# TREATMENT OF WOOD WITH POLYSILICIC ACID DERIVED FROM SODIUM SILICATE FOR FUNGAL DECAY PROTECTION<sup>1</sup>

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**Abstract.** The aim of this study was to investigate safer, more inexpensive chemicals derived from sodium silicate that can be used to protect wood against fungal degradation. Desiccant and surfactant properties of sodium silicate-derived products have been used since the early 19th century and may find application for wood decay protection. In our study, wood was impregnated with 19.5% sodium silicate and acidified with 2.5% phosphoric acid for 2 da to produce polysilicic acid. After 2-wk daily water leaching, leached specimens had 0.2% weight loss by a brown-rot fungus, *Gloeophyllum trabeum*, and weight losses of 3.4 – 5.2% by a white-rot fungus, *Trametes versicolor*. The control had 32.2 and 30.2% weight losses by *G. trabeum* and *T. versicolor*, respectively. Energy-dispersive X-ray analysis showed that polysilicic acid deposited mainly in the cell lumens. Exposure at 90% RH showed that polysilicic acid-treated loblolly pine or sweet gum that had been water-leached with 22 – 34% chemical retention absorbed more moisture than untreated wood. This indicated that decay resistance of polysilicic acid-treated wood is caused by a different mechanism than desiccation. One possible mechanism may be attributed to direct disruption of permeability of fungal cell membranes by the low-molecular-weight polysilicic acid.

Keywords: Fungal decay protection, impregnation, moisture sorption, polysilicic acid, surfactant property.

### INTRODUCTION

The degradation of wood by decay fungi and termites constitutes the major losses of wood products in exterior use. In the past, commercial wood preservatives, including chromated copper arsenate (CCA), creosote, and pentachlorophenol, were used for controlling this degradation. These preservatives are highly effective, longlasting, and cost-effective. In January 2002, the US preservative industry voluntarily phased out CCAtreated wood products in residential construction because of health concerns and replaced them with alkaline copper quaternary compounds and copper boron azole compounds. (Los Angeles Times 2002; Reisch 2002). Copper-based wood preservatives may face restrictions in the future (Schultz and Nicholas 2002). Therefore, noncopperbased wood treatments have been pursued for a considerable time.

Research on noncopper-based wood preservatives has been actively pursued. These include alkyl ammonium compounds (Nicholas and Preston 1980), azaconazole (Valcke and Goodwine 1985), isothiazolone (Greenley 1986), chlorothalonil (Woods and Bell 1990), propiconazole (Goodwine 1990), naphthalyl hydroxylamine (Green et al 2002), and the combination of organic biocides (propiconazole, tebuconazole) with antioxidants (butylated hydroxy toluene, tannic acid), and metal-chelating compounds (phenanthroline, EDTA) (Schultz and Nicholas 2002). Some of these preservatives have shown efficacy in laboratory tests but poor field performance; copper salts are still widely used.

Preliminary tests showed that organoborates from sodium tetraborate (borax) and sodium octaborate (Tim-bor), organosilicates from sodium silicate (water glass), and natural products from trees were effective against wood-decay

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fungi in laboratory soil-block fungal decay tests. Polysilicic acid in combination with boric acid or borax in wood has been evaluated for fungal decay protection, but it only decreases the weight losses by fungi from 2 – 8% (Furuno et al 1992). Poor performance against wood-decay fungi may be attributed to the inability of boron compounds to form covalent or ionic compound with sodium silicate.

