OUTDOOR WEATHERING OF SOL-GEL-TREATED WOOD

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Abstract

Outdoor weathering of wood specimens treated with sol-gel formulations based on methyltrimethoxysilane (MTMOS), hexadecyltrimethoxysilane (HDTMOS), and ferric-zirconia-titania (Fe-Zr-Ti) sol was evaluated. The sol-gel process allowed deposition of a thin film of hybrid inorganic-organic networks (gel) in the wood cell wall that resulted in improved outdoor weathering properties. The sol-gel-treated specimens showed better color retention compared with non-treated control specimens after one-year exposure outdoors. However, in terms of uniformity of color retention, the general appearance of the treated specimens after outdoor exposure was only average to good. Whereas the non-treated control specimens showed slight micro-checks and uniform severe bleaching after outdoor weathering, the sol-gel-treated specimens showed relatively less bleaching that appeared to be confined to some parts of earlywood.

Keywords
Outdoor weathering, sol-gel treated wood, color stability, wood surface photostabilization

Introduction

Wood weathering outdoors is induced by solar radiation (ultraviolet (UV)), visible (Vis), infrared (IR), moisture (dew, rain, snow, and humidity), and temperature and oxygen [1]. Of these factors, Ultraviolet (UV) radiation is the most damaging and is responsible for the primary photochemical degradation of wood surfaces. UV radiation can penetrate wood up to a depth of 75 µm, and visible light radiation can penetrate wood to a depth of 200 µm [2]. Other factors such as blowing wind, sand, dirt, and acid rain can further exacerbate the degradative effects of outdoor weathering on wood [3].

