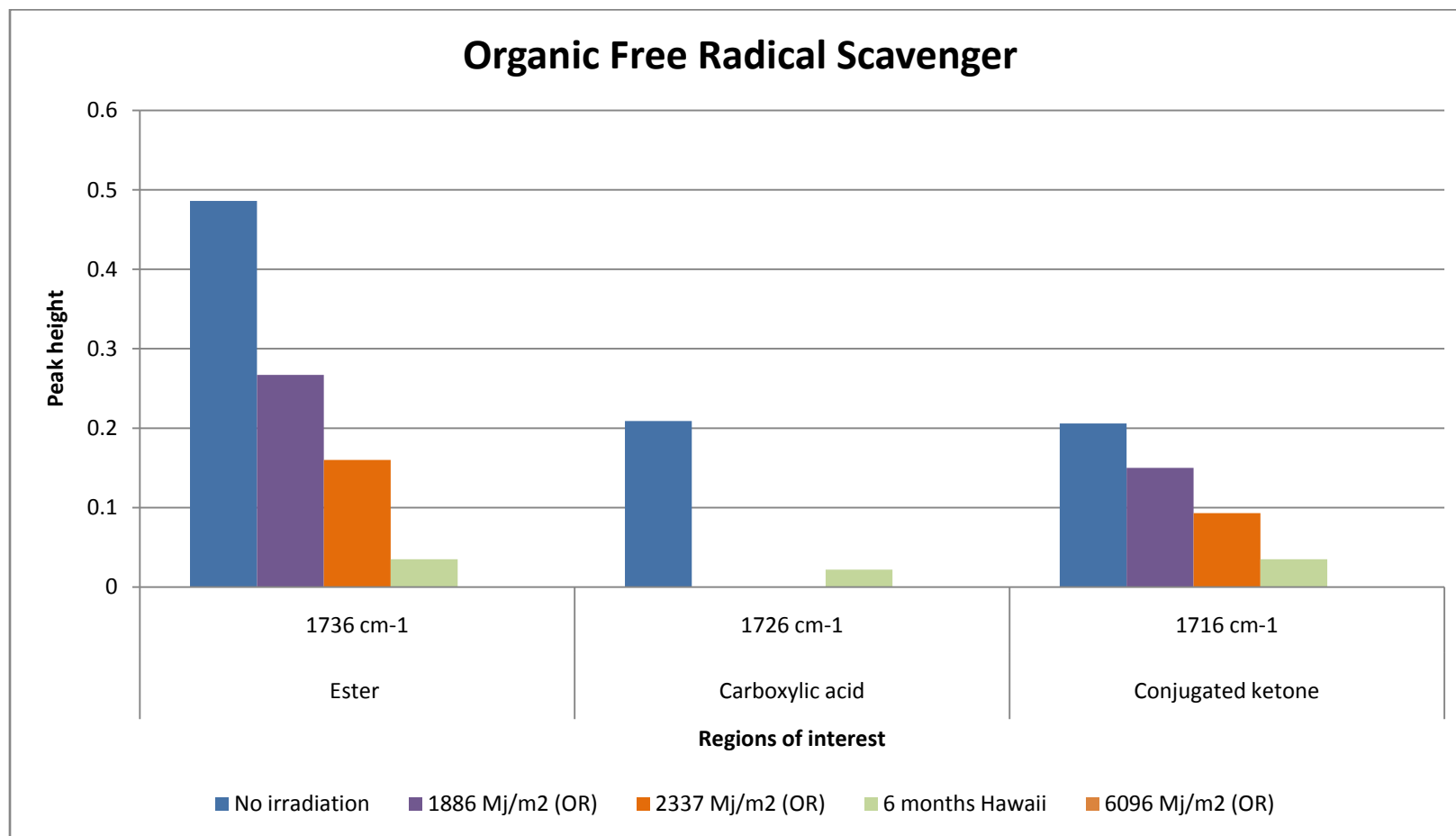


Figure 4.33. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm solution of an organic free radical scavenger and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m² in Eastern Oregon or for six months in Hawaii.

4.4.5 Effects of weathering on loblolly pine samples treated with the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone

The surfaces of the untreated wood and wood receiving most of the treatments used in this study turned brown and then gray with increased solar radiation. Samples treated with the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) turned white and remained so for the duration of the study. This color change appeared drastic to the human eye, but was less substantial when the $L^*a^*b^*$ color judgment method was used (Figure 4.34). While the rapid loss of the tan and brown hues was likely due to the degradation of aliphatics and lignin from the surface, possibly due to the presence of chlorine, the treatment also prevented microbial growth on the surface. The lack of microbial growth was especially evident under tropical conditions and allowed for the direct comparison of UV initiated degradation between the two exposure locations. The resulting data suggests that, discoloration was directly related to the amount of solar radiation received in the presence of DCOIT and the photochemical reactions initiated by it.

DCOIT also affected check development. The number of checks was initially higher on DCOIT treated wood, while the treatment appeared to markedly reduce the number of surface checks on samples after one year of exposure (Figure 4.35). This apparent reduction in checking may have been caused by the presence of cellulose fibers on the surface of the samples that obscured the checks underneath, while the initial increase in the number of checks might have been caused by the rapid degradation of the lignin polymer on the surface. Check development differed little between the tropical and desert exposure locations, suggesting that the type of moisture cycling experienced by the samples was less important for check formation once the lignin was degraded.

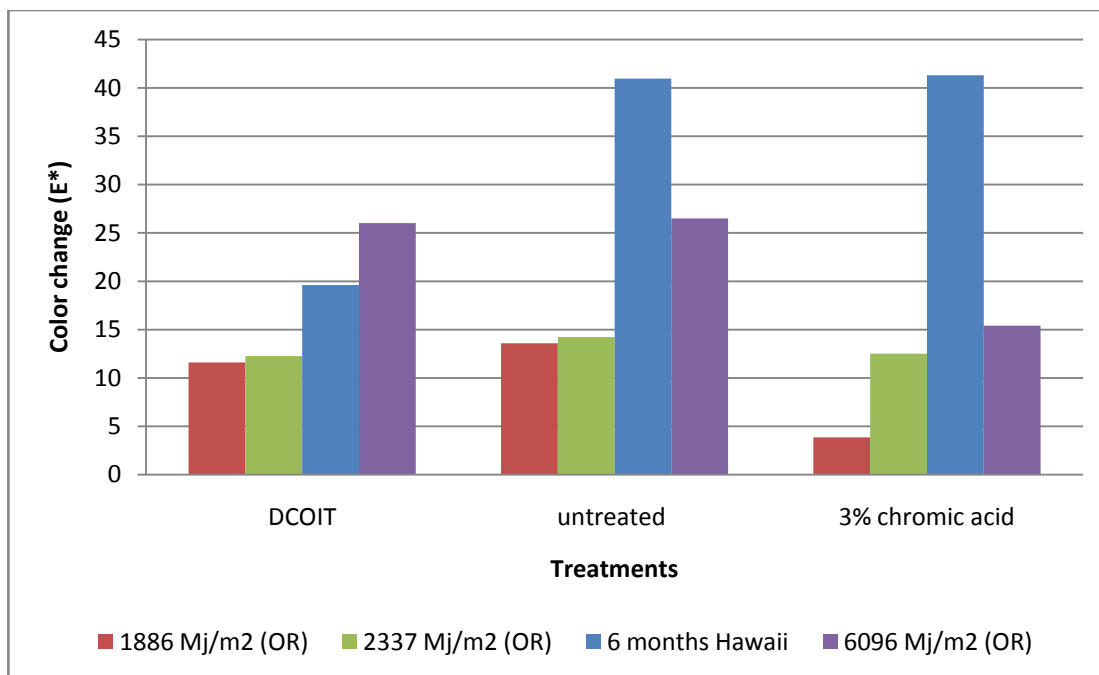


Figure 4.34. Effect of the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) on color fastness for loblolly pine samples exposed to 1886 to 6096 Mj/m² of irradiation in Eastern Oregon or for six months in Hawaii. Untreated and 3% chromic acid treated samples are included as negative and positive controls.

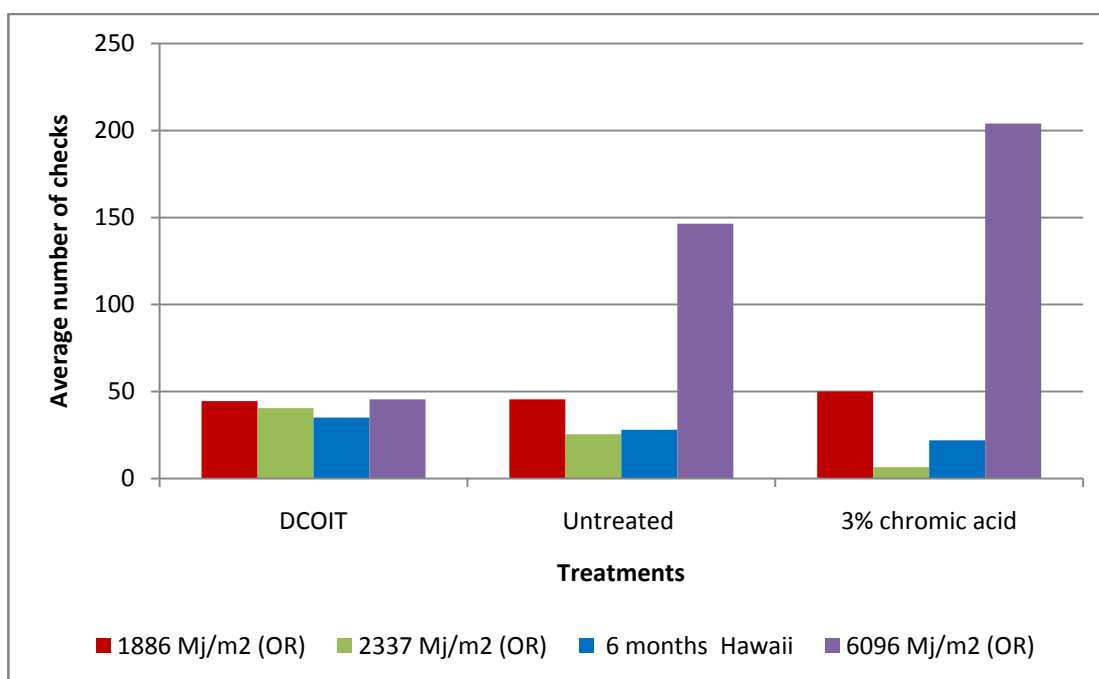


Figure 4.35. Number of surface checks developed in samples treated with the biocide 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) when exposed to 1886 to 6096 Mj/m² of solar radiation in Eastern Oregon or for six months in Hawaii.

The number of aliphatic groups on the surface of samples treated with DCOIT decreased rapidly and then stabilized with increased exposure. One quarter of the initial concentration of aliphatic groups was still present after one year of exposure in the desert and six months in Hawaii (Figure 4.36). This suggests that leaching was not the primary mode of decomposition. Lignin peaks were also severely degraded after only a short exposure period in the desert while lignin was completely removed from samples exposed in Hawaii for six months. However, the fate of the degraded lignin differed between the two exposure locations. FTIR spectra of the samples exposed in Oregon showed the presence of the aromatic lignin peak located between $1660\text{-}1590\text{ cm}^{-1}$, suggesting that the degraded polymer had not been removed from the surface through leaching. This peak was absent in the samples exposed under tropical conditions. Deconvolution of the carbonyl region suggested that all of the components relevant to wood polymers had been lost from the surface when samples were exposed for six months under tropical conditions (Figure 4.37). These results suggest that lignin degradation products were completely removed from the surface through leaching. At the same time, the acid pulping process facilitated by the chlorine in DCOIT degraded the hemicelluloses and cellulose components of the wood. The pulping process appeared to be less efficient under desert conditions, possibly due to the lack of moisture. This combination of removal of lignin decomposition products and bleaching of the carbohydrate fraction resulted in the very bright color. In addition, spectra from samples exposed in Oregon indicated that some carboxylic acid was still present on the surface, confirming that some lignin degradation products were still present after 2337 MJ/m^2 of solar radiation, possibly in the form of organic acids.

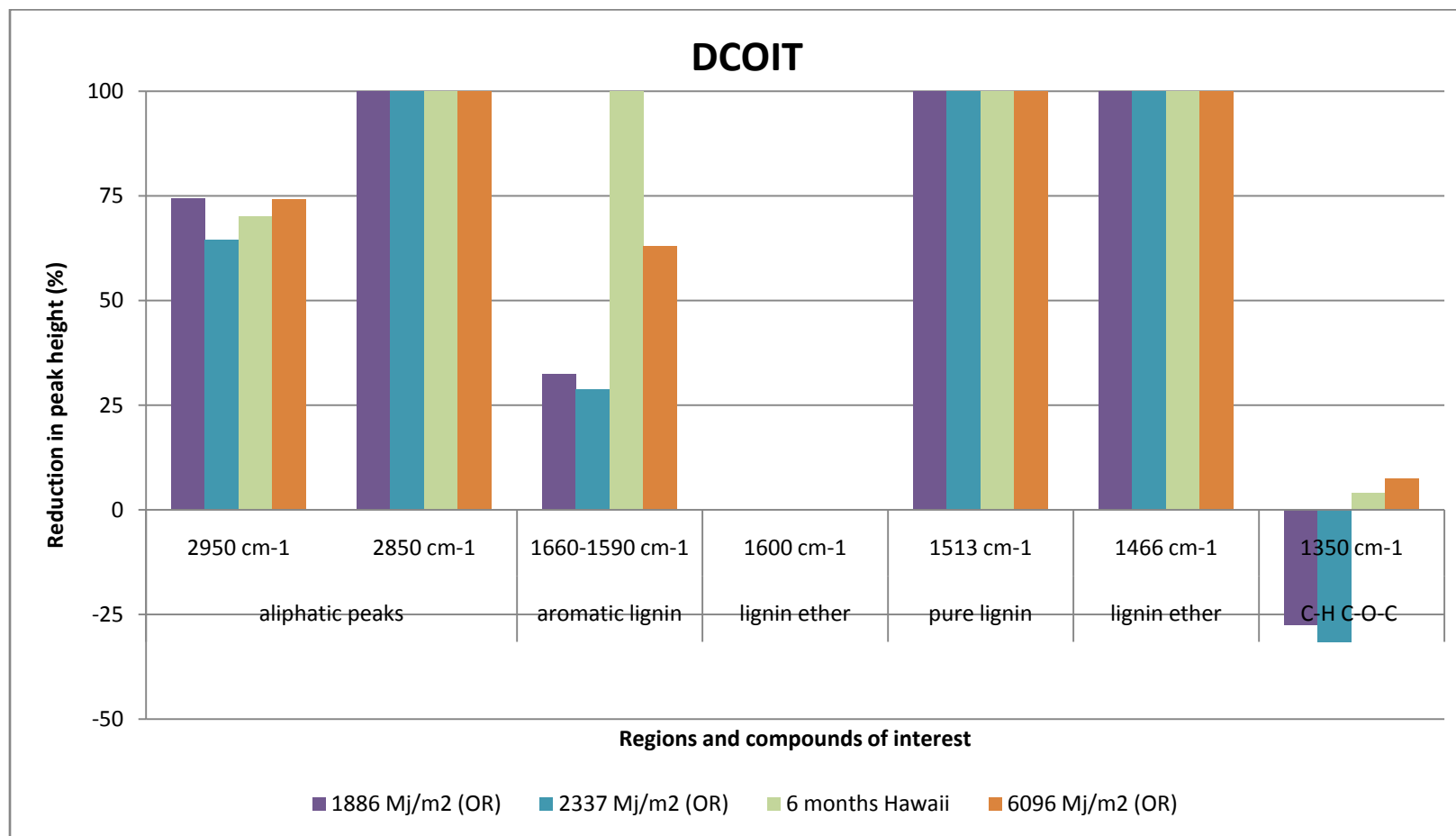


Figure 4.36. Reductions in FTIR peak heights for loblolly pine samples impregnated with a 1000 ppm emulsion of 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed to irradiation dosages ranging from 1886 to 6096 MJ/m² in Eastern Oregon or for six months in Hawaii.

