

# Accelerated Weathering of Wood Surfaces Coated With Multifunctional Alkoxysilanes By Sol-Gel Deposition

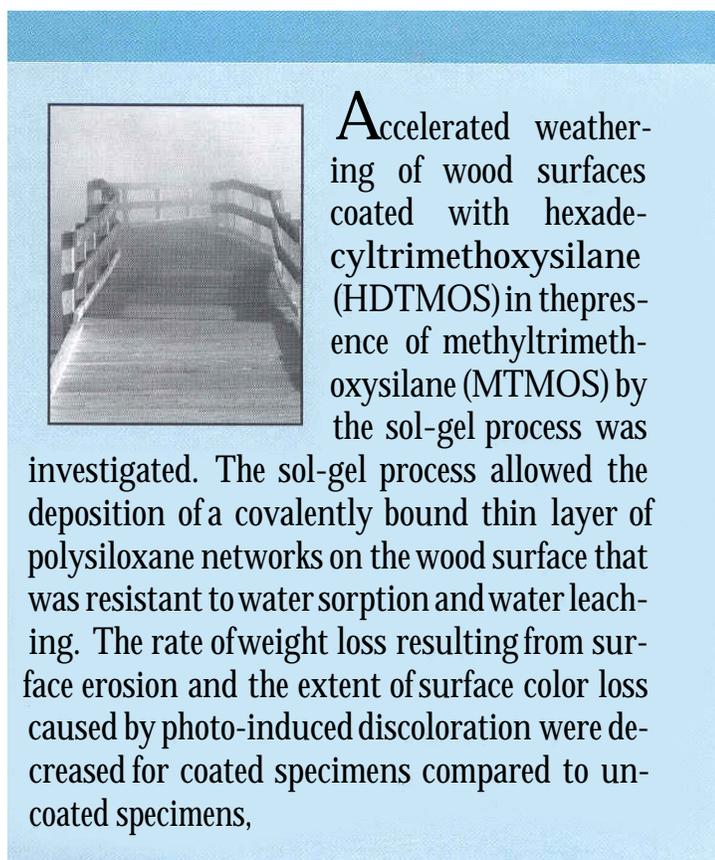
Mandla A. Tshabalala and John E. Gangstad—Forest Products Laboratory\*

## INTRODUCTION

The combined action of moisture and sunlight can cause deterioration of wood surfaces exposed above ground. To control this deterioration, wood surfaces are protected with moisture-excluding and ultraviolet (UV) protective coatings. However, the requirement of low water permeability in a protective coating is often incompatible with many other desirable coating properties, such as adhesion to the wood, ease of application, opacity or color, toughness, abrasion resistance, and chemical stability. The property of moisture impermeability itself may give rise to coating weaknesses that defeat the very purpose of the coating. For example, paint film blistering on wood surfaces can often be traced to water vapor entrapment beneath an impermeable paint film. In addition, paint film checking on wood surfaces is often closely related to dimensional instability of the underlying wood substrate.

Feist and Williams<sup>1-4</sup> observed that small amounts of chromium salts on the wood surface greatly decrease wood weathering. In addition to improving the durability of finishes on wood substrates, chromium salts impart other beneficial properties to wood surfaces, such as fungal resistance, decreased swelling by water, increased water repellency, and enhanced resistance to natural outdoor weathering and extractive bleed. Unfortunately, concerns have arisen about the safe use of chromium-based surface treatments for wood products designed for residential construction. Chromium compounds can have toxic effects on plants, animals, and aquatic life.<sup>5-7</sup> Consequently, alternative technologies are needed that are as effective as chromating technologies in enhancing the durability of wood products in outdoor aboveground applications.

