

## Chapter 27

# Sol-Gel Deposition of Inorganic Alkoxides on Wood Surfaces to Enhance Their Durability Under Exposure to Sunlight and Moisture

Mandla A. Tshabalala

USDA Forest Service, Forest Products Laboratory  
One Gifford Pinchot Drive, Madison, WI 53726-2398

*Wood specimens were coated with sol-gel deposits of aluminum isopropoxide, titanium isopropoxide, or zirconium propoxide in the presence of methyltrimethoxysilane. Both zirconium propoxide and titanium isopropoxide sol-gel deposits reduced water sorption, whereas aluminum isopropoxide sol-gel deposit increased water sorption, compared with uncoated wood specimens. These differences may be ascribed to differences in the distribution of the sol-gel deposits within the surface wood cell walls.*

## INTRODUCTION

To control deterioration caused by exposure to sunlight and moisture, wood surfaces are coated with moisture-excluding pigmented paints. Micronized titanium dioxide that is lattice-stabilized with alumina and coated with aluminum and zirconium organic compounds has been used as a general-purpose pigment in many coating systems, including emulsion paints.<sup>1</sup> The objectives of this study are to develop new technologies for sol-gel deposition of alkoxides of titanium, aluminum, and zirconium on wood surfaces and to evaluate their effect on the durability of wood surfaces exposed to sunlight and moisture.

## BACKGROUND

The sol-gel process allows deposition of inorganic-organic polymeric networks on a wide range of substrates, including wood. Some of these networks have been shown to exhibit high barrier properties with respect to permeation rates of oxygen, water vapor, and volatile organic compounds.<sup>2</sup> A recent study showed that sol-gel polycondensation networks of some alkoxysilanes deposited on a wood surface enhanced its fire and water resistance properties.<sup>3</sup> Another recent study showed that coating of paper or textiles with sol-gel-silica layers containing bound dyes improved leaching stability.<sup>4</sup> In our laboratories we are investigating the effect of accelerated weathering of wood surfaces coated with multifunctional alkoxysilane sol-gel deposits.<sup>5</sup> In this chapter, we present preliminary data on the moisture and light resistance properties of wood specimens coated with sol-gel deposits of titanium, aluminum, and zirconium alkoxides in the presence of methyltrimethoxysilane.

## MATERIALS AND METHODS

Wood specimens were prepared in the form of small thin wafers,  $0.8 \times 15.8 \times 51.3$  mm (tangential, radial, longitudinal), from air-dried loblolly pine (*Pinus taeda L.*) boards. Four sets of labeled wood specimens, each set consisting of quadruplicates, were preconditioned to a constant weight in a controlled humidity room. One set served as the control, and the other three sets were exposed to three different sol-gel formulations.

Sol-gel deposition of the metal alkoxides on the wood specimens was performed under a 15-mm Hg vacuum to facilitate degassing at the interface of the wood surface and the coating solution. A typical coating formulation consisted of an isopropanol solution of the metal alkoxide (MAO), methyltrimethoxysilane (MTMOS), and trifluoroacetic acid (TFA) as a catalyst, in the weight ratio, 6:0.5:0.2, respectively. However, to improve the solubility of aluminum isopropoxide in the coating formulation, the aluminum isopropoxide solution was modified with N-methyl pyrrolidinone (NMP), to give a formulation of 6:3:0.5:0.2, MAO:NMP:MTMOS:TFA, respectively. Isopropanol solutions of the metal alkoxides and NMP were purchased from Sigma-Aldrich (St. Louis, MO). MTMOS was purchased from Fluka (Buchs, Switzerland).

Water leaching experiments were performed as described elsewhere<sup>5</sup> except that duplicate specimens were placed in 100-mL aliquots of distilled water for 24-h intervals for a total of 240 h. The leachate was analyzed for Al, Zr, Ti, and Si.

Photodegradation behavior of wood specimens was evaluated by exposing them to a Xenon arc lamp in a Weather-Ometer®. A radiometer was used to measure the irradiance in the 300- to 400-nm wavelength range. The radiant dosage was estimated by multiplying the measured irradiance with exposure time in hours.

The surface chemistry and morphology of the wood specimens were characterized by SEM and EDXA analysis.

## RESULTS AND DISCUSSION

Weight percent gain of wood specimens after coating with the respective sol-gel deposits is summarized in *Table 1*. Specimens were preconditioned at 65% RH, 26.7°C, before and after coating with the sol-gel deposits.

*Figure 1* shows an example of SEM micrographs of wood specimens before and after sol-gel deposition of aluminum isopropoxide in the presence of MTMOS. The lumen surface of the coated specimen appears to have brighter regions, especially around the bordered pits.