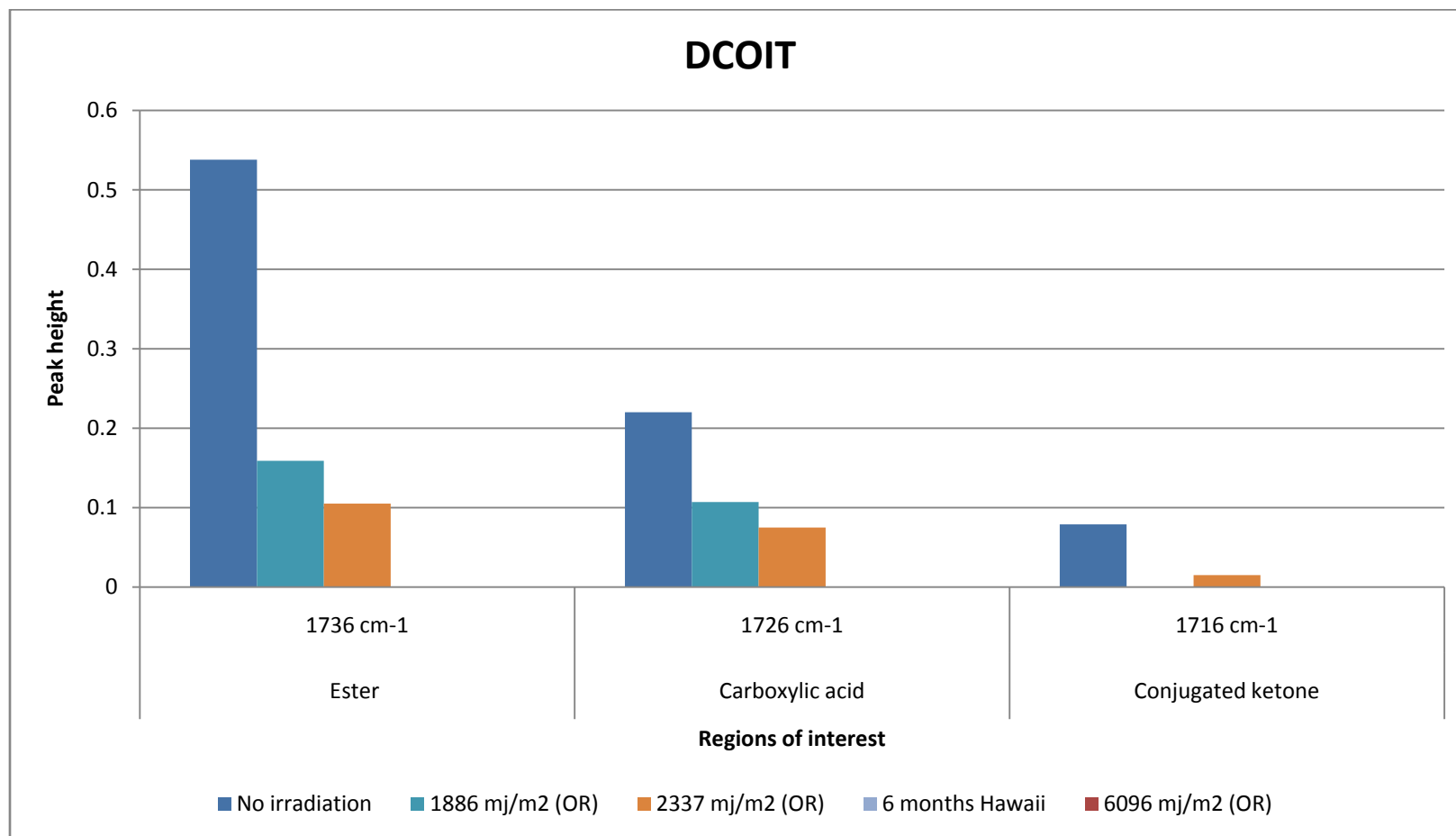


Figure 4.37. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm emulsion of 4, 5-Dichloro-2-n-Octyl-3-Isothiazolinone (DCOIT) and exposed to irradiation dosages ranging from 1886 to 6096 Mj/m^2 in Eastern Oregon or for six months in Hawaii.

4.5 Conclusions

Surface protection systems applied to loblolly pine samples exposed to tropical and desert conditions weathered differently. Exposed samples discolored more readily and checked less frequently under tropical conditions despite receiving similar solar radiation doses. The observations suggest that weathering reflects interactions between radiation and other environmental factors. Darkening in the tropics was primarily driven by microbial growth on the surface, while discoloration under desert conditions was mainly caused by erosion and polymer degradation, resulting in a light gray color. Checking was possibly influenced by moisture cycling. More frequent, but less severe moisture cycles in the tropics result in a higher equilibrium moisture content and thus less checking. Samples exposed in the desert experienced fewer, but more severe moisture cycles due to the relatively low moisture content of the samples between rain events. These cycles result in greater checking. The effects of these climatic factors and the potential for synergy between them merit exploration for those seeking surface treatments capable of performing in a range of exposures.

FTIR analysis indicated that protecting the wood polymers from photo-degradation was difficult to achieve regardless of the exposure site, due to their inability to inhibit absorption of near ultra violet light. Yet some differences were detected. Hemicelluloses and cellulose degradation were generally greater under tropical exposures, possibly due to biological activity and subsequent removal of breakdown products during rain events, while lignin degradation in a number of treatments was reduced compared to the samples exposed under desert conditions. These results suggest that the synergistic relationship between biological and physical weathering should be explored further. The results also illustrate why surface protection systems developed in one climate may be ineffective in another. Thus, prospective surface systems should contain multiple actives and be tested across a broad range of climates, or different systems should be designed for targeted climates.

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Use of Iron oxides to Influence the Weathering Characteristics of Wood Surfaces: a
Systematic Survey of Particle Size, Crystal Shape and Concentration

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5. USE OF IRON OXIDES TO INFLUENCE THE WEATHERING CHARACTERISTICS OF WOOD SURFACES: A SYSTEMATIC SURVEY OF PARTICLE SIZE, CRYSTAL SHAPE AND CONCENTRATION

5.1 Abstract

Surface coatings such as paints and stains have been traditionally used to protect wood surfaces against the effects of weathering. While these systems provided short term protection against lignin loss, discoloration and checking, they also hide the natural beauty of the wood and degrade with time, requiring maintenance or eventual replacement. Infusing the wood with iron oxide pigments may be an alternative method for limiting weathering, providing a transparent method for more permanent protection of the wood surface. An earlier study suggested that the ability of iron oxides to protection against discoloration varied with particle size. In this study, iron oxides with different crystal shapes and particle sizes were investigated along with a carbon black pigment. Samples were exposed to predetermined amounts of solar radiation in the high desert of Eastern Oregon and then evaluated for discoloration, checking and changes in chemical composition. Much higher levels of iron oxide were required than previously thought to prevent discoloration and limit lignin degradation. Large particle sizes that led to greater opacity provided greater protection. The best protection against discoloration and lignin loss was provided by carbon black. The findings also suggested that iron oxides had no effect on checking, indicating that the mechanisms of discoloration and checking are not directly related.

5.2 Introduction

Coatings are an effective means for protecting wood surfaces against weathering. Traditionally, these systems have been used to provide long term protection to the underlying wood for applications such as siding and fences (Williams and Feist 2001, Gorman and Feist 1989). However, these coatings eventually fail and crack or peel, allowing moisture ingress and UV light absorption on the wood surface. This damage results in biotic and abiotic

degradation of the underlying wood (Evans et al 2002). Reapplied film forming coatings on wood products have drastically reduced durability as a result of poor surface adhesion, necessitating the complete and costly removal of the degraded coating prior to reapplication (Kleive 1986). Wood surfaces may also be protected by applying a penetrating stain. These systems generally contain a pigment, water repellent, binder and, frequently, a wood preservative to prevent biotic attack (Williams and Feist 1993). Instead of forming a barrier on the surface, these systems provide protection on the wood cell level. Penetrating stains also allow the natural figure of the wood to remain visible and are easy to reapply. However, stains are prone to checking and fading over time as a result of imperfections in the hydrophobic film and erosion of the pigment (Kiguchi et al 1996). The detrimental erosion of pigments from the surface can be slowed or perhaps even prevented by distributing the pigment throughout the entire cross section through pressure impregnation.

Iron oxides are frequently used as pigments in stains and paints to tint the coating, producing primarily yellow and red tones. These tones are especially desirable for stains, since they naturally augment those of the wood. Low concentrations of iron oxides have also shown promise as wood surface protection agents, reducing lignin loss and discoloration (Schauwecker et al 2010). However, the roles of particle size and shape in performance remain unknown. Iron oxides are found in three principle forms, each with a unique crystal shape: iron (III) oxide (Fe_2O_3), iron (III) oxide-hydroxide ($\text{Fe}(\text{OH})_3$), and magnetite(Fe_3O_4). These crystal shapes absorb, transmit and reflect different wavelengths of light, resulting in colors ranging from yellow to black (Lewis 1995; Schwertmann and Cornell 2000). These interactions with the solar spectrum may allow for the preferential absorbance, reflectance, and transmittance of radiation by the iron oxide, preventing solar radiation from reaching the wood. This would limit or prevent initiation of free radical reactions, thereby preventing lignin degradation, while allowing the natural beauty of the wood to remain visible. In addition to these properties, different particle sizes result in varying degrees of opacity to light in the

visible portion of the solar spectrum. These different particle sizes may further enhance or detract from the protective and visual appeal of iron oxides (Wright and McKenna 2000, Endriss 1998, Felder 1971). However, these iron oxide properties have not been fully investigated in conjunction with wood surfaces. This study investigated the effects of different particle shapes and sizes along with concentrations of iron oxide on the weathering characteristics of loblolly pine (*Pinus taeda*) sapwood.

5.3 Methods

Pigment dispersions of iron (III) oxide (Fe_2O_3 , red), iron (III) oxide-hydroxide ($\text{Fe}(\text{OH})_3$, yellow), magnetite (Fe_3O_4 , black) and carbon black (Table 5.1) were used to examine the effects of different iron oxide chemistries on surface weathering. Particle size was investigated across all three types of iron oxide while concentration was studied by applying different loadings of a 122 nm iron(III) oxide suspension. Clear, flat sawn loblolly pine sapwood (*Pinus taeda* L.) samples (10 mm thick, 85 mm wide and 155 mm long) were prepared from nominal “1x4” stock. One sample from each parent board was assigned to be treated with each compound of interest, to allow for comparisons across compounds.

Iron oxide dispersions were procured from commercial suppliers (Table 5.1) and sonicated for 60 minutes to disperse agglomerations. Particle size was determined immediately after sonication and no more than five minutes before use, using a laser diffraction particle size analyzer (Horiba Partica LA 950, Horiba Instruments, Irvin CA). The loblolly pine samples were weighed before treatment and impregnated using a uniform vacuum/pressure cycle (Table 5.2). After treatment, the samples were reweighed to determine chemical uptake and then reconditioned to a moisture content of 12%. The positive control samples, were brushed with 3% chromic acid (CrO_3 bases) instead of pressure impregnated, since brushing with chromic acid was shown to be effective as a surface protection agent (Black and Mraz 1974). The samples were end sealed using a marine epoxy resin. In addition, one set of sixteen iron oxide impregnated samples were brushed with a 1% m/m solution of

polyvinyl acetate resin (Titebond III, Franklin International Inc.) to determine if a water proofing sealant prevented pigments removal from the surface. Baseline colorimeter measurements were made using a Konica Minolta Chroma Meter (Ramsey, NJ) and a jig to center the colorimeter over the samples.

Table 5.1. Pigments assessed for their ability to reduce weathering of loblolly pine sapwood.

Compound	Color	Particle size (nm)	Concentration (ppm)	Supplier
Iron (III) oxide	Red	122	1000	Rockwood Pigments, Beltsville, MD
Iron (III) oxide	Red	472	1000	Emerald Performance Materials, Charlotte, NC
Iron (III) oxide-hydroxide	Yellow	124	1000	Rockwood Pigments, Beltsville, MD
Iron (III) oxide-hydroxide	Yellow	417	1000	Davis Colors, Los Angeles, CA
Iron (III) oxide-hydroxide	Yellow	1480	1000	Rockwood Pigments, Beltsville, MD
Carbon black	Carbon black	162	1000	Davis Colors, Los Angeles, CA
Magnetite	Black	1074	1000	Davis Colors, Los Angeles, CA
Magnetite	Black	4173	1000	Rockwood Pigments, Beltsville, MD

Table 5.2. Vacuum and pressure conditions used to impregnate loblolly pine sapwood with various pigment systems.