The objective of the present study was to investigate the weathering characteristics of wood surfaces coated



Accelerated weathering of wood surfaces coated with hexadecyltrimethoxysilane (HDTMOS) in the presence of methyltrimethoxysilane (MTMOS) by the sol-gel process was investigated. The sol-gel process allowed the deposition of a covalently bound thin layer of polysiloxane networks on the wood surface that was resistant to water sorption and water leaching. The rate of weight loss resulting from surface erosion and the extent of surface color loss caused by photo-induced discoloration were decreased for coated specimens compared to uncoated specimens,

by the sol-gel process with a combination of methyltrimethoxysilane (MTMOS) and hexadecyltrimethoxy silane (HDTMOS). The alkoxysilanes and sol-gel deposition conditions used in the present study were selected on the basis of previous studies reported by other researchers.<sup>8</sup>

Alkoxysilanes are widely used as crosslinking agents in formulations of paint, ink, adhesives, and water repellents.<sup>9-12</sup> They have also been investigated as possible environmentally acceptable replacements for existing chromating processes for pretreating sheet metal before painting or as corrosion-inhibiting films on

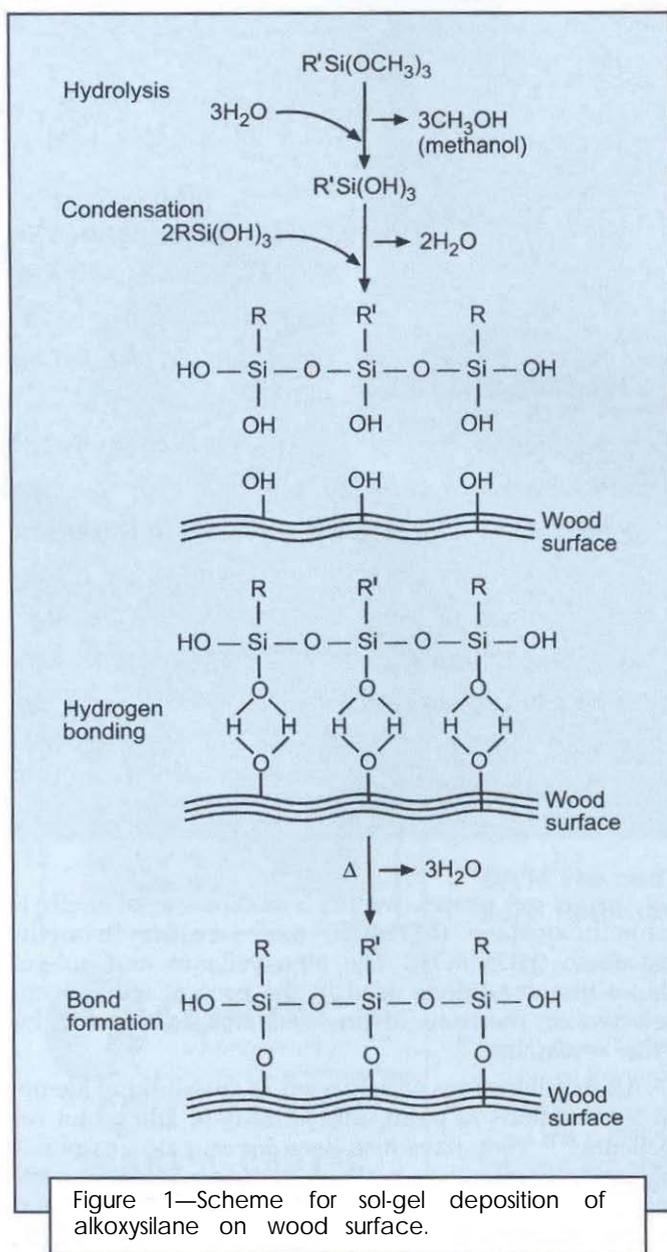
\*USDA Forest Service, One Gifford Pinchot Drive, Madison, WI 53726-2398.

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iron.<sup>13-15</sup> Methyltrimethoxysilane, a multifunctional alkoxy silane, has been shown to be effective for rapid waterproofing of ceramic tiles and blankets used as thermal insulation on aerospace vehicles.<sup>16</sup>

The sol-gel process allows deposition of inorganic-organic polymeric networks on various substrates as a result of controlled hydrolysis and polycondensation of alkoxy silanes.<sup>17-21</sup> Some of these networks have been shown to exhibit high barrier properties with respect to the permeation rates of oxygen, water vapor, and volatile organic compounds.<sup>17</sup> A recent study showed that sol-gel polycondensation networks of some alkoxy silanes deposited on a wood surface enhanced its fire and water resistance properties.<sup>8</sup> Another recent study showed that coating of paper or textiles with sol-gel silica layers containing bound dyes improved leaching stability.<sup>22</sup>

As illustrated in Figure 1, sol-gel deposition consists of several steps, which begin with the hydrolysis of



alkoxy groups by bound water within the wood cell wall to form free silanols and alcohol. The silanols undergo condensation to form polysilanol, which then form hydrogen bonds with the wood surface. Upon heating, these surface hydrogen-bonded polysilanol lose water to form covalent bonds with the wood surface.<sup>8,23</sup>

## MATERIALS AND METHODS

Certain commercial instruments and materials are identified in this paper to adequately describe the experimental procedure. In no case does such identification imply recommendation by the U.S. Department of Agriculture nor does it imply that the instruments or materials are necessarily the best available for the purpose.