Sodium silicate is an important commercial chemical that has four major applications (Willis 1954) as industrial or household detergents, adhesives for corrugated boxes, desiccants for organic liquids or food, and a catalyst for gasoline. Two other applications are as a stabilizer for textile bleaching and water and soil treatments. Sodium silicate is readily available and inexpensive, and polysilicic acid derived from sodium silicate is not harmful to the environment. The surfactant and desiccant properties of products derived from sodium silicate may have application in decay protection of wood. Surfactant properties similar to those of alkyl quaternary ammonium compounds (Nicholas and Preston 1980) may protect treated wood from fungal decay by disruption of the permeability of fungal cell membranes (Eaton and Hale 1993). The desiccant property (Willis 1954) may keep wood dry and thereby protect wood from fungal degradation. The objective of our study was to investigate safer and more inexpensive chemicals derived from sodium silicate for wood protection against fungal degradation and to learn the mechanisms of fungal decay protection, which are not well understood.

#### MATERIALS AND METHODS

## **Impregnation**

Five concentrations (10.5, 13.5, 16.5, 19.5, and 22.5%) of sodium silicate were impregnated into wood and acidified with 2.5 and 5% phosphoric acid for 2 da. For each concentration, 32 blocks were used, which included 20 blocks (10 loblolly pine and 10 sweet gum) for fungal decay tests and the remaining 12 blocks (6 loblolly pine and 6 sweet gum) for weathering

tests. The treatment with one concentration of sodium silicate for decay and weathering tests are described subsequently.

Thirty-two sapwood blocks from two wood species [16 blocks of loblolly pine (*Pinus taeda* L.) and 16 blocks of sweet gum (Liqulambar styraciflua L.); 19 mm in all anatomic directions] were conditioned at 27°C and 30% RH for 3 wk and weighed. The blocks reached EMC after a 3-wk conditioning. They were placed under vacuum at 1.2 kPa for 3 h in a treating cylinder and then impregnated with one of five concentration levels of aqueous sodium silicate solutions (10.5, 13.5, 16.5, 19.5, and 22.5%; 50 mL/block). After impregnation, the blocks were removed from the treating solution, the excess solution wiped from the surface, and weighed to determine the solution absorbed. The blocks were then acidified with 2.5 and 5% phosphoric acid (1.6 L; 50 mL/ blocks) and soaked for 2 da. After soaking, the pH of the solution was measured by a pH meter (ATI Orin pH meter) and the blocks removed from the solution. One-half of the blocks (16 blocks: 8 pine and 8 sweet gum) were leached in distilled water (800 mL; 50 mL/block) daily for 6, 24, and 48 h and then every 24 h for 2 wk according to ASTM D-1413-99 (ASTM 2000). The leached and nonleached blocks were conditioned at 27°C and 30% RH for 3 wk and then weighed before fungal decay tests. For the decay tests, chemical retentions of treated blocks were based on EMC at 27°C and 30% RH before and after treatments. Polysilicic acid was produced in wood by impregnating 10.5, 13.5, 16.5, 19.5, and 22.5% sodium silicate and acidification with 2.5 or 5% phosphoric acid for 2 da had 4 - 8 pH.

The procedure for impregnating and leaching wood blocks treated with sodium silicate for the moisture sorption study were the same as previously described, except two concentration levels of sodium silicate (19.5 and 22.5%; 50 mL/block) and 10 loblolly pine and 10 sweet gum blocks were used in each treating concentration. The silicate-treated blocks were acidified with 5% phosphoric acid (50 mL/block) for 2 da. Five control blocks and treated blocks (5 nonleached;

5 leached) were heated at 105°C for 24 h before and after treatments to obtain oven-dry weights of chemical in the wood. Oven-dry (105°C, 24 h) weight of treated blocks after 4-wk moisture sorption tests was also determined. EMC of the control and treated blocks at 90% RH and 27°C was determined by the increased moisture uptake of the blocks (after 4 wk at 90% RH and 27°C) based on oven-dry weight before treatment. The retention of chemicals in treated blocks was determined based on oven-dry weight before and after treatments. The EMC of treated wood was estimated by subtracting the moisture increase of treated blocks (after 4 wk at 90% RH and 27°C) from the oven-dry weight of chemicals in treated wood and ovendry weight of wood after treatment. Polysilicic acid and salts of phosphoric acid produced in nonleached wood and polysilicic acid produced in leached wood were not prepared separately to correct the moisture contents, which were absorbed by these chemicals after 4-wk moisture sorption.

For Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray analysis (EDXA), five loblolly pine blocks were impregnated with 22.5% sodium silicate and then acidified with 2.5% phosphoric acid (50 mL/block) for 2 da. They were leached with distilled water daily for 2 wk (ASTM 2000). The same procedure for impregnation and water-leaching was used as described previously. One leached block was used for FTIR and EDXA analysis.

### Characterization

Loblolly pine and loblolly pine impregnated with polysilicic acid derived from sodium silicate were characterized by infrared analysis using KBr pellets by a Mattson Galaxy series FTIR 5000 spectrometer (Unicam, UK). Polysilicic acid in treated wood was prepared by impregnating wood blocks with 22.5% sodium silicate and then acidified with 2.5% (50 mL/block) phosphoric acid for 2 da as described previously.

EDXA using a Tracor Northern 5500 energy-dispersive spectrometer (Thermo Noran, Madi-

son, WI) was used to determine the distribution of chemicals in cell walls of loblolly pine across wood cells and wood layers for untreated and silicate treated loblolly pine. The leached block described was also used for EDXA analysis.

Control and treated samples were examined by scanning electron microscopy (Zeiss EVO 40; Carl Zeissd SMT, Peabody, MA) and EDXA. Samples of  $7 \times 7$  mm were microtomed in the transverse direction approximately 0.5 mm below the surface and at the center of the block. Spectra were collected for 100 s from an area of  $4 \times 4$  mm and line scans with 40 spots at 0.5 s each with 10 passes were performed across cell walls from lumen to lumen. Ten fields for each specimen were analyzed. The uncoated specimens were examined in the variable pressure mode at a working distance of 15 mm at 500 pA and 15kV.

## **Fungal Decay Tests**

Fungal decay tests by the soil-block method were conducted according to ASTM D1413 (ASTM 2000). Gloeophyllum trabeum (Pers.: Fr.) Murrill (MAD-617), a brown-rot fungus, was used with loblolly pine blocks and *Trametes* versicolor (L.:Fr.) Quel. (MAD-697), a white-rot fungus, with sweet gum blocks. Five replicate blocks with and without leaching from each concentration and five controls were tested for decay resistance over 12-wk exposure. The extent of fungal attack was determined by weight loss. Because there were too few data points to establish a threshold relationship, statistical analysis of threshold retention by nonlinear regression analysis could not be considered accurate (Steel and Torrie 1960; Nance and Amburgey 1976; Gezer et al 1999). Therefore, threshold values were estimated from 2% weight loss by decay.

#### RESULTS AND DISCUSSION

#### Characterization

*Equilibrium moisture content.* Wood was treated with 19.5% sodium silicate and acidified

Table 1. EMC of polysilicic acid-treated loblolly pine and sweet gum at 90% RH, 27°C.

	Nonleached		Leached		
Treatment	Chemical retention (%) <sup>a</sup>	EMC (%) <sup>b</sup>	Chemical retention (%) <sup>a</sup>	EMC (%) <sup>b</sup>	
Loblolly pine: 19.5% sodium silicate, 5% phosphoric acid 2 da	31.1	32.1	22.0	24.2	
22.5% sodium silicate, 5% phosphoric acid, 2da	38.9	34.1	33.6	31.2	
Control					$18.0^{\rm b}$
					$(16.7)^{c}$
Sweet gum: 19.5% sodium silicate, 5% phosphoric acid, 2 da	32.9	32.9	24.7	25.8	
22.5% sodium silicate, 5% phosphoric acid, 2 da	38.9	34.1	31.3	27.1	
Control					18.2 <sup>b</sup>

<sup>&</sup>lt;sup>a</sup> Based on oven-dry (105°C, 24 h) weight before and after treatments.