Cycle	Time (min)	Pressure/ Vacuum
Initial vacuum	5	25 mmHg
Pressure	10	150 psi
Final Vacuum	5	25 mmHg

5.3.1 Exterior Exposure

Samples were mounted on aluminum supports with the growth rings oriented concave face up. Each sample was secured to the rack by placing one stainless steel M 4.5 screw into each corner of the sample. This limited cupping and warping, forcing stress relief to occur through check development.

Eight replicates per treatment were exposed in the Eastern Oregon high-elevation desert at a site near Klamath Falls (Lat: 42.22, Long: -121.78, elevation of 1250 m) on racks pitched at 45° oriented due south. Solar radiation data was collected daily from an AgriMet weather station operated by the Bureau of Reclamation at the site. Natural precipitation was augmented with non-chlorinated irrigation water sprayed on the samples for 15 min three times a week at sunrise. This delivered approximately 114 liters of water to the samples per watering. Two samples per treatment were harvested after 514, 899 and 1848 MJ/m² irradiation. These irradiation intervals corresponded to multiples of the maximum amount of solar energy the site receives in the two week window surrounding the summer solstice. Harvested samples were reconditioned to 12% moisture content. Care was taken to limit surface contamination by preventing the samples from contacting each other or being contaminated by oils from human hands.

5.3.2 Physical evaluation

The conditioned samples were scanned using a 600 dpi Canon color scanner (Lake Success, NY) and images were stored as .jpg files. Each image was cropped to remove the mounting holes and the threshold command in Adobe Photoshop (Adobe Photoshop version 5.0.2, Adobe Systems Inc.) was used to render them in high contrast black and white. Any remaining anomalies from the wood grain or treatment were removed, allowing clear delineation of surface checks. The surfaces were then evaluated for checks with a surface area of greater than 600 pixels using a custom software package developed by the University of British Columbia and updated by Mississippi State University. (Evans pers. Comm.; Li and Nicholas pers comm.). The software package was used to determine the number and size of checks that would be visible to the casual observer. Colorimeter measurements were repeated and results were compared to the pre-exposure values by calculating E* according to Wypych (2008):

$$E^* = ((L^*_{(i)} - L^*_{(f)})^2 + (a^*_{(i)} - a^*_{(f)})^2 + (b^*_{(i)} - b^*_{(f)})^2)^{0.5}$$

Where:

$L_{(i)}$, $a_{(i)}$ and $b_{(i)}$ describe the initial condition of the sample using the CIELAB color space

$L_{(f)}$, $a_{(f)}$ and $b_{(f)}$ describe the final condition of the sample using the CIELAB color space

5.3.3 Chemical evaluation

FTIR analysis of surface chemistry was conducted on one sample per treatment for a given exposure period. Specimens (~2 mm x 10 mm x 20 mm) were removed from the surface using a carving knife. Six specimens, three from the earlywood and three from the latewood bands were selected. The spatial location of the samples was chosen at random. FTIR spectra were collected using a PerkinElmer Spectrum One FTIR Spectrometer (PerkinElmer Inc., Waltham, MA) in conjunction with a MIRacle (Pike Technologies Inc., Madison, WI) single bounce attenuated total reflection (ATR) probe utilizing a composite diamond crystal. Sixty scans were collected per specimen. After collection, the spectra were baseline corrected and all six spectra collected from one sample were averaged to produce a composite spectrum representing the entire sample using Omic 7.4 software (Thermo Fisher Inc., Waltham, MA). Regions of the spectra relevant to photodegradation of wood were quantified within the software package. Individual peak heights were measured and normalized using the large cellulose and hemicellulose C-O stretching peak at 1033 cm⁻¹. Changes in peak height were expressed as a percent loss, using the unexposed reading as a baseline. The carbonyl region was treated differently due to overlapping peaks in this portion of the spectra. The region between 1750 and 1700 cm⁻¹ was normalized within a treatment and Fourier self deconvolution was applied to resolve overlapping peaks, allowing for the analysis of esters (1736 cm⁻¹), carboxylic acid (1726 cm⁻¹), and conjugated ketones (1716 cm⁻¹).

5.4 Results

Gauge retentions were calculated from the information collected during treatment (Figure 5.1 and 5.2). No statistically significant differentness ($\alpha = 0.05$) were noted for samples treated with a 1000ppm solution of various iron oxides as determined by Tukey's multiple comparison test conducted using SAS version 4.1 (SAS Institute Cary NC 2006), allowing for comparisons between these samples. In addition, there were statistically significant retention increases ($\alpha = 0.05$) between the 500, 5000 and 10000 ppm treatments, allowing for evaluation of concentration effects.

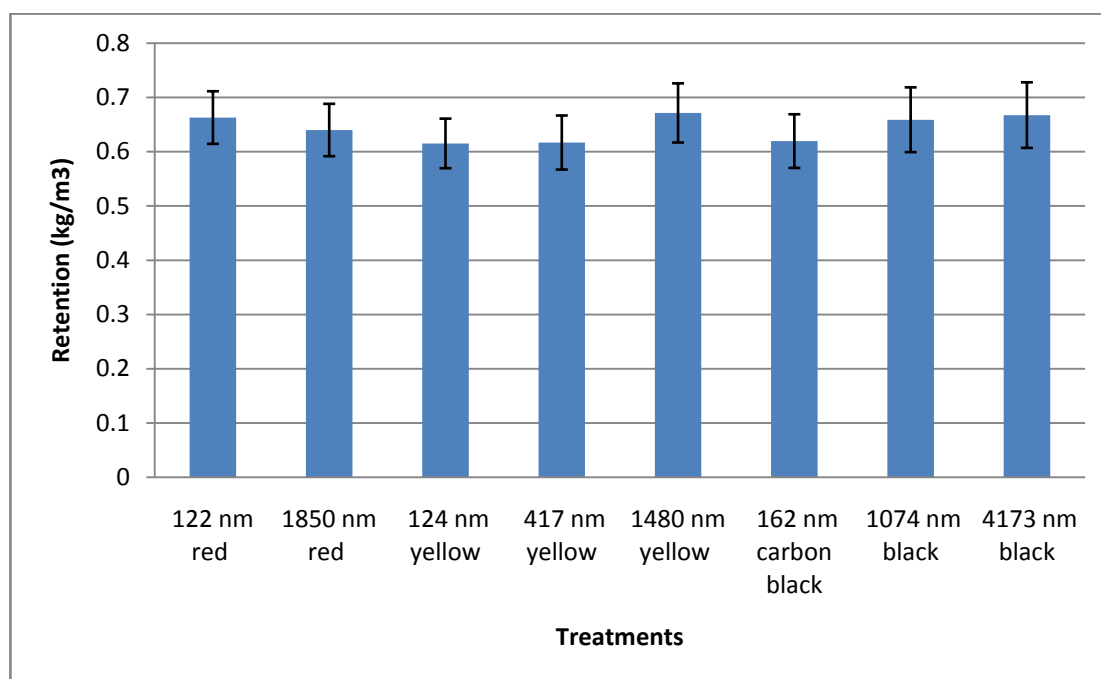


Figure 5.1. Actual retentions for samples treated with 1000 ppm solutions of various iron oxides. Error bars represent one standard deviation about the mean.

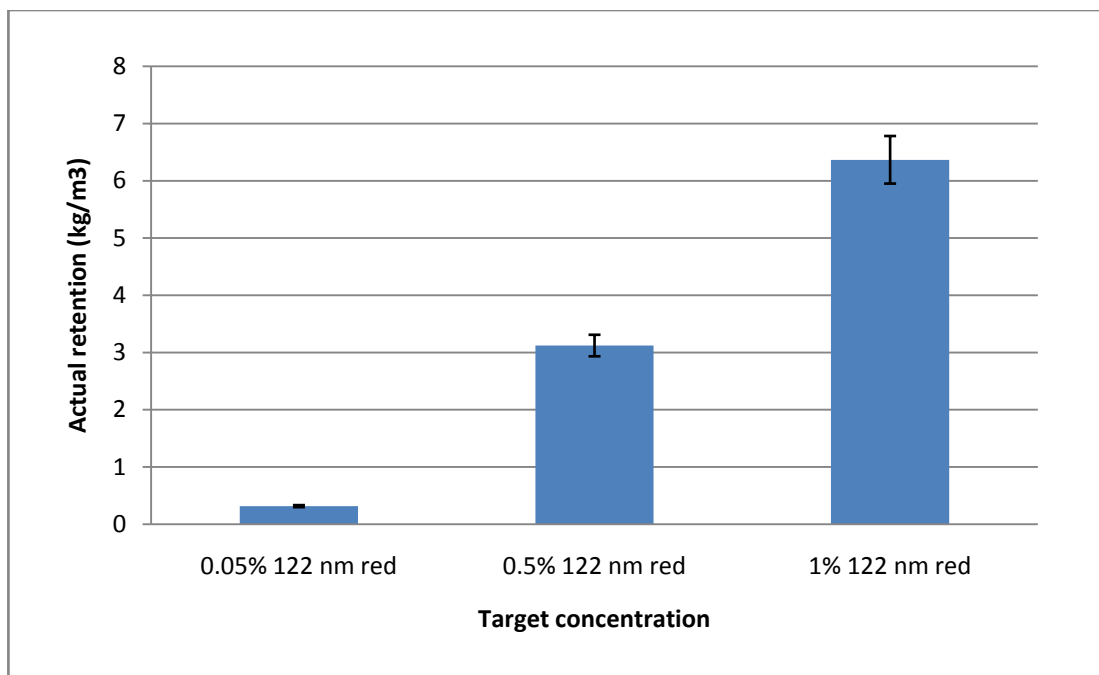


Figure 5.2. Actual retentions for samples treated with 500, 5000, or 10,000 ppm solutions of 122 nm red iron oxide dispersions. Error bars represent one standard deviation about the mean.

Samples were installed at the exposure site in mid-July and removed over three exposure periods. Two replicates were removed from the field after 515 and 900 Mj/m^2 of solar radiation, while the last two replicates and the samples that had been brushed with resin were removed after 1848 Mj/m^2 of solar radiation. Conditions were very similar across all of the exposure periods, with daily radiation decreasing as Fall approached (Table 5.3). Total natural precipitation received at the site was 8.6 mm over the course of the study, with each rain event totaling less than 1.5 mm.

Table 5.3. Climatic conditions during each exposure period.

Irradiation period	Irradiation dose (Mj/m^2)	Time in the field (days)	Average relative humidity (%)
1	514	17	47 (6.4)
2	899	32	48 (6.4)
3	1848	80	53 (9.8)

5.4.1 Development of surface checking

Increased concentrations of 122 nm red iron oxide reduced the number of checks that developed on the surface during the initial 514 MJ/m² of radiation, (Figure 5.3). However, a dose response was no longer discernable after 899 MJ/m² of irradiation. Mean check area data indicated that check size was unaffected by iron oxide concentration (Figure 5.4). Black iron oxides developed the fewest detectable checks over the course of the study (Figure 5.5). The dark color of the pigment may have absorbed UV radiation and converted it into heat, and was dissipated shielding the wood substrate. Samples treated with particles less than 162nm in size developed fewer checks during the first 514 MJ/m² of exposure than those treated with larger particles, with the exception of the red iron oxide (Figure 5.5). Similarly, mean check area was reduced by the yellow and red iron oxide treatments with a mean particle size of less than 124 nm (Figure 5.6) over the first exposure period, although this trend did not continue with additional exposure. The remaining black iron oxides and the other treatments did not affect check area. These results suggest that other mechanisms not controlled by iron oxide color, loading or particle size had a greater influence on check development and size over a prolonged period of time.

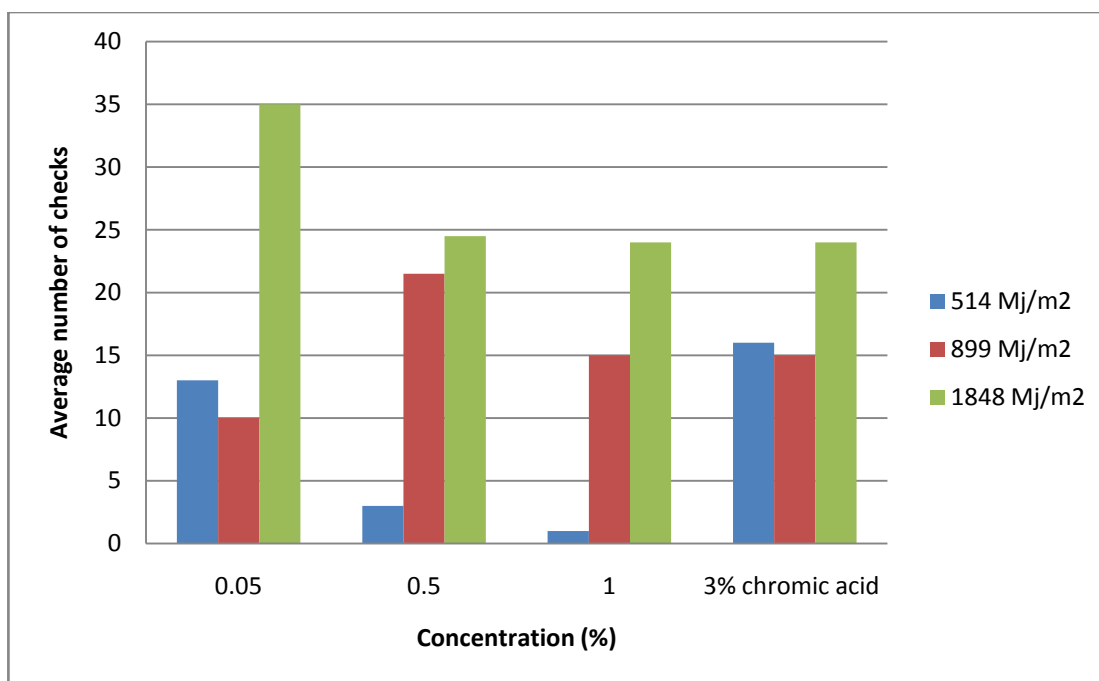


Figure 5.3. Mean number of checks that developed on the surface of samples treated with different loadings of 122 nm red iron oxide and exposed in the Eastern Oregon high desert.