The elemental composition of metal alkoxide sol-gel deposits on the surface of wood specimens was confirmed by EDXA analysis. For example, as shown in *Figure 2*, the EDXA spectra of wood specimens coated with sol-gel deposit of aluminum isopropoxide and MTMOS showed aluminum and silicon peaks.

Table 1—Weight Percent Gain of Wood Specimens after Coating with Sol-Gel Deposits

Sol-Gel Deposit	Weight Percent Gain <sup>a</sup>
Aluminum isopropoxide + MTMOS	.177 ± 2
Titanium isopropoxide + MTMOS	.152 ± 3
Zirconium propoxide + MTMOS	.84 ± 2

(a) Average of four replicates.

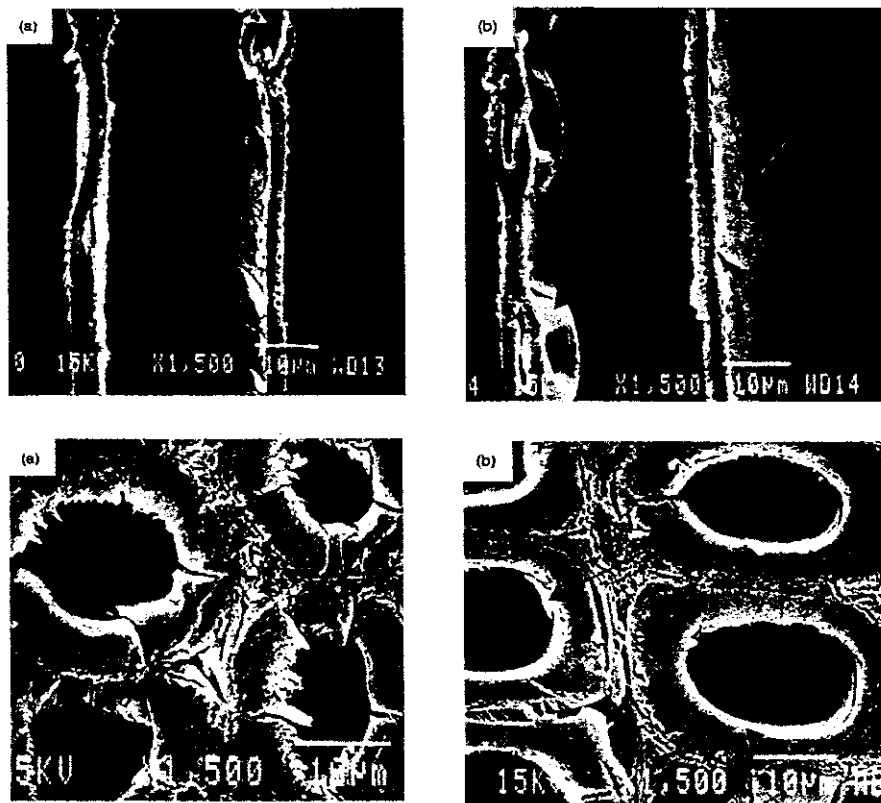


Figure 1—SEM micrographs, tangential view (top) and transverse view (bottom), of wood specimens (a) before and (b) after coating with sol-gel deposit of aluminum isopropoxide in the presence of MTMOS and NMP. Sol-gel deposit appears as bright regions on the lumen surface, especially around bordered pits.

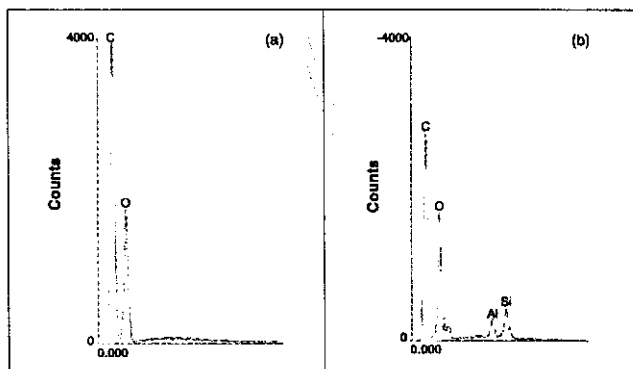


Figure 2—EDXA spectra of wood specimens (a) before and (b) after coating with sol-gel deposit of aluminum isopropoxide and MTMOS. Coated specimen shows aluminum and silicon peaks.