with 5% phosphoric acid for 2 da (Table 1). The EMC at 90% RH and 27°C of nonleached loblolly pine wood was 32.1% with 31.1% chemical weight gain. The EMC for leached blocks was 24.2% with 22% chemical weight gain. For sweet gum, the EMC for nonleached blocks was 32.9% with 32.9% chemical weight gain. For leached blocks, the EMC was 25.8% with 24.7% chemical weight gain. The EMC of the untreated control was 18.0% for loblolly pine, which was close to the literature value (16.7%) (Lee 1998), and 18.2% for sweet gum. The results indicated that the EMC of polysilicic acid-treated loblolly pine blocks were 34.4 to 78.3% higher than the control. For sweet gum treated blocks, the EMC was 41.8 to 80.8% higher than the control.

For wood treated with 22.5% sodium silicate and then acidified with 5% phosphoric acid for 2 da, the EMC of treated nonleached loblolly pine was 34.1 with 38.9% chemical weight gain. For leached blocks, the EMC was 31.2 with 33.6% chemical weight gain. For treated sweet gum, the EMC of nonleached wood was 34.1 with 38.9% chemical weight gain. For leached wood, the EMC was 27.1 with 31.3% chemical weight gain. The results indicated that the EMC of treated loblolly pine was 73.3 to 89.4% higher than the control and 48.9 to 87.4% higher for treated sweet gum wood than the control. Our moisture sorption study at 90% RH showed that the EMC of polysilicic acid-treated loblolly pine and sweet gum was higher than the untreated control. This indicated that polysilicic acid in treated wood did not possess desiccant property. The polysilicic acid prepared by acidification with phosphoric acid may produce products with large pores (pore diameter: 10 - 15 nm, specific gravity: 0.65 - 0.75). These large pores absorb moisture through condensation (hydrated silica), whereas products with small pores (pore diameter: 2.2 - 2.6 nm, specific gravity: 0.37 - 0.43) (silica gel) absorb moisture through adsorption and desorption cycles (sorption hysteresis), which contributes to desiccation. Silica gel with small pore sizes may not be produced in acidifying sodium silicate with phosphoric acid (Eitel 1954; Hubard 1954). Our progress in preparing surfactant organosilicates from water glass led us to suggest that decay resistance of polysilicic acid-treated wood may be attributed to the surfactant property of the lower-molecular-weight polysilicic acids. The lower-molecular-weight polysilicic acids, including dimers and oligomers, may exist as colloid suspensions in aqueous solution and may inhibit fungi in wood by a mechanism similar to surfactant compounds, including alkyl quaternary ammonium compounds, which are based on disrupting the permeability of fungal cell membranes (Eaton and Hale 1993).

Weathering tests. The weathering tests (Table 3) of wood treated with polysilicic acid showed that for nonleached pine wood treated with 2.5% phosphoric acid, weight losses caused by weathering were 0.6, 0.8, 3.7, 3.4, and 4.4% with chemical retentions of 16.3, 20.4, 25.7, 29.6, and 34.2%, respectively. For leached wood, weight losses were small, 0.1 – 0.2%,

b Average of five replicates; weight of moisture absorbed by the blocks after 4 wk at 90% RH, 27°C based on oven-dry weight before treatments.

<sup>&</sup>lt;sup>c</sup> Number in parentheses is the literature value.

Table 2.	Assignment of Fourier	transform infrare	d spectroscopy	bands of loblolly	pine and	loblolly pine in	npregnated
with polys	silicic acid with 22.8%	weight gain after v	water leaching.				