It is widely recognized that lignin, one of the main chemical components of wood, is a strong UV radiation absorber. Photodegradation of lignin chromophores, containing coniferylaldehyde and α-carbonyl groups and various quinodic structures, leads to formation of radicals that further depolymerize lignin and other chemical components of wood, cellulose, and hemicellulose [4]. Figure 1 shows examples of such chromophores, A and B [5]. These radicals undergo further photochemical reactions as illustrated in Figure 2 to form colored compounds that absorb in the violet-blue region of the visible light spectrum [6–8]. Absorption of visible light leads to photo bleaching of the wood surface. Thus, the wood-weathering process is a competition between color-generating reactions initiated by UV radiation, and color bleaching reactions caused by Vis radiation. In addition to causing loss of original color, weathering degrades the integrity of the wood surface and impairs performance of applied exterior wood coatings [9, 10].
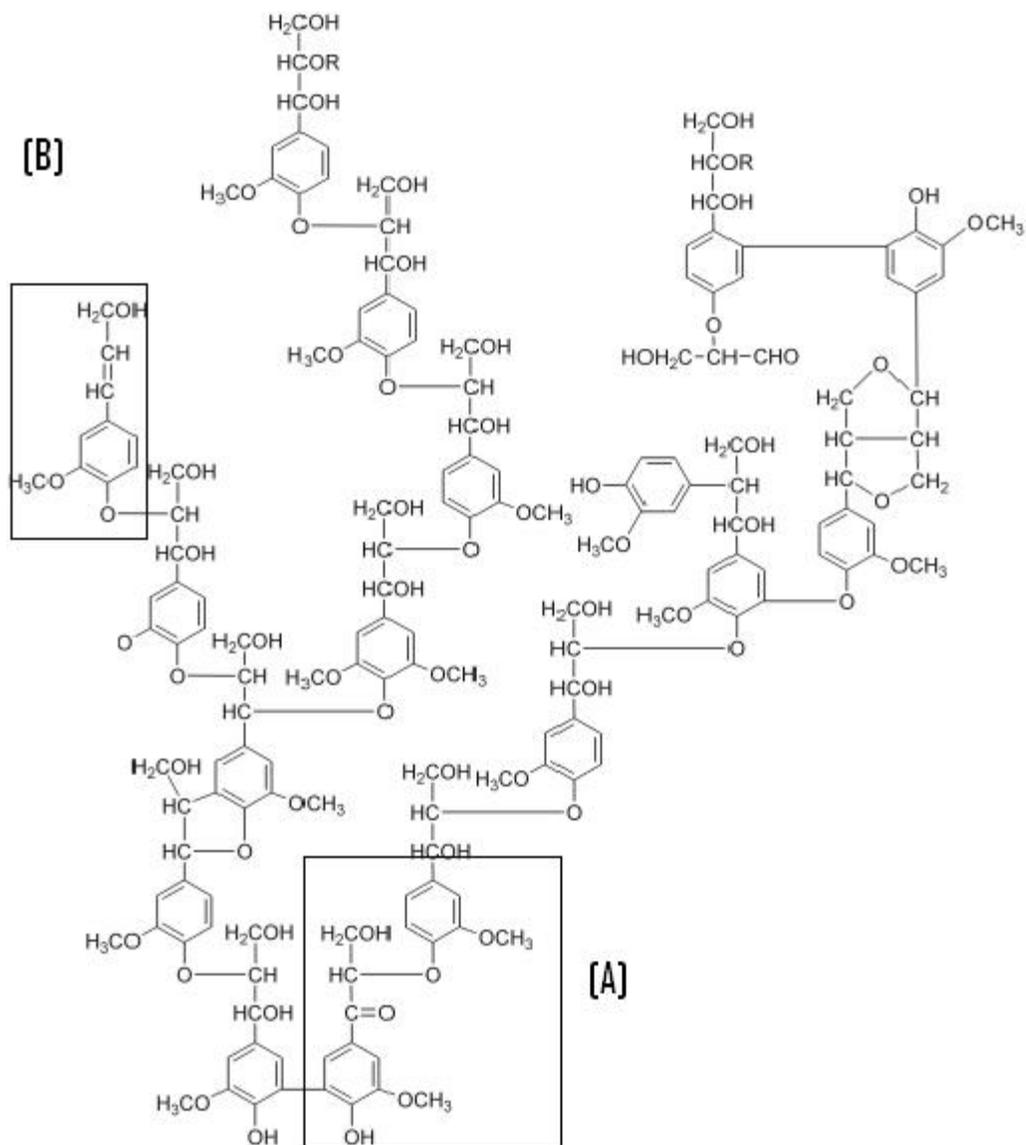
Figure 1: Schematic of lignin structure illustrating chromophores, A and B, that lead to the formation of colored compounds, which absorb in the violet-blue region of the visible light spectrum [6, 11].
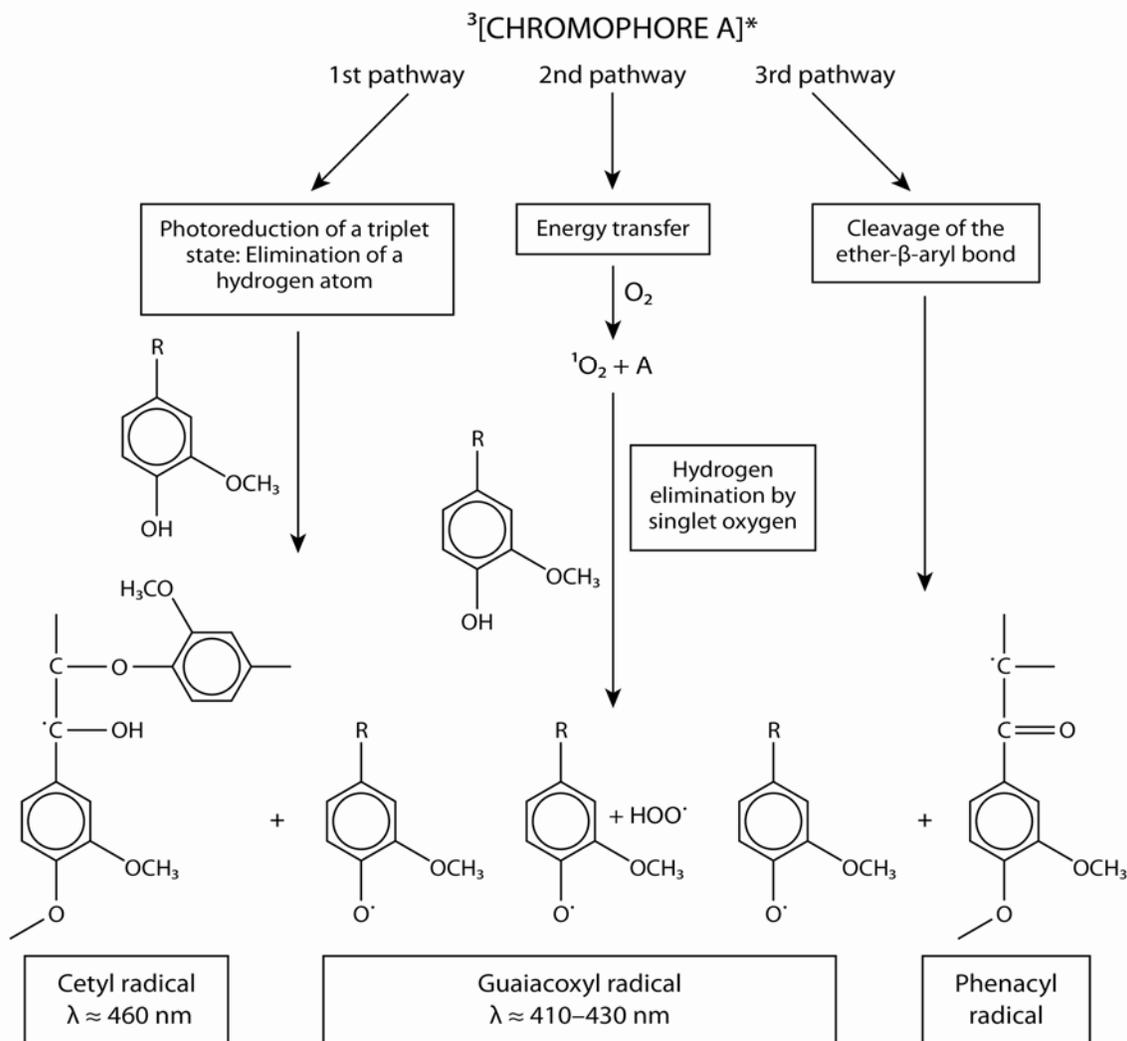
Figure 2: Mechanism of free radical formation from lignin photodegradation [6].