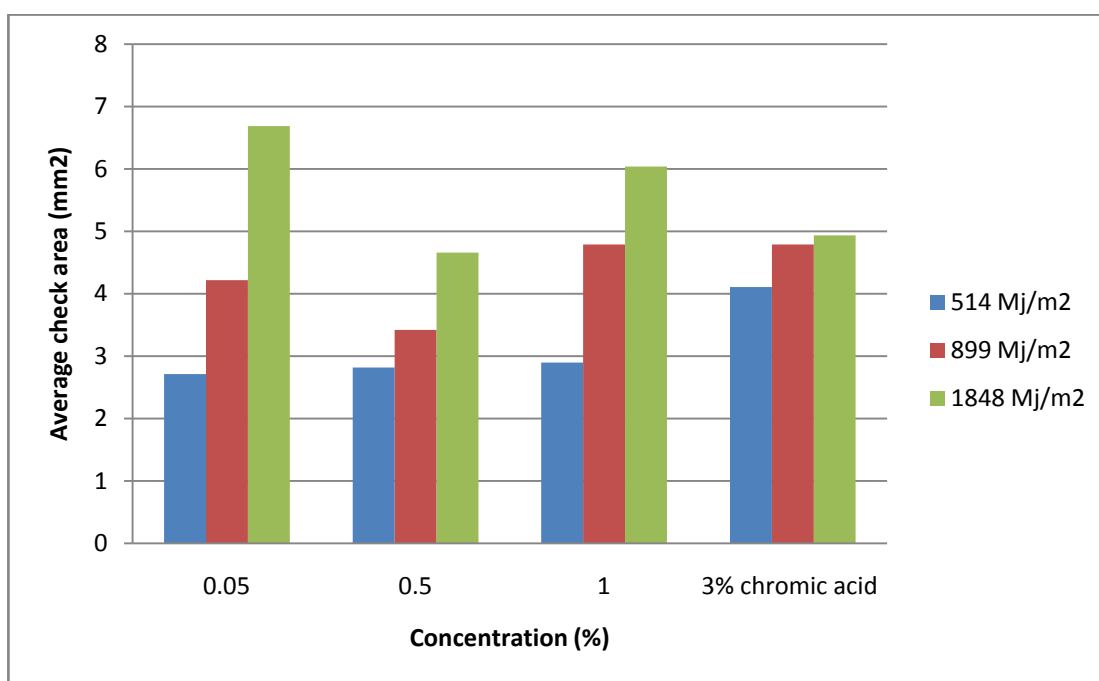


Figure 5.4. Mean check area on the surface of samples treated with different loadings of 122 nm red iron oxide and exposed in the Eastern Oregon high desert.

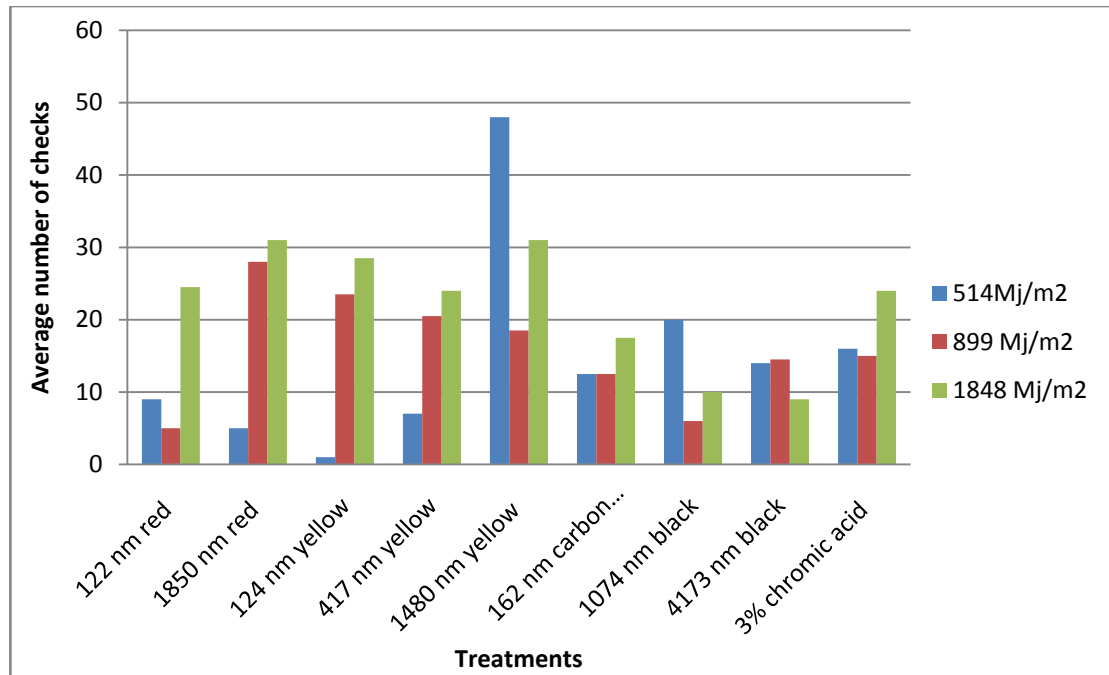


Figure 5.5. Mean number of checks that developed on the surface of samples treated with various iron oxide dispersions (1000 ppm) and exposed in the Eastern Oregon high desert.

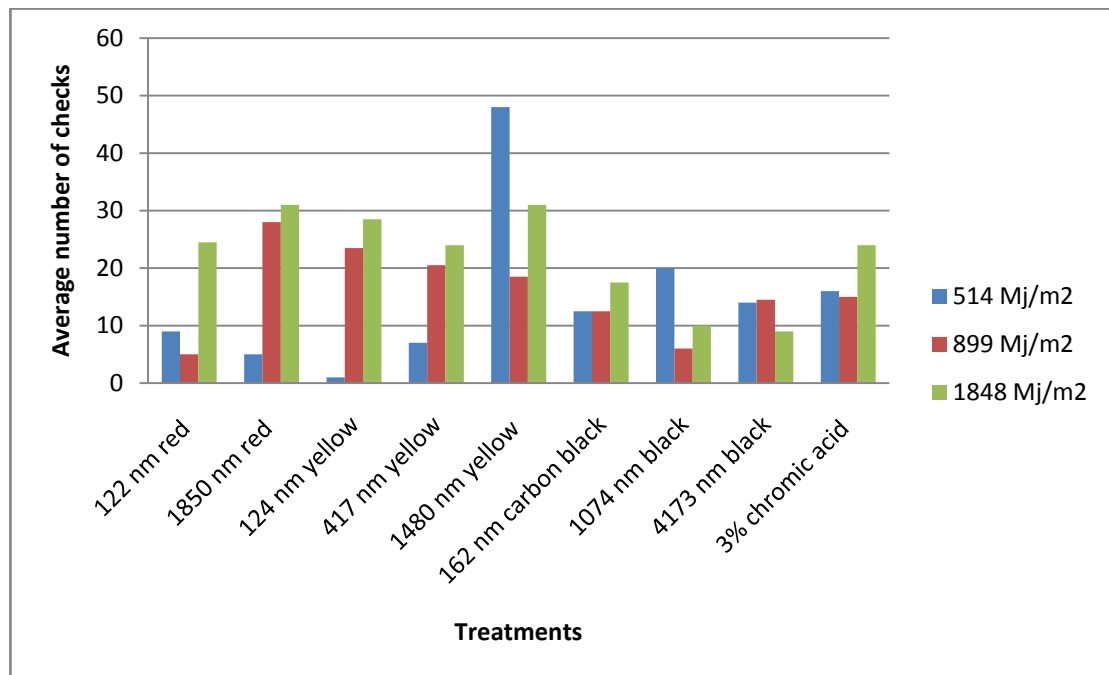


Figure 5.6. Mean check area on the surface of samples treated with various iron oxide dispersions (1000 ppm) and exposed in the Eastern Oregon high desert.

Resin brushed onto the surface was evaluated because we thought it might reduce loss of iron oxide particles from the sample surface, thereby extending treatment efficacy. In addition, it was thought that the resin would provide some protection from water sorption and thus reduce checking resulting from moisture cycling. However, the number of checks that developed on the surface of samples after 1848 Mj/m^2 of radiation was greater with than without resin (Figure 5.7 and 5.8) while mean check area was unaffected. These data suggest that surface sealing binders may worsen checking by preventing wood movement on the microscopic level.

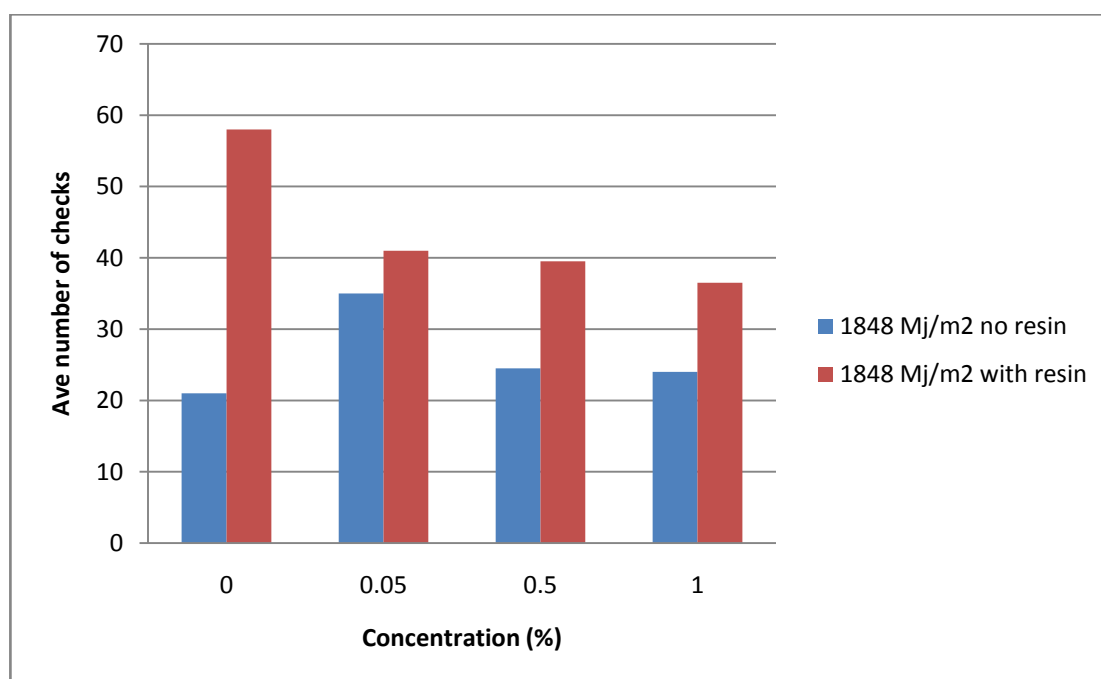


Figure 5.7. Mean number of checks on the surface of samples treated with different levels of 122 nm red iron oxide, with and without 1% resin brushed onto the surface, and exposed to 1848 Mj/m^2 of radiation in the high desert of Eastern Oregon.

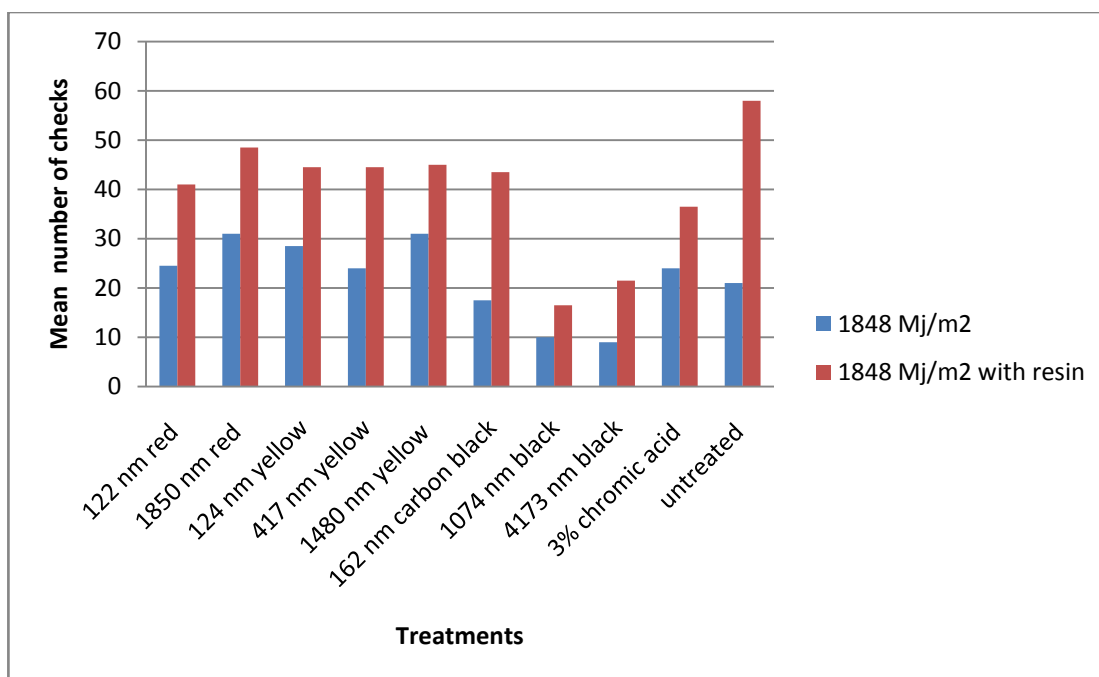


Figure 5.8. Mean number of checks on the surface of samples treated with different iron oxide dispersions (1000 ppm), with and without a resin topcoat and exposed to 1848 MJ/m² of radiation in the high desert of Eastern Oregon.

5.4.2 Discoloration of iron oxide treated samples

The dry conditions prevailing at the test site resulted in abiotic discoloration dominating on the sample surface, due to effects of water, wind and solar radiation. There was a significant dose response on samples treated with different doses of 122 nm iron oxide (Figure 5.9), although the level of protection was lower than that found with 3% chromic acid treatment. In addition, the amount of discoloration did not increase with increased solar radiation exposure, suggesting that the iron oxide either masked additional discoloration or prevented the surface from weathering into the gray tones normally associated with advanced exposure. Discoloration across different forms and particle sizes of iron oxide varied and no clear patterns emerged, possibly due to the low retentions evaluated (Figure 5.10). However, the data suggested that darker pigments with a particle size of 1000-2000 nm provided more protection. The addition of resin on the surface, intended to slow iron oxide loss, did not influence discoloration, suggesting that this compound did not serve its intended purpose or

that the exposure time was not long enough to delineate the effects of the binder (Figures 5.11 and 5.12).