Polymer or wood	Frequency (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment	References
Loblolly pine	3600 - 3000	bvs	H-bonded OH of wood	Marchessault (1962)
	2929 - 2800	S	C-H and C-H <sub>2</sub> stretching	
	1632	S	OH stretching of adsorbed water,	
			Hydroxy ketone of flavanols	
	1600 - 1515	S	Aromatic $C = C$ of lignin	
	1425	S	CH <sub>2</sub> symmetrical bending	
	1380	m	C–H bending	
	1059	S	C–O stretching	
Loblolly pine impregnated with polysilicic acid	3600 – 3200	bvs	H-bonded OH of wood and polysilicic acid asymmetric Si–O–Si stretching	Colthup et al (1964) Marchessault (1962
	2929 - 2800	S	C-H and C-H <sub>2</sub> stretching	
	1632	S	OH stretching of adsorbed water, hydroxy ketone of flavanols	
	1600 - 1515	m	Aromatic $C = C$ of lignin	
	1425	m	CH <sub>2</sub> bending	
	1380	m	C-H stretching	
	1100	VS	Symmetric Si-O-Si stretching	

a b, broad; s, strong; v, very; m, medium.

with chemical retentions of 7.0 - 20.5%. For treatment with 5% phosphoric acid, weight losses for nonleached wood were 4.5, 2.2, 1.5, 2.3, and 4.1% with chemical retentions of 20.4, 22.8, 27, 31.1, and 36.3%, respectively. For leached wood, weight losses were also small, ranging from 0.1 to 0.2% with chemical retentions ranging from 11.5 to 26.3%. For sweet gum treated with polysilicic acid (Table 4), weight losses for nonleached wood treated with 2.5% phosphoric acid were small, 0.2 - 1%, with chemical retentions between 16.6 – 39%. For leached wood, weight losses were 0% with chemical retentions of 12.5 - 26.1%. For treatment with 5% phosphoric acid, weight losses for nonleached wood were 0.7 - 2.9% with chemical retentions of 23.3 -40%. For leached wood, weight losses were 0% with chemical retentions of 12.5 and 30.5%. These weathering tests indicated that larger weight losses for nonleached wood may attribute to the dehydration of salts, including salts of phosphoric acid. The small weight losses of leached wood may indicate that polysilicic acid in wood was not dehydrated during the weathering tests. The weathering losses of wood blocks were used to correct the weight losses by fungal decay.

The retention of polysilicic acids in pine wood was 16.3 - 36.3% for the nonleached wood and

7.0 – 26.3% for leached wood (Table 3). The results indicated that approximately one-third of polysilicic acid-derived products in pine wood were leached out by water. These water-soluble products are salts of phosphoric acid and water-soluble extractives from wood.

Fourier transform infrared spectroscopy absorptions of loblolly pine impregnated with polysilicic acid derived from sodium silicate. Infrared (IR) spectra of loblolly pine and loblolly pine impregnated with polysilicic acid are described in Table 2 and Fig 1. Only IR absorptions of loblolly pine impregnated with polysilicic acid are described subsequently. Very strong and broad IR absorption at 3200 to 3600 cm<sup>-1</sup> is attributed to H-bonded OH stretching vibration of wood and polysilicic acid, and a strong IR absorption at 1100 cm<sup>-1</sup> is attributed to symmetric Si-O-Si stretching vibration of polysilicic acid (Marchessault 1962; Colthup et al 1964). These IR data indicated that polysilicic acid was formed in wood. In addition to these absorptions, the following IR absorptions characteristic of wood (Marchessault 1962) were also found:  $2800 - 2900 \text{ cm}^{-1}$  (medium intensity), C-H and C-H<sub>2</sub> stretching; 1456 cm<sup>-1</sup> (medium intensity), lignin and CH2 symmetric

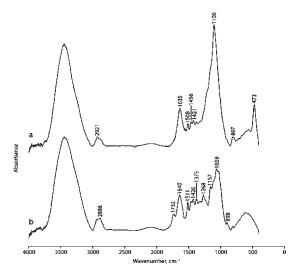
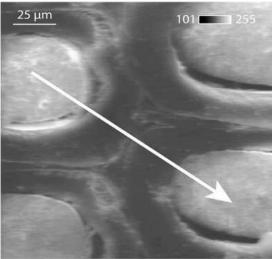


Figure 1. Fourier transform infrared spectroscopy (FTIR): (a) loblolly pine wood impregnated with polysilicic acid with 22.8% weight gain after water leaching and (b) loblolly pine.

bending;  $1421 \text{ cm}^{-1}$  (medium intensity),  $CH_2$  bending; and  $1508 \text{ cm}^{-1}$  (medium intensity), aromatic C = C stretching of lignin.