The focus of contemporary approaches to protecting wood from weathering is photostabilization of the wood surface against the action of UV radiation. These approaches rely on use of organic UV absorbers to block UV radiation from reaching the wood surface and on hindered amine light stabilizers (HALS) for scavenging radicals formed from lignin photolysis reactions. In recent years, there has been increased interest in the use of inorganic UV blockers for photostabilization of wood surfaces. Inorganic UV blockers incorporated as nanoparticles in wood clear coatings block UV radiation from reaching the wood surface by scattering and absorption while remaining transparent to visible light [12]. Inorganic UV blockers can also be deposited on the wood surface by plasma-enhanced chemical vapor deposition (PECVD) or by sol-gel deposition methods.

Denes *et al.* [13], Denes and Young [14], and Podgorski *et al.* [15] modified wood surfaces with polysiloxanes under cold plasma conditions to create water-repellent characteristics and to minimize damage caused by weathering. Recently, Bente *et al.* [16] reported plasma treatment of wood surfaces with a mixture of silane/nitrogen gases to create water-repellent characteristics

using a dielectric-barrier gas discharge at atmospheric pressure. The advantages of PECVD methods are intensity and efficiency. Furthermore, they are dry processes and are confined only to the outermost layers of the wood surface. One major disadvantage of PECVD methods is their requirement for expensive vacuum systems. However, dielectric-barrier gas discharge at atmospheric pressure may change that situation if simple equipment is developed that can maintain a good homogeneous gas discharge for plasma treatment of wood.

Brebner and Schneider [17] modified wood by sol-gel deposition of alkoxysilanes to decrease its hygroscopicity and improve its anti-swelling efficiency. Tanno *et al.* [18] reported sol-gel treatment of wood with a mixture of 3-trimethoxysilyl-propyl-carboxymethyl-decylmethyl ammonium hydroxide (TMSAH) inner salt and 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) to improve its antimicrobial resistance. In our laboratories, we have demonstrated that sol-gel deposition of thin barrier films using a mixture of multifunctional alkoxysilanes on wood improves its moisture-resistance properties [19] and its color stability under exposure to accelerated weathering conditions [20]. One major advantage of sol-gel deposition methods is that they allow low-temperature deposition of nanoparticle metal oxide thin films on wood surfaces that block UV radiation by scattering.