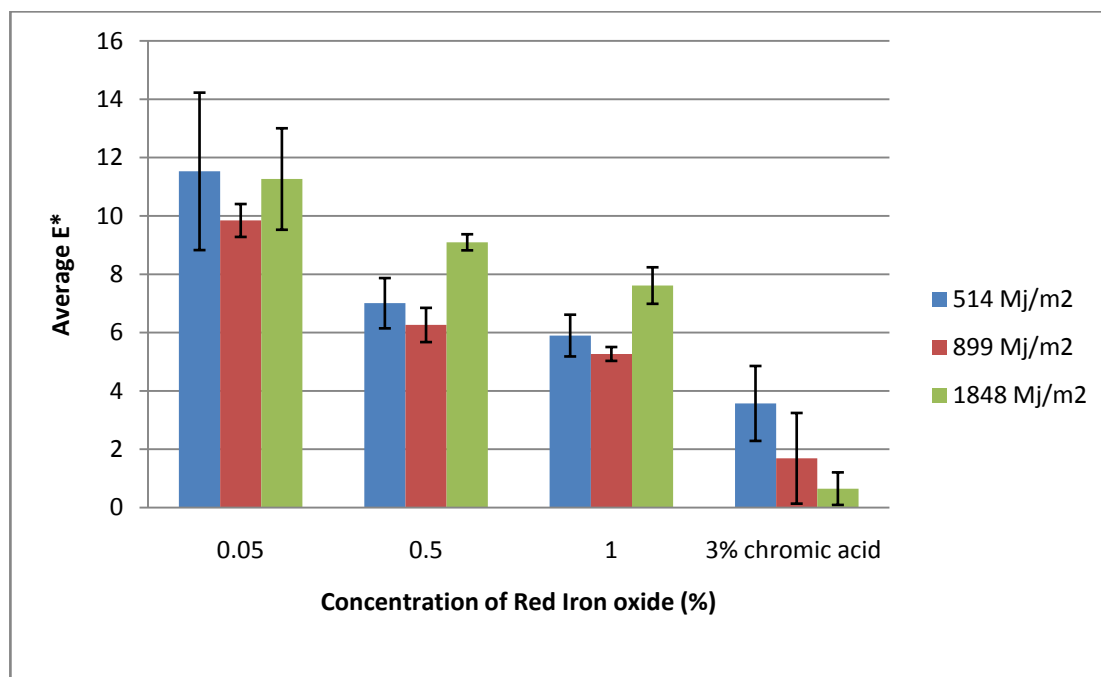


Figure 5.9. Mean discoloration of samples treated with different loadings of 122 nm red iron oxide and exposed in the Eastern Oregon high desert. Error bars represent one standard deviation about the mean.

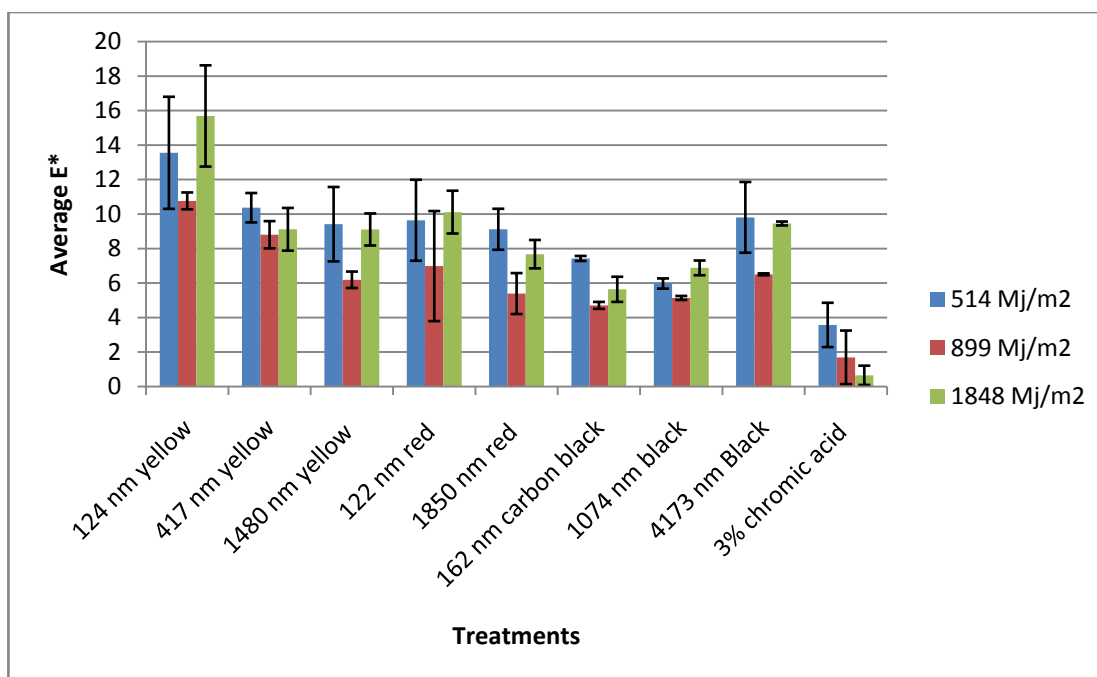


Figure 5.10. Mean discoloration of samples treated with various iron oxides dispersions (1000 ppm) and exposed in the Eastern Oregon high desert. Error bars represent one standard deviation about the mean.

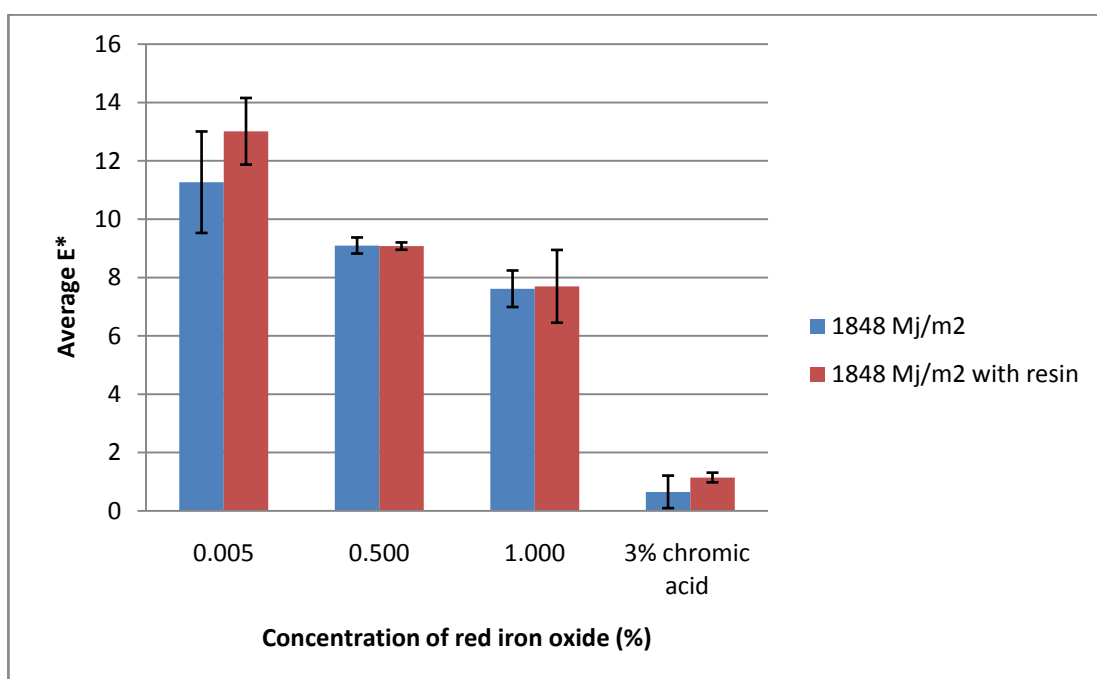


Figure 5.11. Mean discoloration of samples treated with different levels of 122 nm red iron oxide, with and without 1% resin brushed onto the surface, and exposed to 1848 MJ/m² of irradiation in the high desert of Eastern Oregon. Error bars represent one standard deviation about the mean.

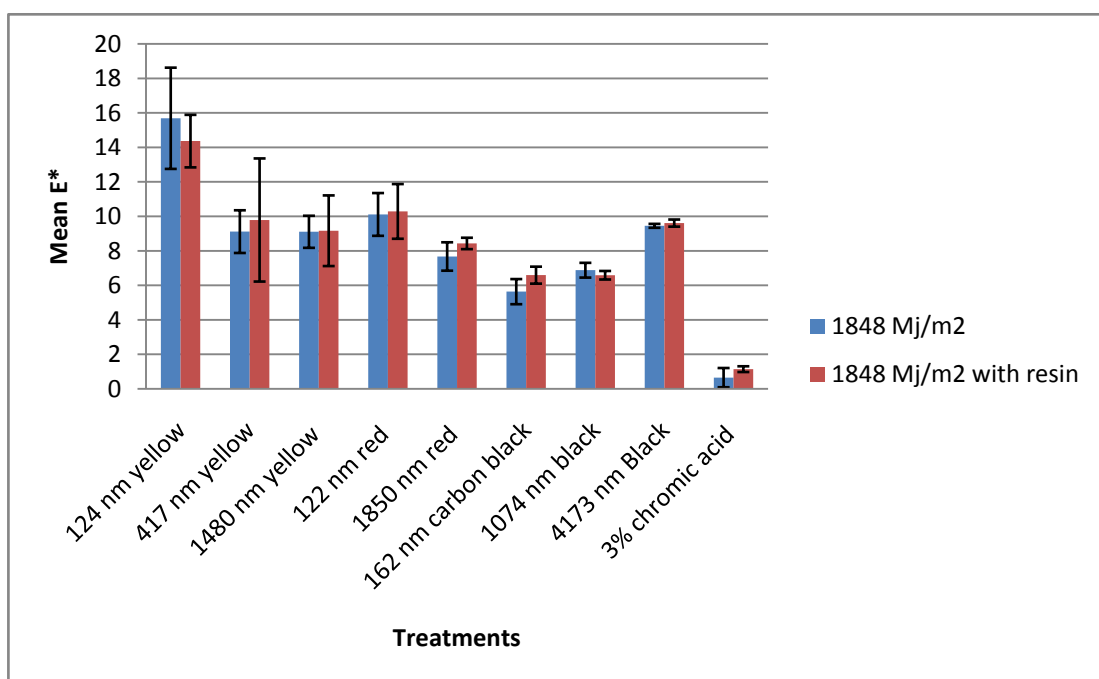


Figure 5.12. Mean discoloration of samples treated with different dispersions of iron oxide (1000 ppm), with and without a resin topcoat, and exposed to 1848 MJ/m² of irradiation in the high desert of Eastern Oregon. Error bars represent one standard deviation about the mean.

5.4.3 Changes in chemical composition

Analysis of FTIR spectra data was complicated because the absorbance characteristics of the iron oxide prevented clear analysis of the aromatic lignin region (1660-1590 cm⁻¹) and the carbonyl region (1740-1700 cm⁻¹) (Figure 5.13). While FTIR spectra were collected from the samples brushed with resin before exposure, these data are not discussed since the resin did not improve weathering characteristics of the samples and caused further interference in the carbonyl region of the spectra.

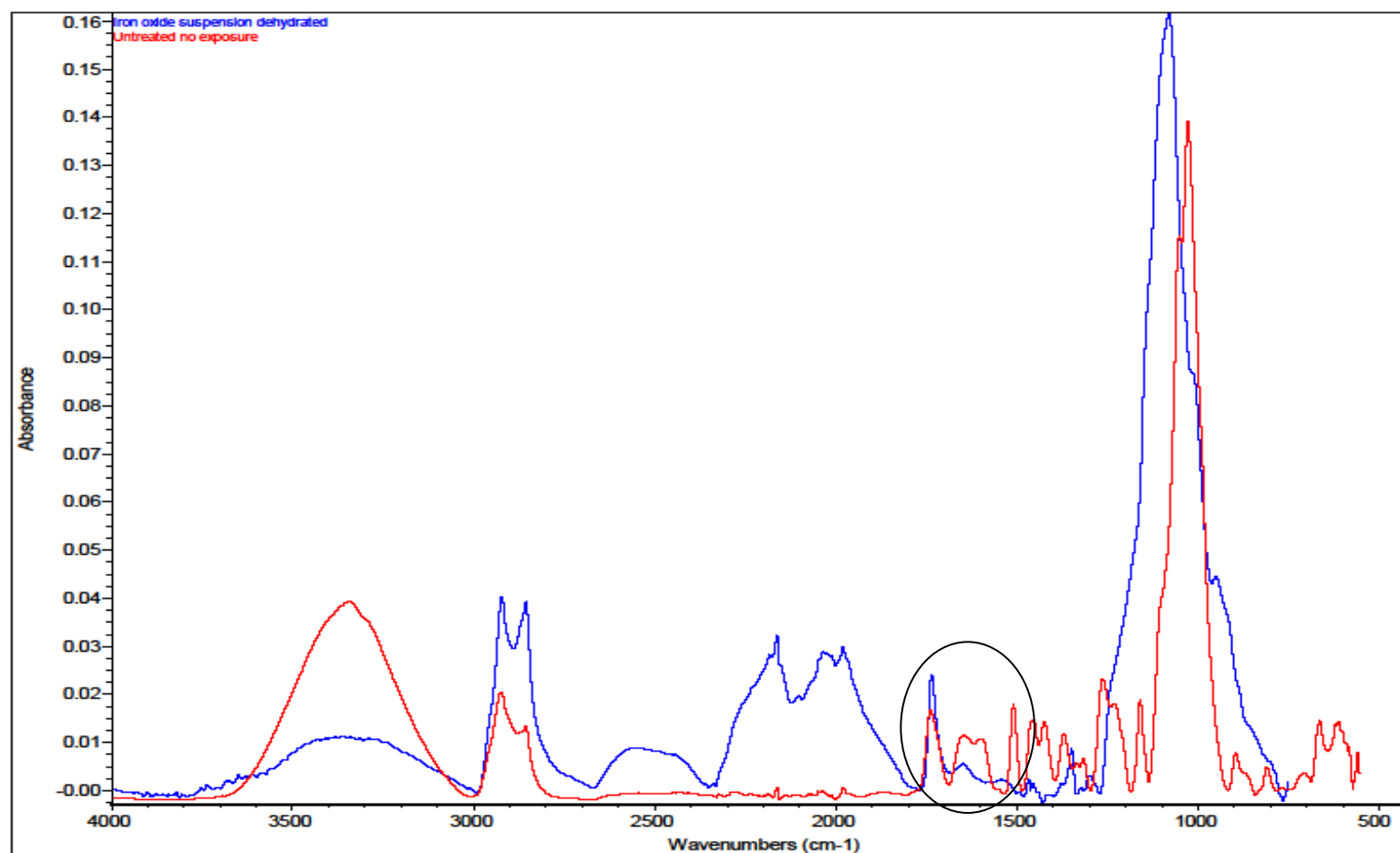


Figure 5.13. FTIR spectra of dehydrated iron oxide suspension compared to untreated, unexposed loblolly pine with the area of interest highlighted.