Energy-dispersive X-ray analysis of loblolly pine impregnated with polysilicic acid. EDXA of loblolly pine impregnated with polysilicic acid derived from sodium silicate after water leaching showed that polysilicic acid was deposited mainly in cell lumens. The Si count of about 1700 of polysilicic acid in a cell lumen compared with Si count of 100 in an adjacent cell wall indicated 17 times more silicone in the cell lumen than in the cell wall (Fig 2). Furthermore, EDXA also revealed that silicone was distributed more in the surface layers of wood than in the center because the Si count is about 23,000 for the surface layers compared with a 60 count near the center (Fig 3). The EDXA study indicated that sodium silicate impregnated in loblolly pine can reach only the surface layers of wood and little penetrated into the center portion. One possible explanation of surface deposition of polysilicic acid was that after impregnation, sodium silicate was rapidly polymerized from the wood acidity (pH 4.5 - 6.5).



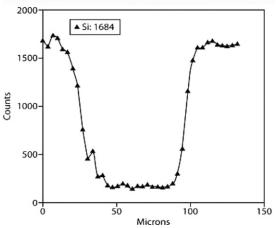


Figure 2. Energy-dispersive X-ray analysis (EDXA) of loblolly pine impregnated with polysilicic acid with 22.8% weight gain after water leaching.

The polymerized silicates were unable to penetrate into cell wall layers and remained on the surface layers of cell lumens.

## **Fungal Decay Evaluation**

Polysilicic acids formed in situ in wood cell lumens resisted decay by a brown-rot fungus, *G. trabeum*, and decreased weight loss by a white-rot fungus, *T. versicolor*. The results of fungal decay tests with a brown- and white-rot fungus are as follows.

**Brown-rot fungus.** The results of decay tests of loblolly pine treated with 10.5, 13.5, 16.5, 19.5, and 22.5% sodium silicate and acidified with 2.5% phosphoric acid for 2 da (Table 3) showed that for nonleached wood, weight gain of 20.4% polysilicic acid prevented decay by *G. trabeum* with 0.9% weight loss. For leached

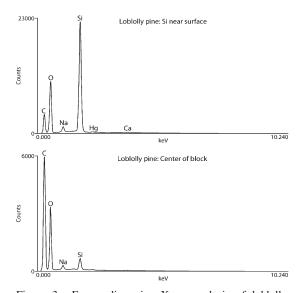


Figure 3. Energy-dispersive X-ray analysis of loblolly pine impregnated with polysilicic acid with 22.8% weight gain after water leaching.

wood, weight gain of 20.5% polysilicic acid prevented decay by *G. trabeum* with 0.1% weight loss. Nonleached wood was acidified with 5% phosphoric acid for 2 da and showed a weight gain of 31.1% polysilicic acids, preventing decay by *G. trabeum* with weight loss of 2.1%. For leached wood, weight gain of 26.3% polysilicic acids prevented decay by *G. trabeum* with weight loss of 0%. The control had 32.2% weight loss by *G. trabeum*.

White-rot fungus. Decay tests of sweet gum wood treated with 10.5, 13.5, 16.5, 19.5, and 22.5% sodium silicate solutions and acidified with 2.5% phosphoric acid for 2 da (Table 4) showed that for nonleached wood, weight gain of 32% polysilicic acids prevented decay by G. trabeum with weight loss of 1%. Leached wood had 3.4% weight loss by T. versicolor. Acidified with 5% phosphoric acid for 2 da, nonleached wood with a weight gain of 30.1% polysilicic acid prevented decay by T. versicolor with weight loss of 1.3%. For leached wood, it only decreased weight losses. The control had 30.6% weight loss by T. versicolor. These decay tests with G. trabeum and T. versicolor showed that sodium silicate solutions acidified with 2.5% phosphoric acid performed better than wood acidified with 5% phosphoric

Table 3. Effect of polysilicic acid on weight losses of loblolly pine decayed by Gloeophllum trabeum in a 12-wk soil-block fungal decay test of nonleached (NL) and leached (L) specimens.