This paper deals with *in situ* sol-gel deposition of hybrid inorganic/organic thin films on wood substrates with the goal of improving their outdoor weathering properties. Because such hybrid inorganic/organic thin films have high barrier properties with respect to permeation rates of oxygen and water vapor [21], as well as UV radiation-blocking properties, they could be useful in retarding the weathering process of wood in several ways. First, because of their nanoparticle morphology, they can scatter UV radiation, and obstruct it from reaching the wood surface, thus reducing the probability of initiating photodegradation. Second, because of their high barrier properties to permeation by oxygen, they can limit availability of oxygen, which participates in the photodegradation of wood surfaces [22]. Third, by including a sol-gel precursor with hydrophobic properties in the sol-gel formulation, the resulting hybrid inorganic/organic thin film can limit moisture access to the wood surface, thus reducing swelling of the wood cell wall. Swelling and shrinking of the cell wall exacerbates the degradative effects of wood weathering. Finally, since sol-gel silica thin layers on textiles and paper improve the leaching stability of bound dyes [23], it is conceivable that they can also improve the leaching stability of wood extractives that give wood its natural color.

The objective of this study was to evaluate the weathering performance of sol-gel-treated wood specimens compared with non-treated control specimens. After 342 days of outdoor weathering, each specimen was evaluated for color change, surface erosion, micro-checks, and general appearance.

Experimental

Materials and Methods

Specimens for outdoor weathering were prepared in the form of 3-inch by 4-inch by 1/4-inch (76.2-mm by 101.6-mm by 6.35-mm, radial, longitudinal, tangential) mini-boards from 46-inch (1168.4-mm) beveled western redcedar boards that had been stored at 27°C and 30% relative humidity (RH). Six replicates of each specimen were treated layer-by-layer with the sol-gel components and according to the protocols described in Table 1. L1, L2, and L3 denote sol-gel layers 1, 2, and 3, respectively, with L3 as the topmost layer, L2 as the middle layer, and L1 as the bottom layer. Preparation of the Fe-Zr-Ti sol has been described previously [24].

Table 1. Specimen treatment scheme for outdoor weathering

Treatment ID	Sol-gel layers	Treatment protocol
WT1	L1: MTMOS[a] L2: Fe-Zr-Ti[b] L3: HDTMOS[c]	Layers were applied without drying period between applications
WT2	L1: MTMOS L2: HDTMOS L3: Fe-Zr-Ti	Layers were applied without drying period between applications
WT3	L1: MTMOS L2: Fe-Zr-Ti L3: HDTMOS	Layers were applied with 24-h drying period between applications
WT4	L1: MTMOS L2: HDTMOS L3: Fe-Zr-Ti	Layers were applied with 24-h drying period between applications
Non-treated	None	None
[a] Methyltrimethoxysilane. [b] Ferric-Zirconia-Titania sol. [c] Hexadecyltrimethoxysilane.		

Treated and non-treated specimens were securely fastened to a 342.9-mm by 406.4 mm (13.5-inch by 16-inch) wooden frame with stainless steel fasteners, each frame holding four treated and one control specimen (Figure 3). The frames were placed at the Valley View test site (Madison, Wisconsin), facing due south at a 45° vertical angle. Table 2 presents a summary of monthly averages of temperature and relative humidity measurements recorded at the test site during outdoor exposure.

The color of each specimen was measured at five contiguous spots with a Technidyne Micro S-5 Brightimeter (Technidyne Corporation, New Albany, Indiana). Surface erosion and micro-checks were assessed visually with a Wild Heerbrugg Photomakroskop M400 light microscope (Wild Heerbrugg AG, Gais, Switzerland). General appearance of the specimens was assessed visually and reported on a scale of 1–10, with 1 indicating poor appearance and 10 indicating very good appearance.

Figure 3: Outdoor weathering of sol-gel-treated and non-treated (control) wood specimens.

Results and Discussion

Color change measurements

Color measurements were determined according the CIE L*a*b* system of three parameters. The L* axis represents the lightness and varies from 100 (white) to zero (black). The a* coordinates represent chromaticity with +a* for red and –a* for green; and the b* coordinates represent chromaticity with +b* for yellow and –b* for blue. L*, a* and b* were measured before and after 342 days of outdoor weathering. These values were used to calculate the resulting color change, ΔE*, according to the following equations:

$$\Delta L^* = L^*_{(f)} - L^*_{(i)} \tag{1}$$
$$\Delta a^* = a^*_{(f)} - a^*_{(i)} \tag{2}$$
$$\Delta b^* = b^*_{(f)} - b^*_{(i)} \tag{3}$$
$$\Delta E^* = \{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\}^{1/2} \tag{4}$$