5.4.4 *Effect of iron oxide concentration on chemical composition*

FTIR analysis indicated that the primary lignin peak (substituted aromatic) located at 1513 cm^{-1} was retained when samples were impregnated with more than 0.5% of 122 nm red iron oxide, although substantial losses occurred before the peak stabilized (Figure 5.14). These results suggest that elevated retentions of red iron oxide reduce free radical formation and lignin degradation caused by UV light. The improvement in lignin retention provided by these treatments exceeded the protection provided by brushing 3% chromic acid on the wood surface and was similar to the protection provided by a hydroxyphenylbenzol UV inhibitor investigated in an earlier study (Schauwecker et al 2011). However, the lignin ether peak at 1466 cm^{-1} did not show the same dose response as seen in the primary lignin peak (Figure 5.15). Earlier studies suggested that this peak was less sensitive to degradation than the primary lignin peak (Schauwecker et al 2011). In addition, impregnating samples with iron oxide or brushing them with chromic acid did not protect the aliphatic region, suggesting that extractives associated with the natural color and decay resistance of the wood were being removed from the surface (Figure 5.16). These data suggest that retaining even a small amount of the lignin significantly improved color retention.

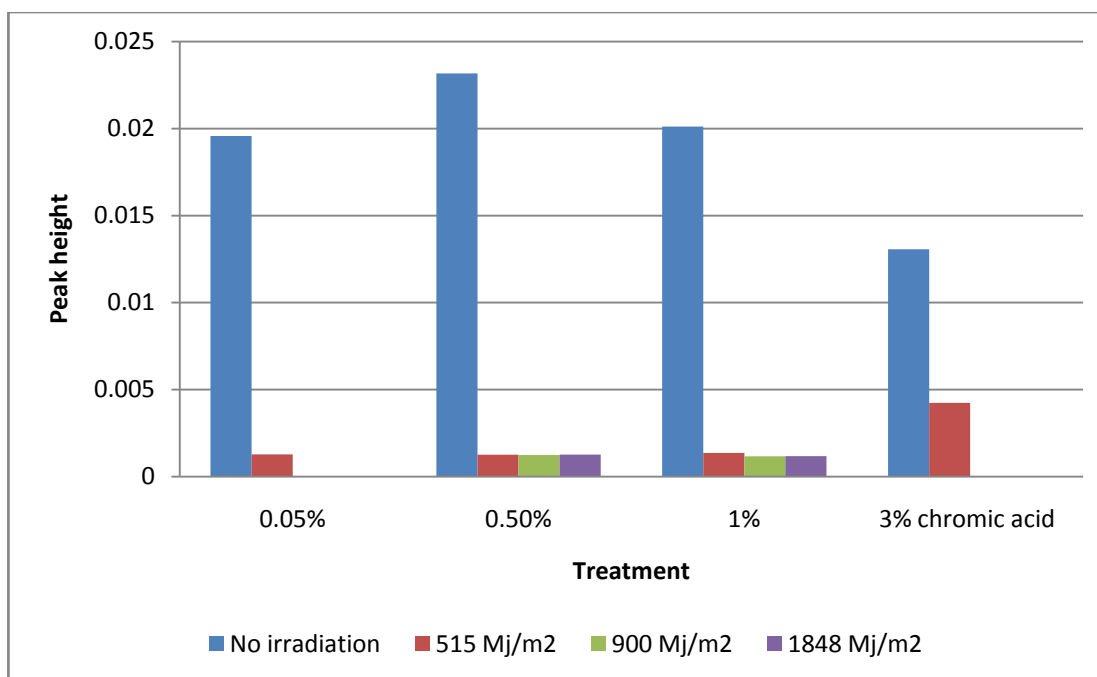


Figure 5.14. Reduction in the primary lignin peak (at 1518 cm^{-1}) in FTIR spectra for samples treated with various loadings of 122 nm red iron oxide or brushed with 3% chromic acid and exposed to irradiation dosages ranging from 515 and 1848 MJ/m^2 in Eastern Oregon.

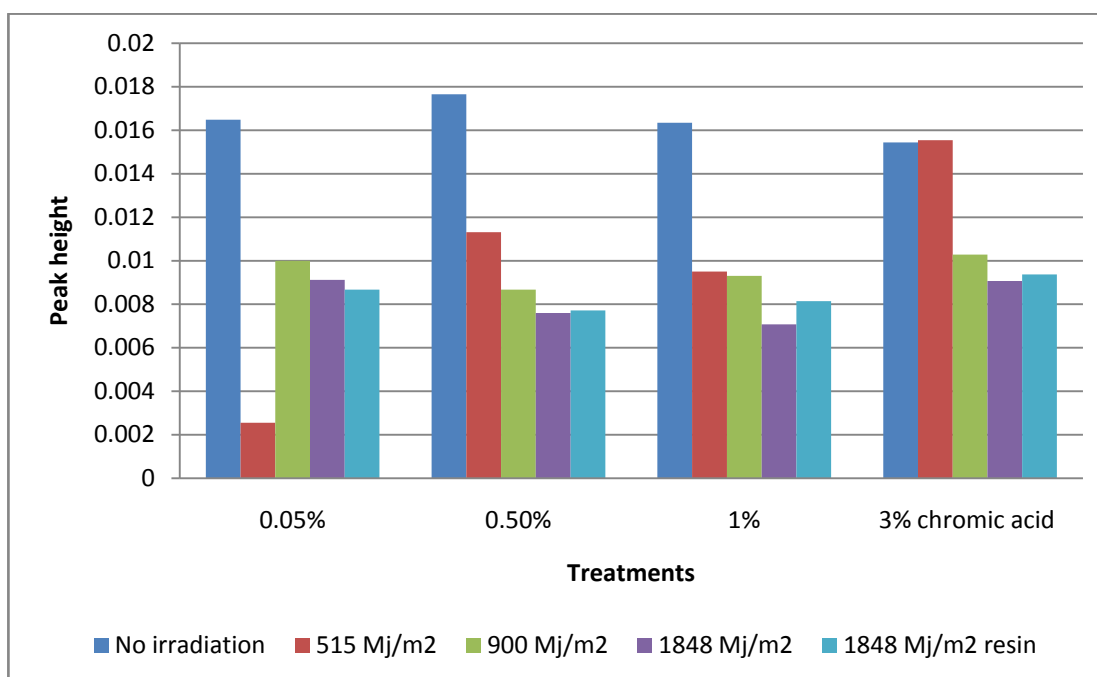


Figure 5.15. Reduction in the lignin ether peak (1466 cm^{-1}) in FTIR spectra for samples treated with various loadings of 122 nm red iron oxide or brushed with 3% chromic acid and exposed to irradiation dosages ranging from 515 and 1848 MJ/m^2 in Eastern Oregon.

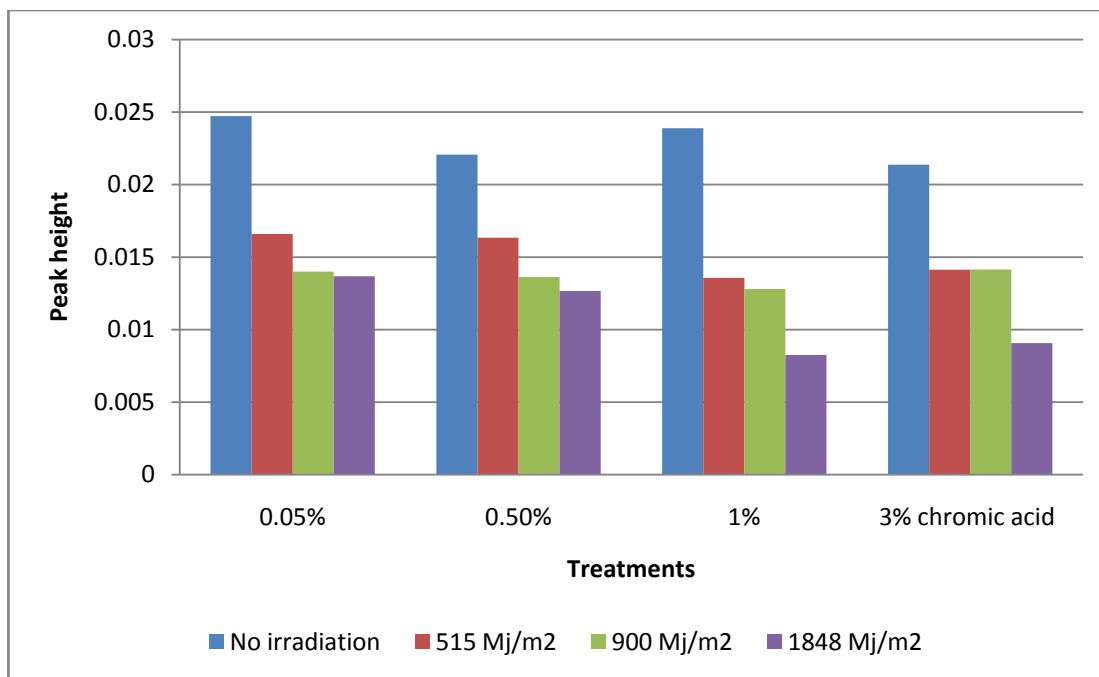


Figure 5.16. Reduction in the aliphatic peak (2950 cm^{-1}) in FTIR spectra for samples treated with various loadings of 122 nm red iron oxide or brushed with 3% chromic acid and exposed irradiation dosages ranging from 515 and 1848 Mj/m^2 in Eastern Oregon.

5.4.5 Effects of various iron oxides

Improvements in lignin protection occurred with increasing yellow iron oxide particle size, as evidenced by the pure lignin peak and reinforced by the lignin ether peak at 1466 cm^{-1} (Figures 5.17-19). However, the first lignin ether peak at 1600 cm^{-1} was rapidly lost. In addition, FTIR spectra suggested that larger yellow iron oxide particles resulted were associated with larger residual aliphatic peaks suggesting that some of the extractives on the wood surface were protected for a longer period of time. These results, and those obtained by monitoring discoloration, suggest that larger yellow iron oxide particles result in a more opaque surface that limits the amount of solar radiation reaching the wood surface this limits the potential for free radical reactions. Spectra collected from samples treated with red iron oxides of similar particle size indicated that these compounds provided less protection for the lignin and the aliphatic region than comparable yellow iron oxide pigments (Figures 5.20-21). These data demonstrate the importance of crystal shape when selecting pigments for this

application, since crystal shape determines which regions of the solar spectra are absorbed, reflected or transmitted. Data collected from the low retention red iron oxides also reinforced the pattern observed in the yellow iron oxides, indicating that larger particles provided more protection and that fade resistance at low retentions was dominated by the removal of the pigment itself rather than lignin retention.

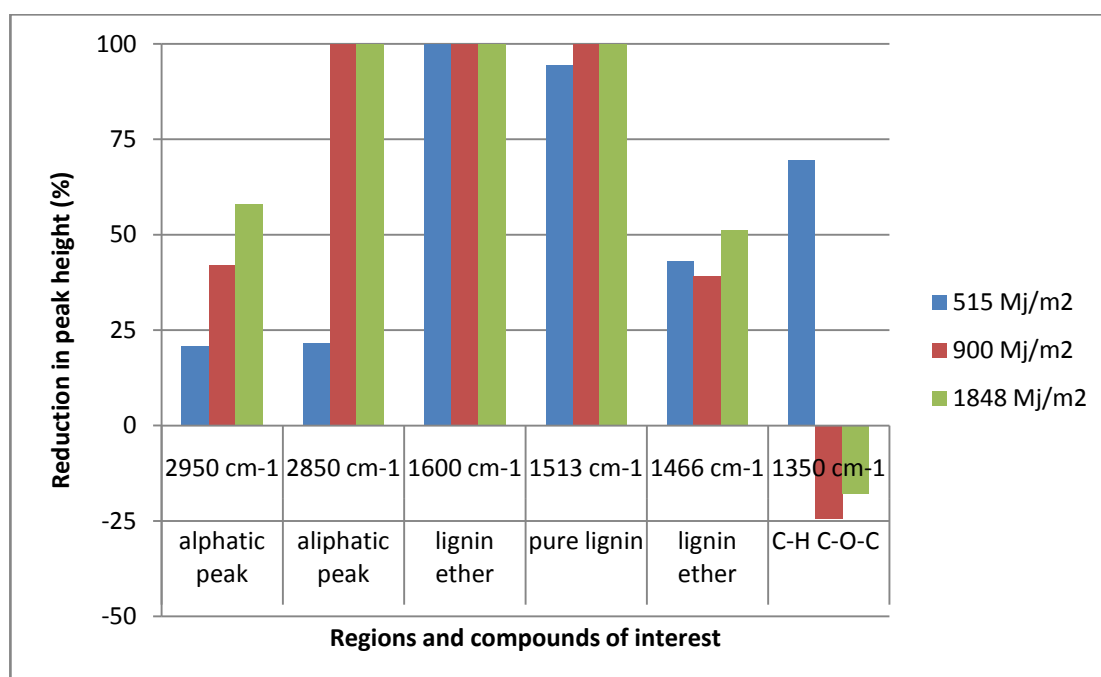


Figure 5.17. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 124 nm yellow iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 Mj/m² in Eastern Oregon.