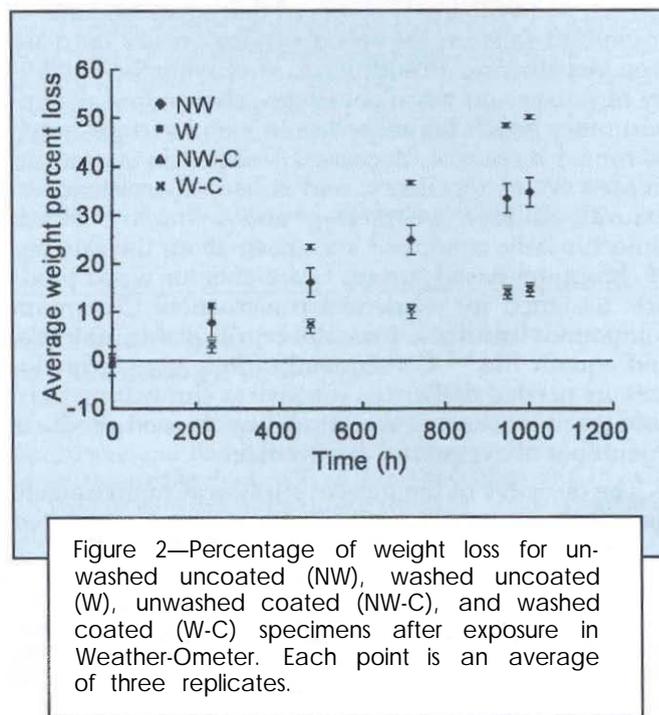
### Materials

N-methyl-2-pyrrolidinone (NMP) and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (Milwaukee, WI). Hexadecyltrimethoxysilane (HDTMOS) and methyltrimethoxysilane (MTMOS) were purchased from Fluka (Milwaukee, WI). Methanol was purchased from Fisher (Fair Lawn, NJ).

Wood specimens were prepared in the form of small thin wafers, 0.8 x 15.8 x 51.3 mm (tangential, radial, longitudinal) from air-dried loblolly pine (*Pinus taeda* L.) boards. Before weighing, labeled specimens were always preconditioned to a constant weight in a controlled humidity room.

### Removal of Extractives

To remove extractives from the outer surfaces, weighed specimens were extracted for 24 hr in a Soxhlet apparatus with an aqueous solution of NMP containing



one part by volume NMP and nine parts by volume distilled water. Specimens were allowed to air dry under the hood for approximately two hours before being transferred to a controlled humidity room to condition at 65% relative humidity (RH), 26.7°C. After conditioning, the weight of each specimen was recorded; all specimens were kept in the controlled humidity environment until further experimentation. Specimens subjected to this procedure will be referred to as "washed " and those not subjected to this procedure as "unwashed. "

**Coating of Wood Specimens**

Ten replicates each of washed and unwashed specimens were weighed and placed in a coating solution at room temperature and under a 15-mm Hg vacuum for three days. Specimens were coated under vacuum to facilitate the removal of gases at the solid-liquid interface. The coating solution consisted of methanol, HDTMOS, MTMOS, and TFA in a volume ratio of 40:20:5:1. After coating, specimens were dried in an oven at 65°C for 24 hr. At the end of the drying period, specimens were allowed to cure for 24 hr in an oven at 105°C. After curing, specimens were placed in a vacuum desiccator to cool to room temperature overnight. Thereafter, specimens were placed in a controlled humidity room and allowed to condition at 65% RH, 26.7°C. Specimens were weighed after conditioning.