ΔL*, Δa*, and Δb* are differences between the initial (i) and final (f) values; the higher the ΔE* value, the greater the color change. As illustrated in Figure 4, after 342 days of outdoor weathering, control specimens showed the greatest color change, whereas the treated specimens showed color change that increased in the order WT2 > WT1 ≈ WT4 > WT3. These results suggest that inclusion of drying steps between application of successive layers (WT3 and WT4) resulted in better weathering performance compared to no drying steps between successive layers (WT1 and WT2). In addition, treated specimens with HDTMOS as top layer (WT1 and WT3) performed better compared with those with Fe-Zr-Ti as top layer (WT2 and WT4). Evidently, HDTMOS, a hydrophobic alkoxysilane, limited moisture access to the wood surface and helped to slow down the rate of weathering.

Surface erosion and micro-checks

Surface erosion of the specimens after 342 days outdoor weathering was evaluated by light microscopy. Figure 5 shows light microscopy images of non-weathered specimens and specimens exposed outdoors for 342 days. The non-treated controls showed washboard-like erosion of the earlywood. The treated specimens showed a pattern of micro-checks with no discernible erosion. However, WT2 and WT4 showed less micro-checking compared with WT1 and WT3.

General appearance

Figure 6 shows images of the specimens at the start and after 30, 100, 280, and 342 days of outdoor weathering. At the start (Day 0), the non-treated specimens had a very light reddish tint, whereas the treated specimens had a reddish-brown color. After 30 days outdoor exposure, the non-treated control specimens showed more severe color change compared with the treated specimens. Among the treated specimens, WT2 and WT4 showed slightly greater color change compared with WT1 and WT3. After 100 days, all specimens showed different extents of color reversion, with the non-treated controls being more intense compared with all the treated specimens except for WT3. The most dramatic surface color changes occurred after 280 days exposure during the spring months. The non-treated control showed severe bleaching with a grayish hue. Among the treated specimens, WT2 and WT4 showed more bleaching compared with WT1 and WT3. After 342 days exposure, during the fall season, the non-treated control specimen showed very severe bleaching and graying. The treated specimens showed different extents of milder bleaching, with WT2 and WT4 more bleached than WT1 and WT3.

The general appearance scores assigned visually to the specimens after 100 and 342 days of outdoor weathering are shown in Table 3. All specimens except for WT1 received the same scores. WT1 received a slightly lower score primarily because of dark brown blotches, which gave the appearance of non-uniform color bleaching.
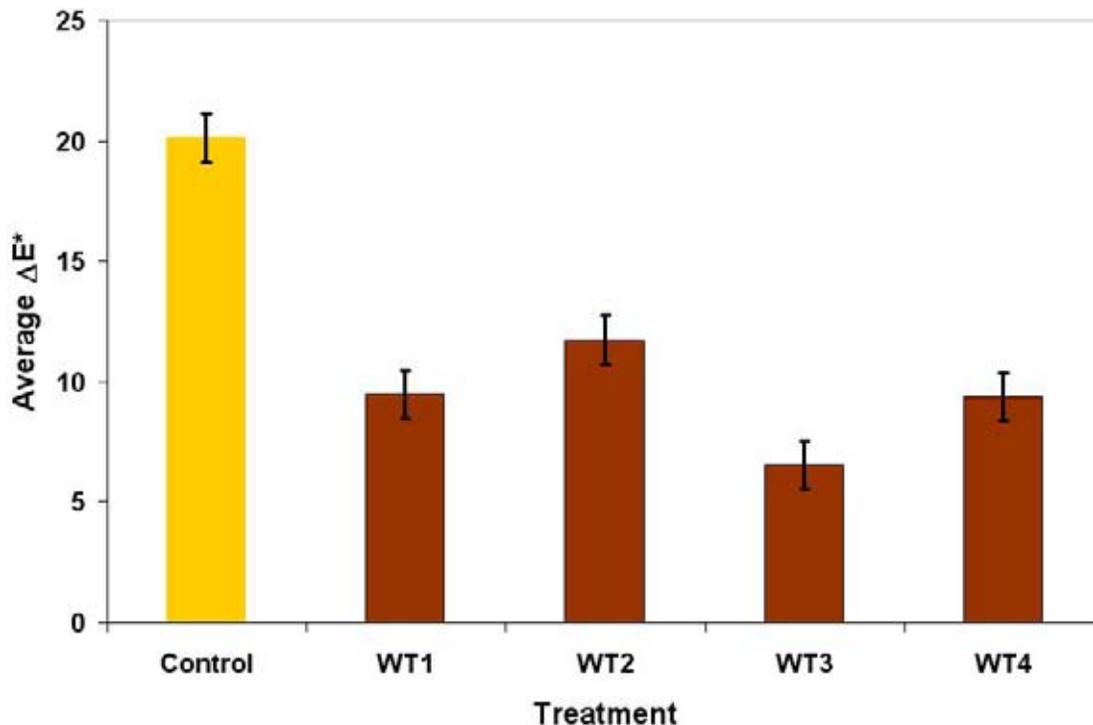