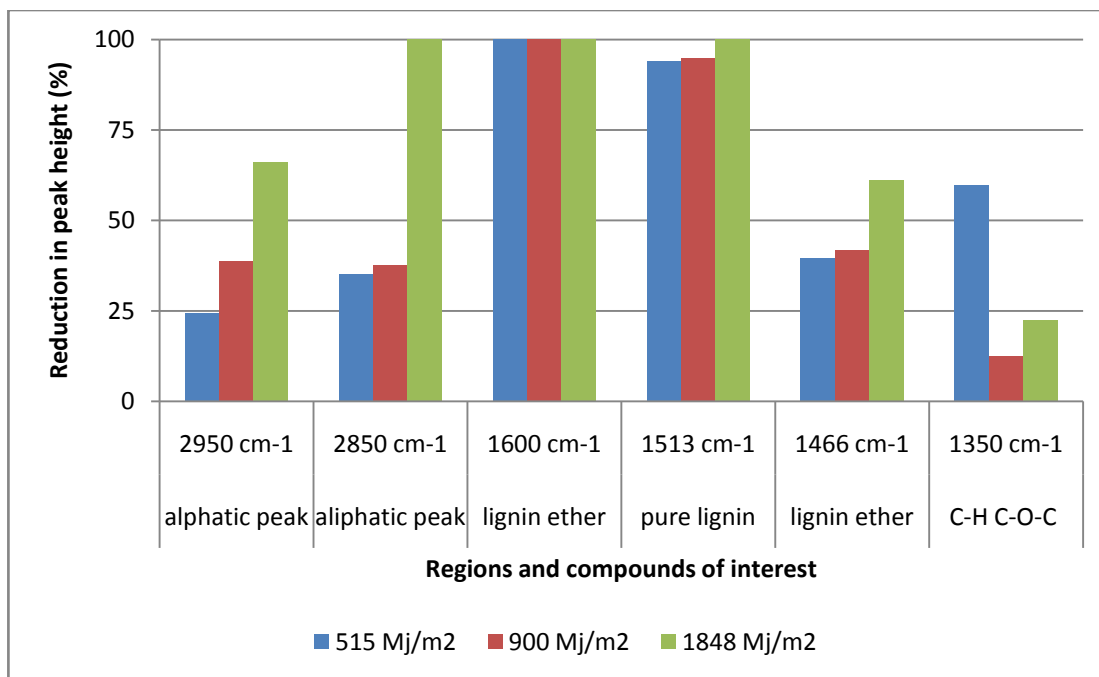


Figure 5.18. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 417 nm yellow iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

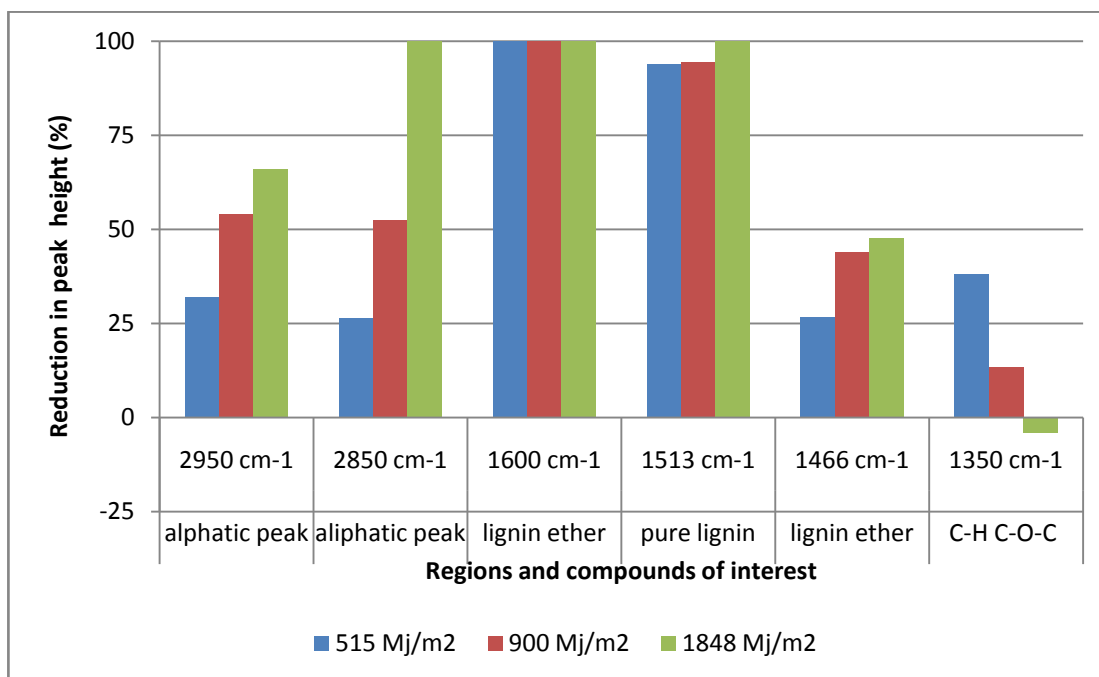


Figure 5.19. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 1480 nm yellow iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

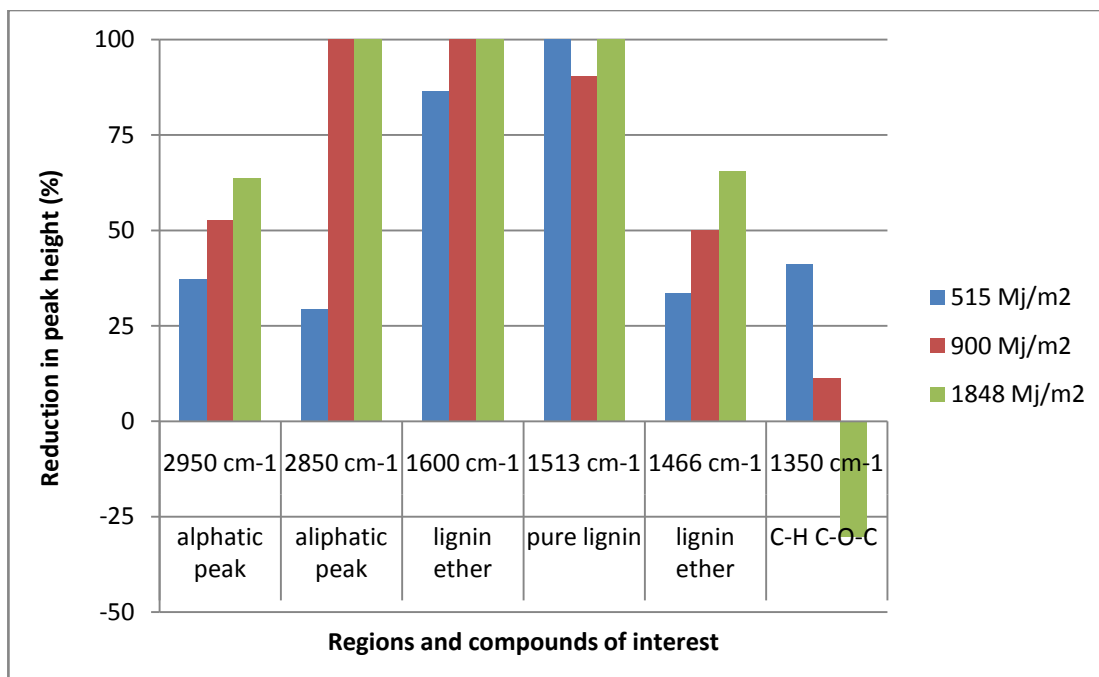


Figure 5.20. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 122 nm red iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

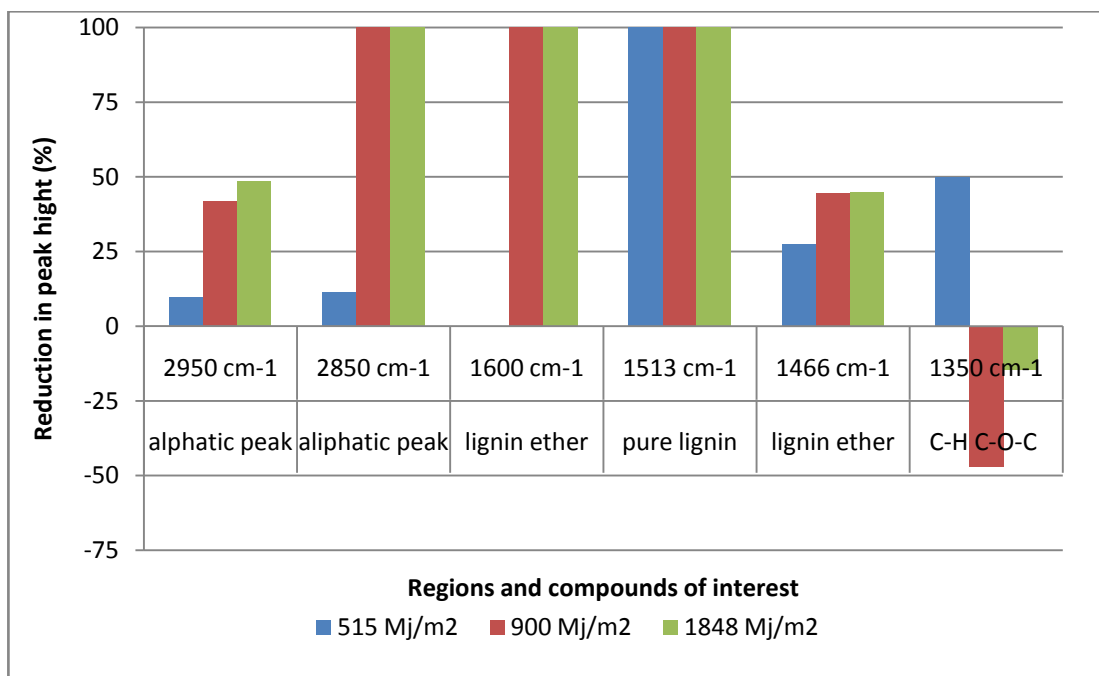


Figure 5.21. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 1850 nm red iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

Spectra indicated that black iron oxide treated samples rapidly lost all lignin components regardless of particle size (Figures 5.22-23). In addition, these samples lost more of the aliphatic peaks than their red and yellow counter parts. This was surprising since the 1074 nm black iron oxide exhibited the least amount of color change. These results suggest that even though lignin loss is important to degradation of wood surfaces, the effects can be masked by pigment retention on the surface, especially early during the weathering process.

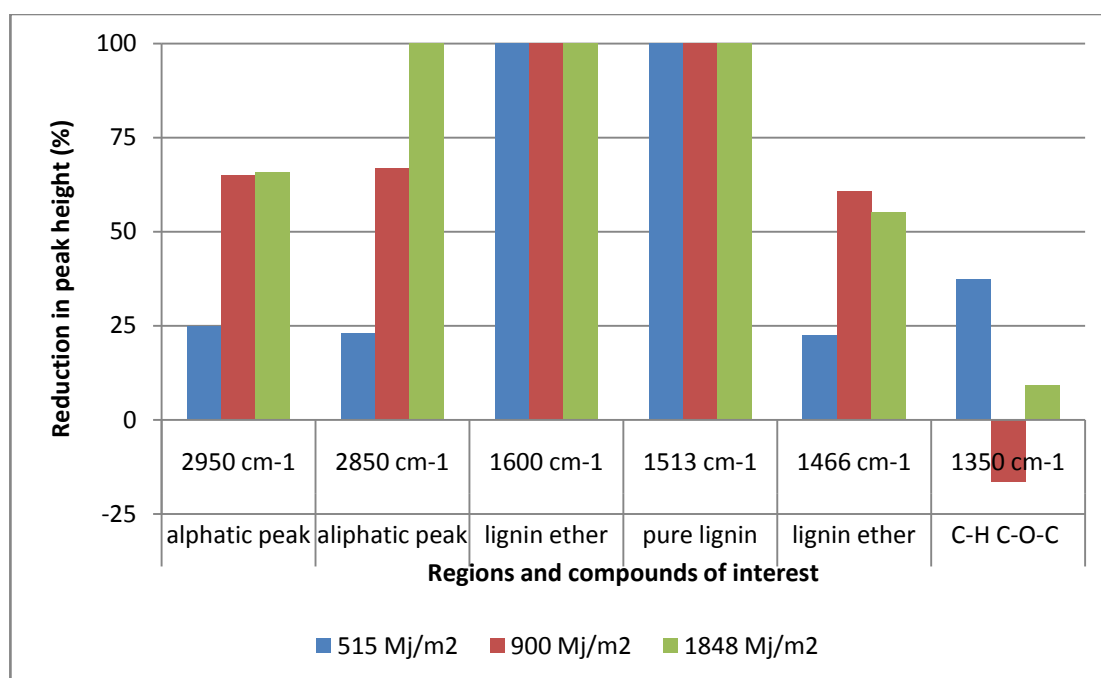


Figure 5.22. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 1074 nm black iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

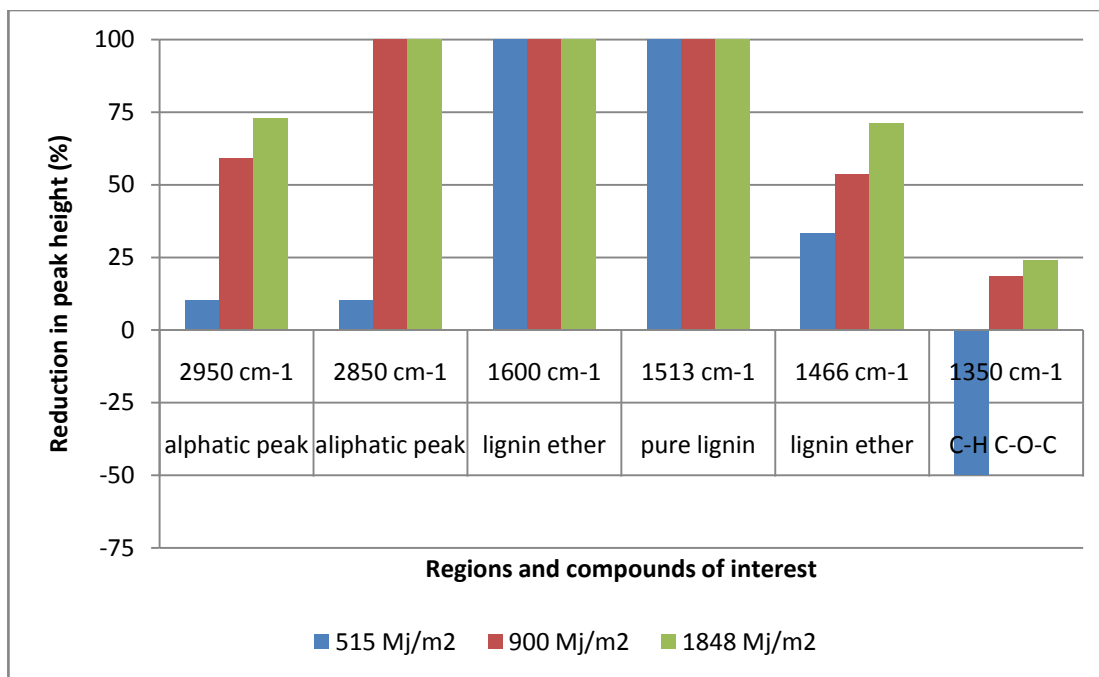


Figure 5.23. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 4173 nm black iron oxide particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

Carbon black, a well known UV inhibitor used in the polymer industry, was included in this study to serve as a surrogate for small particle size black iron oxide because the magnetic properties of magnetite made it difficult to achieve fine grinds and prevent agglomerations in dispersions (Funt et al 1993). In addition, weathering studies conducted in Arizona using a high density polyethylene matrix suggested that the protective properties of carbon black and iron oxide were similar (Polymer Processing Company 2010). FTIR evaluation of samples treated with 162 nm carbon black suggested that this compound protected lignin at the same levels found with similar sized red and yellow iron oxide particles (Figure 5.24). However, carbon black did not protect aliphatic components as well as the iron oxide suspensions. Deconvolution of the carbonyl region was conducted for this compound since the pigment did not interfere with the analysis. These data suggest that the addition of carbon black stabilized the carboxylic acid content on the wood surface throughout the exposure period (Figure 5.25), indicating that carbon black slowed, but did not arrest lignin degradation. However, degradation of the ester peak suggested that hemicellulose was still being lost from the

surface. In addition, the increase in the conjugated ketone peak suggested that the cellulose content on the surface increased with time indicating that carbon black slowed but did not completely prevent degradation. These results, in combination with the discoloration data, suggest that higher loadings of carbon black should be investigated further, especially in applications where dark colored materials are desired.