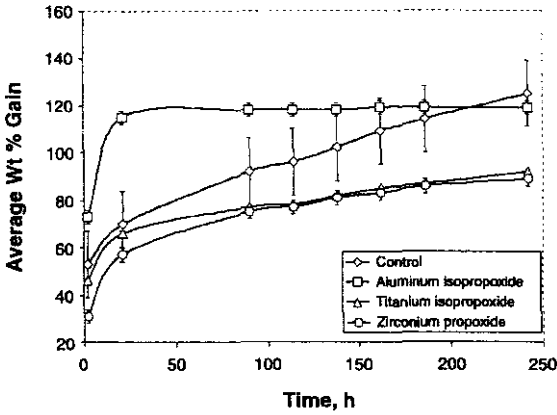


Figure 3—Water sorption of wood specimens before and after coating with different sol-gel deposits. (Each point is an average of duplicates. The titanium and zirconium alkoxide plots coincide after time, 100 h, and the markers obscure error bars. Note that the plot of the control specimens showed a greater variability in water sorption compared with plots of coated specimens.)

Water sorption behavior of wood specimens coated with sol-gel deposits of different metal alkoxides in the presence of MTMOS is shown in Figure 3. Sol-gel deposits of titanium and zirconium alkoxides reduced the mass of water sorption by 30% to 40%, while that of aluminum alkoxide initially increased it by about 20%. These differences in water sorption behavior may be related to differences in the distribution of the sol-gel deposits within the cell wall.<sup>6</sup> To form an effective moisture barrier, the sol-gel deposits not only must be distributed on the surface of the lumen, but must extend into the cell wall. As shown in Figure 1(b), the

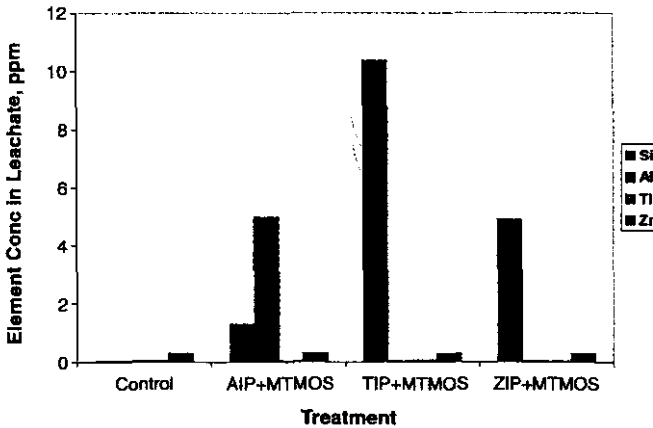


Figure 4—Water leaching of woodspecimens before and after coating with the different sol-gel deposits. (Note that the specimens coated with aluminum propoxide (AIP) showed considerable leaching of aluminum compared to the specimens that were coated with titanium tip or zirconium propoxide zip.)

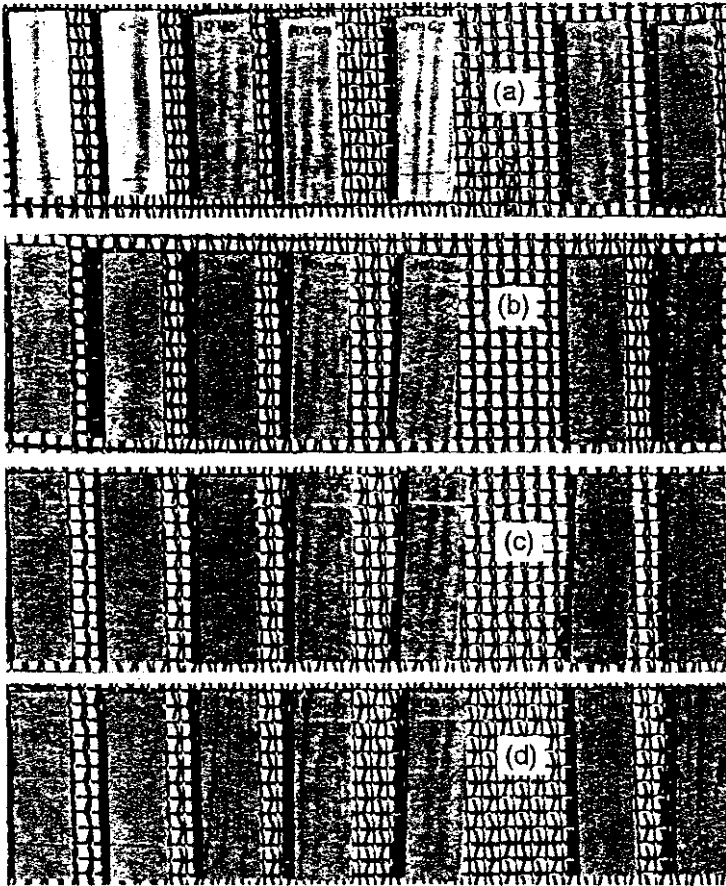


Figure 5—Surface color of wood specimen (a) before and after exposure in a Weather-Ometer to (b) 8 kW-hr/m<sup>2</sup>, (c) 30 kW-hr/m<sup>2</sup>, and (d) 50 kW-hr/m<sup>2</sup> of photo radiation of wavelength 300 to 400 nm. The first two specimens on the left are uncoated controls;.....controls, C1 and C2

aluminum isopropoxide sol gel deposit appeared to be concentrated around the surface of the bordered pits.