**Accelerated Weathering**

Three replicates each of coated and uncoated specimens were exposed for 1,000 hr in an Atlas Weather-Ometer (Atlas Electric Devices Company, Chicago, IL). Specimens were exposed to 102 min of UV radiation and 18 min of combined UV radiation and water spray per two-hour cycle. The radiant energy of the UV lamp, which has 295-300 nm cut-off inner and outer filters made of borosilicate glass, was assumed to be very close to that of natural unfiltered sunlight.

To evaluate the rate of weight loss resulting from surface erosion, specimens were removed from the Weather-Ometer at predetermined intervals, preconditioned first at 30% RH and then at 65% RH, weighed, and returned to the Weather-Ometer for further exposure for a total of 1,000 hr. Before specimens were returned to the Weather-Ometer, their surface color was observed and recorded as not bleached, slightly bleached, or strongly bleached.

**Water Sorption Properties**

Three replicates each of coated and uncoated specimens were removed from the vacuum desiccator, weighed, and placed in distilled water at 25°C in a 120-mL Qorpak bottle equipped with a cap. After equilibrating for 24 hr, specimens were removed from the distilled water and blotted dry with a sheet of absorbent paper. Wet specimens were quickly weighed and returned to the distilled water to equilibrate for an addi-

Table 1—Surface Color Change

Specimen ID	Description	Extent of Surface Color Change	
		240 hr-exposure	1,000 hr-exposure
NW . . . . .	Unwashed controls	Not bleached	Strongly bleached
W . . . . .	Washed controls	Slightly bleached	Strongly bleached
NW-C . . . . .	Unwashed coated	Not bleached	Not bleached
W-C . . . . .	Washed coated	Not bleached	Not bleached

tional day. This procedure was repeated each day for all specimens for the following eight days. To saturate specimens with water, on day eight a vacuum was applied to all specimens in the water and then released. Thereafter, each specimen was blotted dry and weighed quickly as before.

**leaching Characteristics**

Three replicates each of weighed coated and uncoated specimens were placed in 50-mL distilled water at room temperature in a Qorpak bottle equipped with a cap. After each specimen was soaked for 192 hr, the leachate water was transferred to a clean bottle, a fresh 50-mL aliquot of distilled water was added, and the specimen was soaked for another 192hr. This procedure was repeated three more times for a total of 960 hr for each specimen. The leachate water collected from each specimen was analyzed for silicon by inductively coupled plasma spectrometry (ICP).

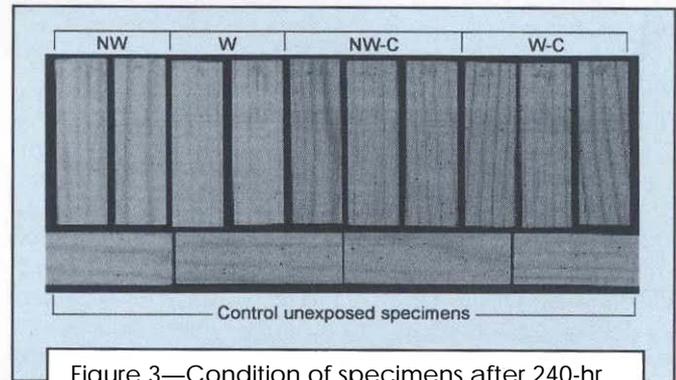


Figure 3—Condition of specimens after 240-hr exposure in Weather-Ometer.

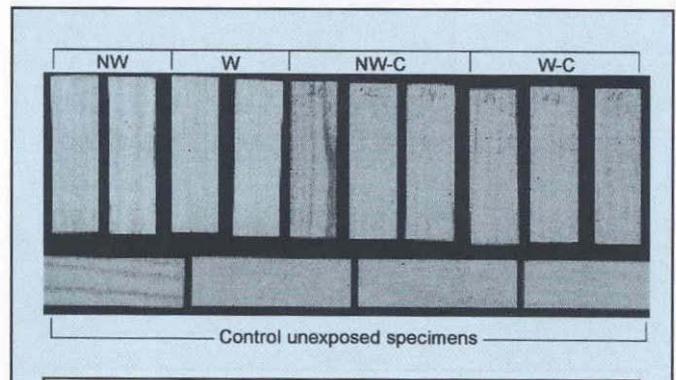


Figure 4—Condition of specimens after 1,000-hr exposure in Weather-Ometer.