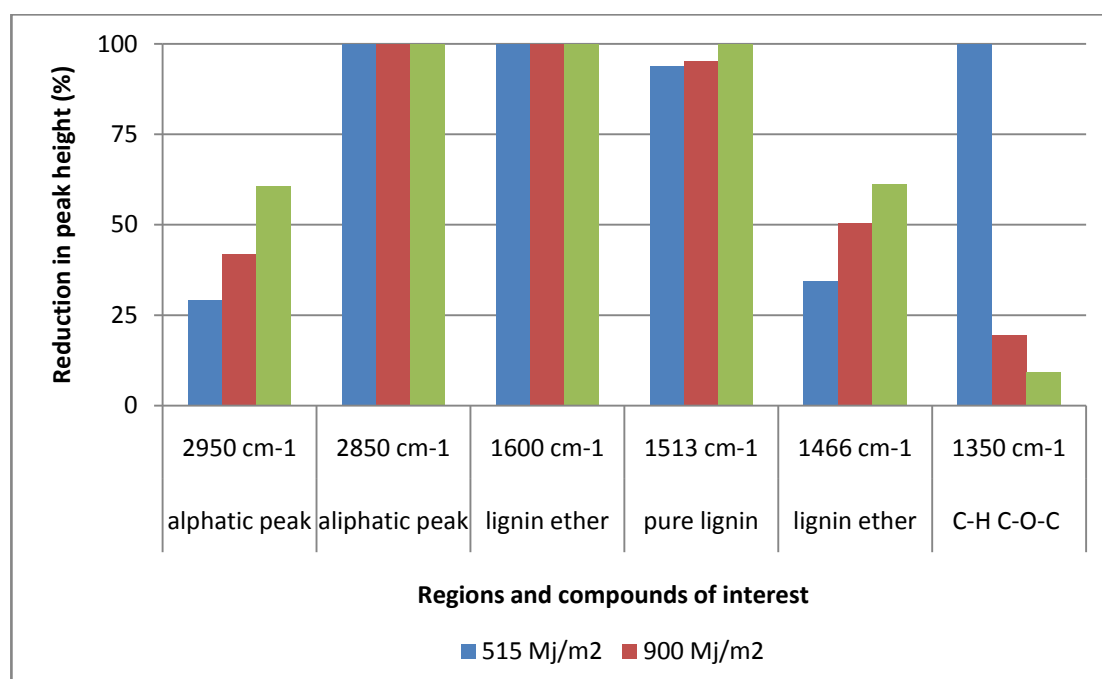


Figure 5.24. Reduction in FTIR peak height for loblolly pine samples impregnated with a 1000 ppm dispersion of 162 nm carbon black particles and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

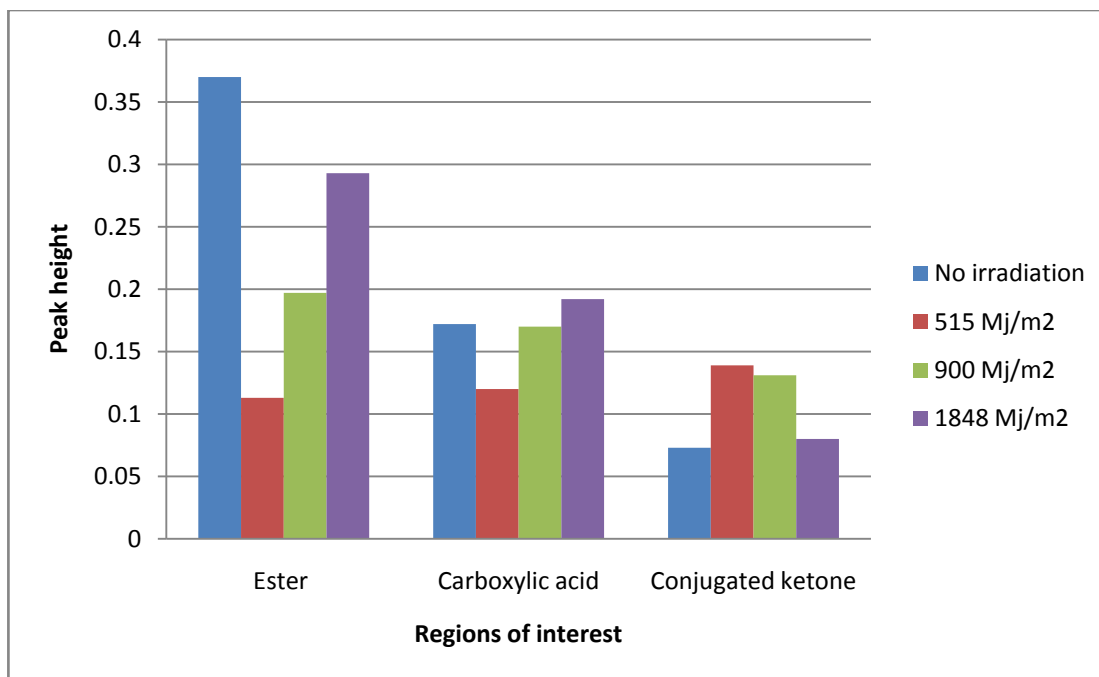


Figure 5.25. FTIR peak heights for the carbonyl region of loblolly pine samples impregnated with a 1000 ppm dispersion of 162 nm carbon black and then exposed to irradiation dosages ranging from 515 to 1848 MJ/m² in Eastern Oregon.

5.5 Conclusions

Yellow and red iron oxides reduced wood surface discoloration and provided some protection to the lignin polymer, the most susceptible component of the lignocellulose matrix (Schauwecker et al 2011). A follow up study assessing different forms of iron oxide showed that discoloration and lignin losses were reduced with increasing retentions of 122nm red iron oxide. In addition, a direct correlation was observed between iron oxide retention and checking after the first 515 MJ/m² of solar irradiation. However, there was no long term protection from checking, suggesting that the mechanisms leading to discoloration and checking differed. This study indicated that retentions similar to those used to protect wood against biological decay with chromium copper arsenate (CCA) or alkaline copper quaternary compound (ACQ) were required to prevent discoloration.

Comparisons of different iron oxides at a fixed retention indicated that carbon black and 1074nm black iron oxide produced the greatest discoloration reductions. FTIR data

suggested that while the black iron oxides masked the effects of solar irradiation, the carbon black dispersion protected the lignin and the wood surface. No clear trends were detected within the red iron oxide treatments; however, the colorimetry data suggested that red iron oxides provided more protection against discoloration than yellow iron oxide of similar particle size. This difference was most likely due to masking since these compounds failed to provide additional lignin protection. A direct relationship was observed between yellow iron oxide particle size and color retention. A similar relationship was also observed when lignin retention was investigated, with larger yellow iron oxide particles providing greater protection. These findings suggest that increased opacity results in better protection. Most importantly, the wood grain was still clearly visible even when treating with the largest particle sizes. These data indicate that further research should focus on yellow iron oxides and carbon black dispersions at higher retentions, since these compounds provided the greatest lignin protection. Such research should investigate other formulations of iron oxide dispersions, various doses and an increased range of particle sizes on other economically important wood species.

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6. CONCLUSION

Population growth in a world with limited non-renewable resources requires more efficient use and reuse of raw materials. Humans have exploited wood and wood based derivatives since the Stone Age and wood continues to play a large role as an industrial feed stock in the petroleum era. However, in order to reduce the environmental footprint of the human population, the role of wood based materials must expand. A major drawback of wood based building materials is their poor weathering characteristics, preventing exposed wooden members from being used in outdoor applications for extended periods of time when both structural integrity and aesthetic appeal are important. The interactions of wood surfaces and atmospheric variables leading to weathering have been extensively investigated, but our understanding remains incomplete and continues to evolve. Preventing weathering can be addressed using solutions tied to the same underlying principles: preventing moisture ingress and obscuring the surface of the material. These objectives are most easily obtained through the application of paints and heavily pigmented stains. Most other methods for preventing weathering do not produce significant improvements and those that show promise are associated with either significant environmental or economic drawbacks.

None of the treatments investigated in this study provided substantial protection from weathering over an extended period of time, but some compounds, especially iron oxides and petroleum based water repellents, provided some protection. However, compounds from within a given group of materials could not be interchanged without affecting performance. These findings suggest that melt point, particle shape, size and possibly other variables unique to a given compound greatly affected their ability to prevent weathering. In addition, compounds that reduced discoloration did not prevent checking, suggesting that the mechanisms leading to discoloration and checking were not directly related.

6.1 Future directions

The results suggest more research is required to understand the effects of climate on the weathering of wood surfaces. While previous studies have evaluated the effects of a single variable, such as acid rain or high elevation, on weathering, there is little work on how the weathering of wood surfaces is altered in different climates, especially in the presence of surface protective compounds. While it is advantageous to evaluate potential surface protectant systems in harsh climates, since exposure in such locations reduces time to market, weathering indexes should be developed to allow for data correlation to regions where these products are more likely to be employed. Such indexes could be developed by relating climate variables such as relative humidity fluctuations, precipitation, solar radiation and temperature, to weathering variables, especially checking, discoloration or lignin loss. This data could be generated by exposing matched samples in strategic locations across the world in conjunction with weather stations, allowing for correlation of climatic variables and the weathering properties of wood. Similar indexes have been developed in the wood preservation industry and are extremely useful when harsh locations are used to quickly evaluate the potential performance of a new wood preservative. In addition, such indices could be used to develop the service life predictions needed in life cycle analysis models, a necessity for green building certification regimens.

The tropical exposure location clearly showed that abiotic weathering does not occur in a vacuum, but reflects interactions with microorganisms. The effects of biotic forces on weathering are unknown; results from this work suggest that the presence of fungi leads to increased discoloration and loss of degradation products. Thus, the microbial role in the weathering of wood surfaces should be investigated further. Such studies could be conducted by artificially aging wood surfaces, colonizing them with different fungal strains, and comparing surface chemistry after set exposure. The effect of dark colored (melanin containing) fungi to shade the wood surface from solar radiation should be evaluated by exposing samples pre-

colonized with pigmented or non-pigmented strains of *Ophiostoma piliferum*. After set exposure periods, samples would be evaluated to determine if changes in the weathering characteristics on the surfaces can be identified, particularly related to lignin degradation.

The evaluation of checking is critical to understanding the surface degradation of wood. Check assessment is tedious and time consuming. Until recently it was performed by manually measuring the length and width and sometimes depth of individual checks. This process limited replication and the number of variables that could be evaluated. The advent of computer aided image analysis has allowed for more rapid evaluation of checks in two dimensions. However, the data obtained is incomplete since the system does not collect check depth data. Depth information could be compiled using ultrasound or x-ray tomography methods. Such tools would lead to qualitative and possibly quantitative three dimensional maps of the surface, providing additional information on check propagation as surfaces weather. While these methods have already been applied to study the voids within wood composites and the weathering of coatings, they have not been applied directly to wood surfaces. Strain fields, precursors to check formation, should also be evaluated to gain a greater understanding of the forces that must be overcome to prevent check formation. While strain fields can be evaluated using advanced light imaging techniques, these methods need areas of high contrast, requiring the surface to be coated and thus making it difficult to apply to wood surfaces at this time. Therefore, advances in image analysis methods are needed in order to gain a greater understanding of the strain fields that develop on wood surfaces as they are exposed to solar radiation and moisture cycling.

Chemical evaluation of wood surfaces is frequently used as a tool for studying changes in cellulose, hemicellulose and lignin components on the surface. Traditionally this has been accomplished through wet chemistry or use of IR or FTIR techniques. Recent advances in microscopy have allowed for the collection of both visible and chemical data from the same area. For example, these techniques could determine if lignin was lost primarily from

the middle lamella regions or from the secondary cell wall. These findings could lead to the development of treatments targeted at specific cell wall layers. In addition, there is little data on the chemical changes to the protective compounds while deployed on wood surfaces. A greater understanding of how these compounds interact with the wood polymers and how they are degraded or depleted could lead to early predictions of service life. In the addition, such findings could also be used to develop better grafting systems, allowing the compounds to be directly attached to the cell wall components where they are needed and making them less susceptible to leaching or physical degradation.

The evaluation of different groups of candidate surface protection compounds has shown the complexity of the weathering. The results also illustrate the seemingly obvious observation that individual compound properties are important when selecting chemicals for this application. Additional groups of compounds such as zinc and zirconium containing materials should be evaluated for their effects on surface performance along with detailed studies on the behavior of individual compounds within a group. Future studies should focus on different petroleum and non-petroleum based waxes since data from this dissertation suggests that melt point is important in determining water repellency. Likewise, different silicon and titanium dioxide formulations should be evaluated along with different organic UV light inhibitors and free radical scavengers. However, the likelihood of identifying a single compound that will prevent all aspects of weathering on wood surfaces is extremely small. Instead the search should concentrate on the potential for synergy between compounds selected from different groups of materials. Thus, studies evaluating combinations of water repellents, pigments and organic UV inhibitors employed in tandem should be carried out.

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