Resistance to water leaching of the sol-gel deposits is illustrated in *Figure 4*. Titanium and zirconium sol-gel deposits showed high resistance to water leaching. As shown by the relatively high concentration of aluminum ( $5.0 \pm .43$  ppm) found in the water leachate, the aluminum sol-gel deposit was not as resistant to water leaching as were the titanium and zirconium alkoxides. All the coated specimens showed some leaching of silica, and the specimens coated with titanium isopropoxide/MTMOS deposits showed the highest concentration of silica ( $10.4 \pm 1.8$  ppm) in the leachate.

*Figure 5* shows the surface color of the wood specimens before and after a radiant dosage of 8, 30, and 50 kW-h.m<sup>2</sup>. The coated specimens showed progressively less severe discoloration from an initial light brown to a dark brown. By contrast, the uncoated control specimens (C1 and C2) showed more severe discoloration from light yellow to light brown.

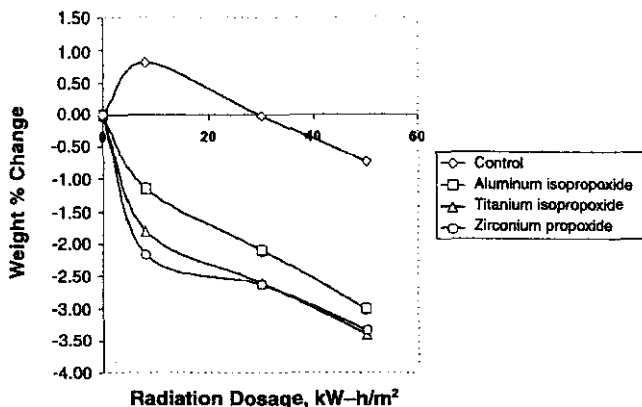


Figure 6—Weight change of specimens after exposure to photo radiation of wavelength 300 to 400 nm in a Weather-Ometer. (Each point is an average of duplicates, and the markers obscure error bars.)

Figure 6 shows plots of weight change of the specimens as a function of radiant dosage. The coated specimens showed an initial high rate of weight loss that appeared to be steadily decreasing after a dosage of 30 kW-h/m<sup>2</sup>. By contrast the control specimens showed an initial high rate of weight gain followed by weight loss at a rate comparable to that of the coated specimens. The observed weight increase may be consistent with the formation and temporary accumulation of hydroperoxides in the surface layers of the wood specimens.<sup>7</sup> The subsequent loss of weight may be consistent with the decomposition of accumulated hydroperoxides, accompanied by the liberation of volatile compounds from the surface layers of the specimens.<sup>8</sup> For the coated specimens, the apparent absence of an initial weight increase suggests that the sol-gel deposits may have affected both the penetration of light and the permeation rates of oxygen to the surface moieties of wood that are susceptible to photooxidation to hydroperoxides. Both light and oxygen are essential for photooxidation of wood components via the hydroperoxide pathway. The observed weight loss may be due to liberation of volatile components of the wood via an alternative photodegradation pathway, such as radical formation by hydrogen abstraction followed by bond rearrangement and decarbonylation.<sup>9</sup>

## CONCLUSION

Sol-gel deposition of titanium isopropoxide and zirconium propoxide in the presence of MTMOS on wood specimens decreased their tendency to absorb water. However, sol-gel deposition of aluminum isopropoxide in the presence of MTMOS and NMP appeared to increase the tendency of wood specimens to absorb water up to a certain limit. The control specimens continued to absorb additional amounts of water even after 240 h of soaking. Because the aluminum isopropoxide coating solution was modified by addition of N-methyl pyrrolidinone to improve the solubility of aluminum isopropoxide in isopropanol, its presence may have led to a different distribution of the sol-gel deposit within the surface wood cell walls.

Experiments on the effect of sol-gel deposits on the action of light on the wood specimens are still in progress. Thus far, it appears that most of the sol-gel deposits that have been investigated in the current work affect, to varying extents, both light penetration and permeation

rate of oxygen to those wood surface components that are susceptible to photooxidation, thereby promoting a degradation pathway that is slightly different from that of uncoated specimens. Hence, contrary to expectations, the sol-gel deposits obtained under the current experimental conditions appeared to result in more severe weight loss in the coated wood specimens compared to the control specimens. Additional experiments are in progress to understand the photooxidation of wood specimens coated with these sol-gel deposits.

## ACKNOWLEDGMENTS

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