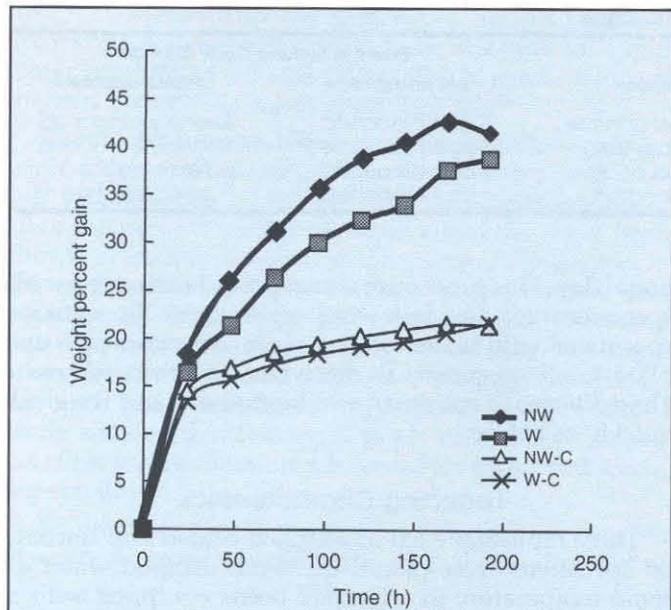


Figure 5—Percentage of weight gain for specimens soaked in distilled water at 25°C. Each point is an average of three replicates.

### Surface Properties

Surface morphology of specimens was obtained by scanning electron microscopy (SEM) on a Jeol JSM-840 scanning electron microscope (Jeol USA, Inc. Peabody, MA). Images were obtained at 15 kV and recorded on Polaroid film.

The surface chemistry was analyzed by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and energy dispersive X-ray analysis (EDXA). The DRIFT infrared spectra were obtained on a Mattson Galaxy 5020 FTIR instrument (Mattson Instruments, Madison, WI) equipped with a deuterated triglyceride sulfate (DTGS) detector. The scan range was 4000-700  $\text{cm}^{-1}$  with a 4- $\text{cm}^{-1}$  resolution; 128 scans were collected. EDXA was carried out on a Tracor Noran TN-5500 energy dispersive X-ray analyzer (ThermoNoran, Middleton, WI). Analysis was carried out at 15 kV with a detector take-off angle of 40° and a collection time of 60 sec.

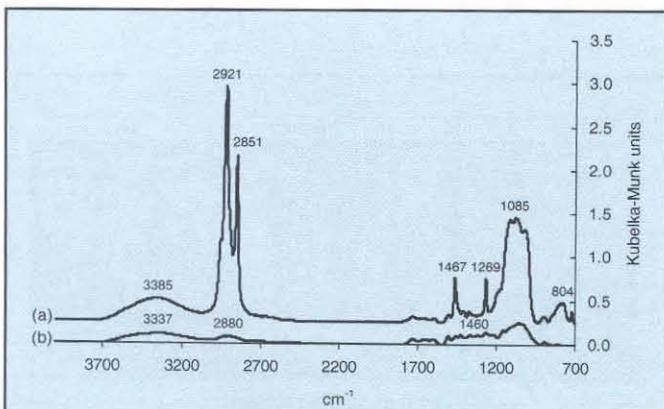


Figure 6—Representative DRIFT spectra of (a) coated and (b) uncoated specimens.

## RESULTS AND DISCUSSION

### Weathering Characteristics

**RATE OF WEIGHT LOSS**—As shown in Figure 2, the rate of weight loss of coated specimens was noticeably less than that of uncoated specimens. After 1,000-hr exposure in the Weather-Ometer, coated specimens showed an average weight loss of approximately 15%, compared to 50% weight loss showed by washed uncoated specimens. The rate of weight loss was highest for washed uncoated specimens followed by unwashed uncoated specimens. There was no significant difference between the rate of weight loss of washed and unwashed coated specimens.