Figure 4: Color change of specimens after 342 days outdoor weathering.
(Error bars indicate ± standard deviation for five replicate measurements.)

Table 2. Monthly averages of temperature and relative humidity measurements at the test site during outdoor exposure of wood specimens

Month	Temperature (°F)	RH (%)
Fall 2007 September 2007	NA[a]	NA
October 2007	57.5 ± 7.8 ($n = 22$)[b]	86.5 ± 10.2 ($n = 22$)
November 2007	NA	NA
Winter 2007 December 2007	23.3 ± 7.0 ($n = 31$)	96.8 ± 4.0 ($n = 31$)
January 2008	20.0 ± 14.5 ($n = 31$)	92.1 ± 7.6 ($n = 31$)
February 2008	20.3 ± 9.1 ($n = 16$)	92.1 ± 7.2 ($n = 16$)
Spring 2008 March 2008	32.2 ± 8.6 ($n = 31$)	85.1 ± 8.7 ($n = 31$)
April 2008	49.4 ± 9.7 ($n = 30$)	80.3 ± 13.1 ($n = 30$)
May 2008	57.9 ± 5.7 ($n = 26$)	73.1 ± 10.2 ($n = 26$
Summer 2008 June 2008	69.3 ± 4.9 ($n = 17$)	85.6 ± 10.0 ($n = 17$)
July 2008	NA	NA
August 2008	NA	NA
[a] NA is data not available. [b] n is number of replicates.		

Table 3. General appearance scores[a]

Time (days)	WT1	WT2	WT3	WT4	Non-treated
100	3 ± 1 ($n = 4$)[b]	6 ± 3 ($n = 3$)	5 ± 1 ($n = 4$)	5 ± 1 ($n = 4$)	5 ± 0 ($n = 4$)
342	3 ± 1 ($n = 4$)	4 ± 1 ($n = 3$)	6 ± 0 ($n = 4$)	4 ± 1 ($n = 4$)	5 ± 1 ($n = 4$)
[a] On a scale of 1–10, 1 is "poor appearance" and 10 is "very good appearance." [b] n = number of replicates.					