An earlier study compared weight percent loss of  $\text{CrO}_3$ -treated and control extracted southern pine sapwood blocks (2.4 x 2.4 x 0.6 cm, tangential by longitudinal by radial) and reported a weight percent loss of 4.8% and 9.0%, respectively, after 1800-hr exposure in the Weather-Ometer.<sup>24</sup> Compared to  $\text{CrO}_3$  treatment, the sol-gel alkoxy silane treatment reported in the present study appears to be more effective in reducing weight loss after accelerated weathering. As stated in the previous paragraph, the weight percent loss was approximately 15% for the sol-gel alkoxy silane coated specimens compared to 50% for control washed specimens.

**EXTENT OF SURFACE COLOR CHANGE**—Table 1 summarizes observations of the extent of surface color change of specimens after 240-hr and 1,000-hr exposure in the Weather-Ometer. Coated specimens showed very little surface color change even after 1,000-hr exposure. After 240-hr exposure, the surface color of coated specimens had not changed compared to that of the control samples, which had not been exposed to accelerated weath-

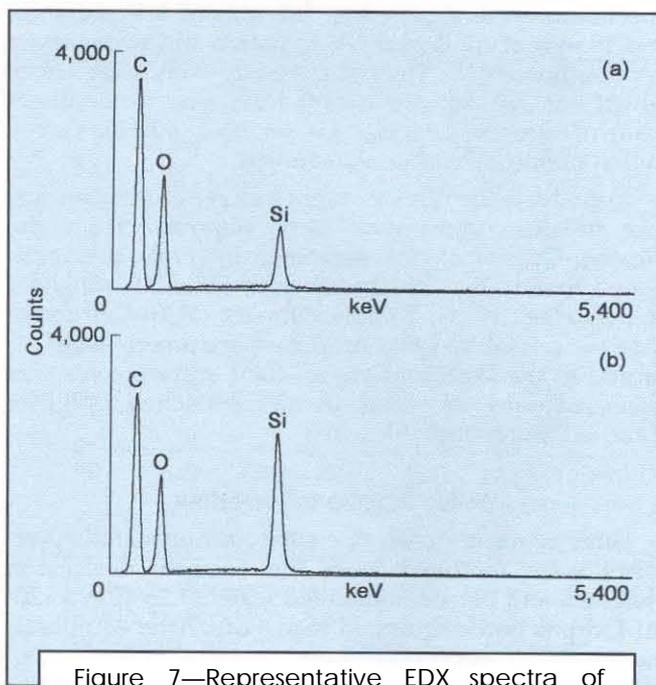


Figure 7—Representative EDX spectra of coated wood specimens (a) before and (b) after 1,000-hr exposure.

Table 2—Weight Loss of Specimens after Leaching with Water for 960 hr

Specimen ID	Description	Average Weight Gain after Coating (g)	Weight Loss from Leaching (%)	Silicon Loss from Leaching ( $\mu\text{g}$ )
NW	Unwashed uncoated	—	0.40	0
W	Washed uncoated	—	1.1	0
NW-C	Unwashed coated	$0.0944 \pm 0.006^a$	0.91	$236 \pm 3^a$
W-C	Washed coated	$0.0761 \pm 0.004^a$	1.3	$214 \pm 3^a$

(a) Average of three replicates.

ering (Figure 3). On the contrary, the surface color of uncoated specimens showed bleaching; washed uncoated specimens showed a greater extent of bleaching than did unwashed uncoated specimens. This trend in the extent of surface color change between coated and uncoated specimens persisted throughout the entire exposure period (Figure 4).

### Water Sorption Properties

Coated specimens showed a measurable decrease in liquid water sorption compared to uncoated specimens (Figure 5). The rate of weight loss as well as the extent of surface color change of specimens subjected to accelerated weathering appears to be directly related to their

rate of liquid water sorption; that is, the lower the rate of liquid water sorption the lower the rate of weight loss and the lesser the extent of surface color change.