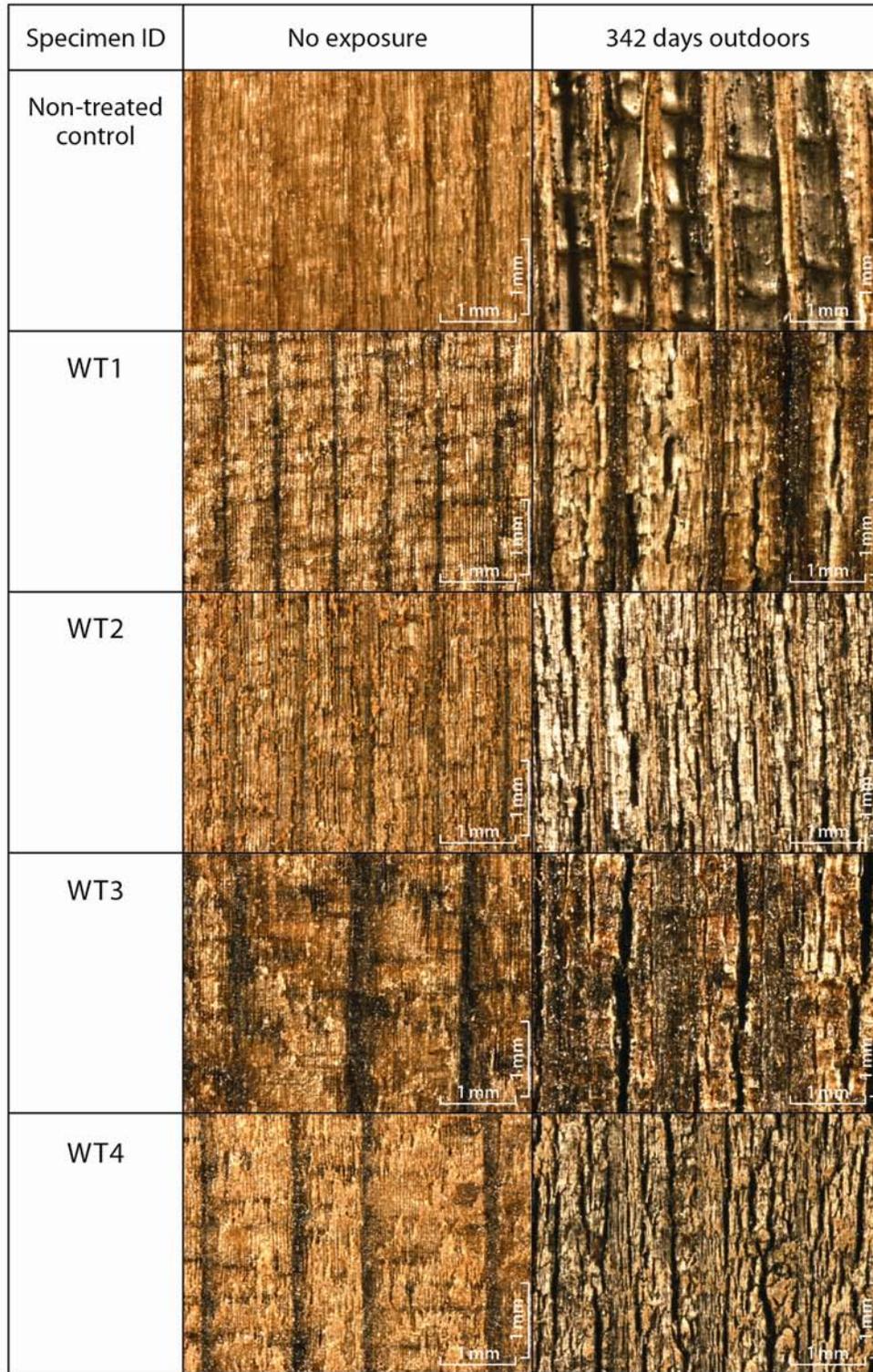| Specimen ID	No exposure	342 days outdoors
Non-treated control		
WT1		
WT2		
WT3		
WT4		

Figure 5: Light microscopy of non-weathered and weathered wood specimens.
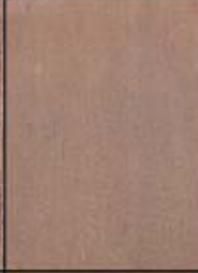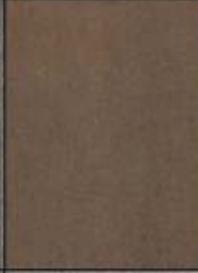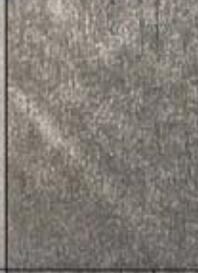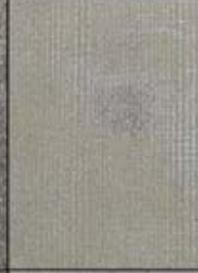
Figure 6: Images of specimens at various outdoor-exposure intervals.

Conclusions

Sol-gel thin films deposited in the wood cell walls of wood surfaces improved outdoor weathering properties by two mechanisms. The UV-blocking effect of the Fe-Zr-Ti layer interfered with one or more of the lignin photodegradation pathways described in Figure 2. The moisture-excluding effect of the MTMOS (Methyltrimethoxysilane) and HDTMOS (hexadecyltrimethoxysilane) layers limited the degradative stress of swelling and shrinking of the wood cell wall.

The effectiveness of these thin films in improving outdoor weathering properties of the wood surface depended on three factors: the chemistry of the sol-gel precursors, the order of deposition of the sol-gel layers on the wood surface, and inclusion of a drying step between depositions of successive layers. Specimens with the hydrophobic (HDTMOS) sol-gel top layer performed better compared with specimens with the UV-blocking (Fe-Zr-Ti) sol-gel top layer. Inclusion of a drying step between depositions of successive sol-gel layers resulted in better weathering properties compared with deposition of successive layers without intervening drying steps.

Acknowledgments

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