### Leaching Characteristics

Although the percentage of weight loss after 960-hr leaching was approximately 1% of the initial weight of each coated specimen, measurable amounts of silicon were detected in the leachate water. As Table 2 shows, the amount of silicon lost by leaching accounted for only a small fraction of the original weight gain of specimens resulting from coating. These results indicate that in addition to leaching of the coating as a silicon-containing surface moiety, a large fraction of weight loss

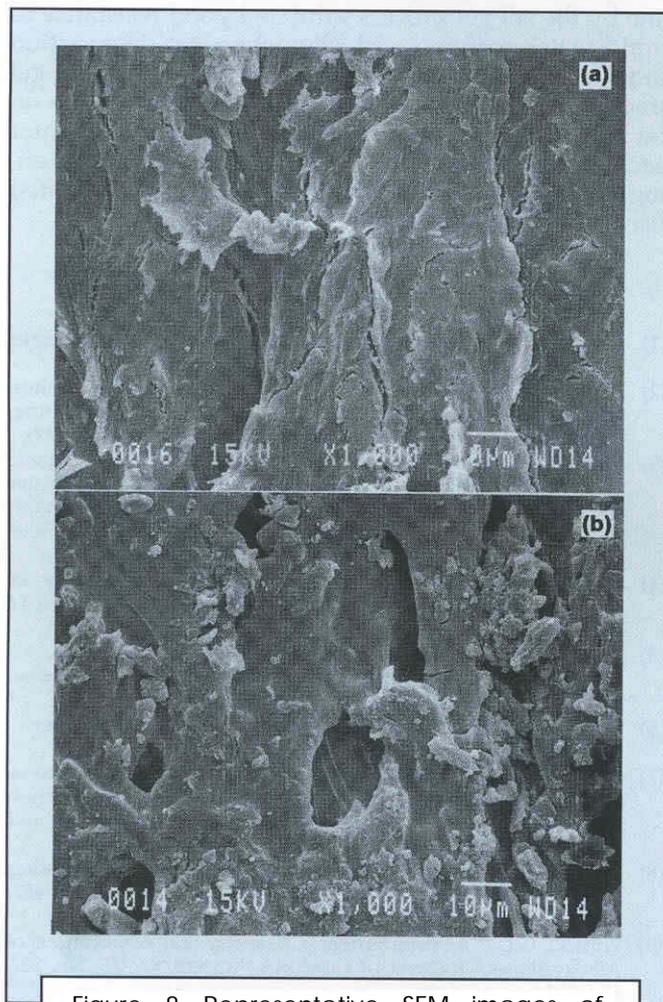


Figure 8—Representative SEM images of coated wood specimens (a) before and (b) after 1,000-hr exposure.

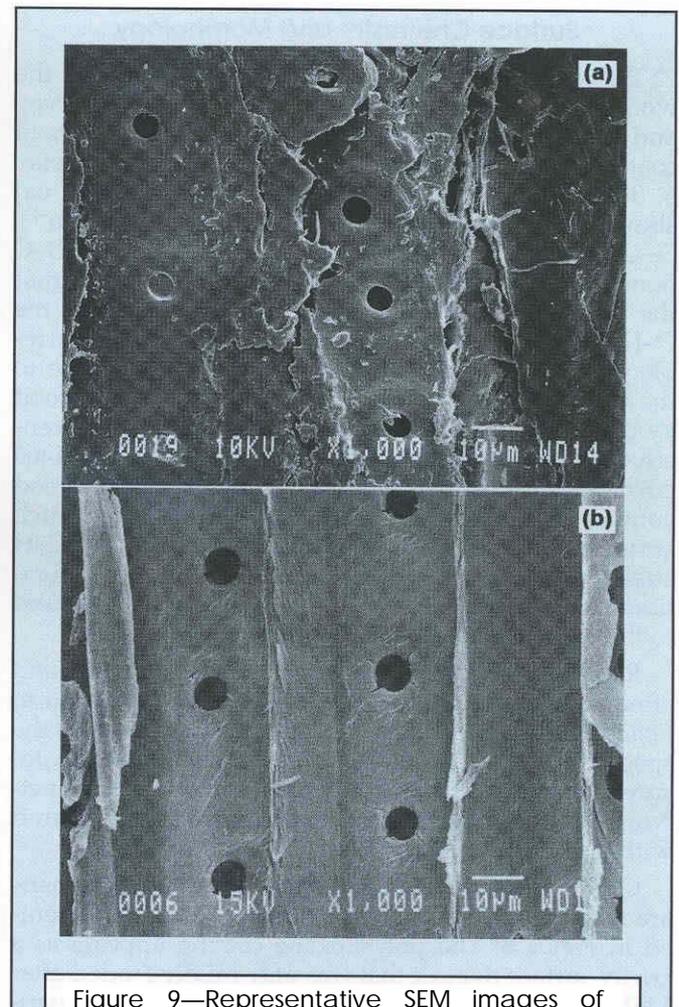


Figure 9—Representative SEM images of uncoated wood specimens (a) before and (b) after 1,000-hr exposure.

Specimen Description	O/C Ratio		Si/C Ratio		Weight Loss after 1000 hr <sup>a</sup> (%)
	Before Weathering	After Weathering	Before Weathering	After Weathering	
Unwashed uncoated. . . . .	0.44	0.72	0	0	34.69 ± 4.6
Washed uncoated . . . . .	0.46	0.68	0	0	50.13 ± 0.45
Unwashed coated . . . . .	0.59	0.30	0.51	0.89	14.67 ± 1.5
Washed coated . . . . .	0.54	0.53	0.38	1.05	14.92 ± 1.1

could be accounted for by nonsilicon containing surface moieties. These nonsilicon containing surface moieties could be water-soluble extractives or residual NMP that was trapped in the wood cell wall, or both. However, judging by the percentage of weight loss (0.4%) of the unwashed uncoated controls, it is reasonable to assume that the predominant nonsilicon containing moiety may be NMP residue trapped in the wood cell wall. Other researchers have observed that water-soluble organic solvents, when applied in aqueous solution, can become entrapped in the wood cell wall to such an extent that prolonged oven drying does not remove them, but the solvents can readily leach out when exposed to liquid water.<sup>25</sup>

### Surface Chemistry and Morphology

The chemistry of the polysiloxane deposit on the wood surface was analyzed by DRIFT and XPS survey and high-resolution XPS spectra.<sup>26</sup> The DRIFT spectra of coated and uncoated specimens are compared in Figure 6. The spectrum of the coated specimen (Figure 6a) shows peaks resulting from Si-OH bonds (3385 cm<sup>-1</sup>), Si-CH<sub>3</sub> bonds (1269 cm<sup>-1</sup>), Si-O, Si-C, and Si-O-C bonds (804 and 1085 cm<sup>-1</sup>).<sup>20</sup> It is important to note that the broad peak centered around 3337 cm<sup>-1</sup> due to the O-H stretch of the wood components (Figure 6b) was replaced by the peak centered around 3385 cm<sup>-1</sup> due to the O-H stretch of the polysilanol bound to the wood by the sol-gel process. In addition, the weak peaks centered around 2880 cm<sup>-1</sup> due to the C-H stretch and 1460 cm<sup>-1</sup> due to the C-H bending vibrations of the wood components were replaced by sharper and much stronger peaks at 2921 and 2851 cm<sup>-1</sup> due to the C-H stretch and at 1467 cm<sup>-1</sup> due to the C-H bending vibrations of the long hydrocarbon chain of HDTMOS bound to the wood by the sol-gel process.

Representative EDX spectra of specimens before and after exposure in the Weather-Ometer are presented in Figure 7. The presence of a significant silicon peak in the spectra of coated specimens even after 1,000-hr exposure supports the proposition that the polysiloxane network deposited by the sol-gel process is strongly bound within the wood cell wall.

Changes in surface morphology of coated specimens are reflected in the representative SEM images presented in Figure 8. The polysiloxane coating appears as a crusty surface deposit that was only mildly eroded after 1,000-hr exposure in the Weather-Ometer. By comparison, the surface of uncoated specimens was severely eroded after 1,000-hr exposure, as evidenced by the

complete degradation of tori and appearance of small cracks at the edges of the pit pores (Figure 9). Note that the surface Si/C ratio of coated specimens increased two to three times after 1,000-hr exposure, whereas the O/C ratio decreased slightly (Table 3). This supports the proposition that accelerated weathering of coated specimens removes water-soluble oxygen-rich compounds and enriches the surface with water-resistant C-Si-O-Si polymeric networks.

## CONCLUSIONS

Wood specimens coated with a combination of methyltrimethoxysilane and hexadecyltrimethoxysilane by the sol-gel process exhibited good resistance to liquid water sorption and photochemical degradation under accelerated weathering conditions. The sol-gel process formed a thin film of polysiloxane networks on the wood surface that was not only resistant to water leaching but also improved the leaching stability of endogenous wood coloring components and mitigated discoloration of the wood.

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