	Chemical retention (%, w/w) <sup>a</sup>		Weight losses (%) <sup>b</sup> by weathering		Weight losses (%) <sup>c</sup> by G. trabeum	
Treatment	NL	L	NL	L	NL	L
2.5% phosphoric acid 2 da:						
sodium silicate solution (%, w/w)						
10.5%	16.3	7.0	0.6	0.1	5.4 (5.3)	49.0 (3.5)
13.5%	20.4	13.6	0.8	0.2	0.9(0.6)	37.4 (4.9)
16.5%	25.7	11.2	3.7	0.1	1.1 (0.7)	37.5 (6.1)
19.5%	29.6	20.5	3.4	0.1	0.4(0.8)	0.1 (0.1)
22.5%	34.2	20.1	4.4	0.1	1.4 (0.6)	0.2(0.1)
5% phosphoric acid 2 da: sodium silicate solution (%, w/w)						
10.5%	20.4	11.5	4.5	0.2	33.1 (2.6)	9.6 (2.6)
13.5%	22.8	14.2	2.2	0.2	28.7 (2.6)	6.7 (0.30)
16.5%	27.0	19.3	1.5	0.1	40.0 (5.6)	5.2 (3.4)
19.5%	31.1	21.4	2.3	0.1	2.1 (0.5)	20.0 (11.6)
22.5%	36.3	26.3	4.1	0.0	1.3	0 (0)
Control						32.2 (3.2)

<sup>&</sup>lt;sup>a</sup> Chemical retention based on weight at 27°C, 30% RH for 3 wk before and after silicate treatments.

b Based on 12 wk in growth chamber at 27°C and 70% RH and conditioned for 3 wk at 27°C and 30% RH before and after test, average of three replicates.

c Average of five replicates; numbers in parentheses are SDs, based on weights of blocks conditioned At 27°C and 30% RH for 3 wk before and after decay tests.

Table 4. Effect of polysilicic acid on weight losses of sweet gum wood decayed by Trametes versicolor in a 12-wk soil-block fungal decay test of nonleached (NL) and leached (L) specimens.

	Chemical retention (%, w/w) <sup>a</sup>		Weight losses (%) <sup>b</sup> by weathering		Weight losses (%) <sup>c</sup> by T. versicolor	
Treatment	NL	L	NL	L	NL	L
2.5% phosphoric acid 2 da:						
sodium silicate solution (%, w/w)						
10.5%	16.6	12.5	0.0	0.0	25.3 (2.0)	28.3 (2.3)
13.5%	20.4	15.4	0.0	0.0	23.8 (6.6)	23.7 (6.9)
16.5%	27.8	21.6	0.2	0.0	13.7 (8.0)	23.3 (3.5)
19.5%	32.0	23.5	1.0	0.0	1.0 (0.8)	3.4 (3.1)
22.5%	39.0	26.1	0.0	0.0	2.5 (0.8)	3.8 (5.3)
5% phosphoric acid 2 da: sodium silicate solution (%, w/w)						
10.5%	23.3	12.5	2.9	0.0	18.3 (5.5)	27.9 (4.3)
13.5%	24.3	16.0	0.8	0.0	3.5 (0.6)	12.0 (4.7)
16.5%	30.1	20.9	1.9	0.0	1.3 (5.5)	23.8 (1.6)
19.5%	34.5	24.9	0.7	0.0	4.9 (2.5)	13.3 (4.1)
22.5%	40.0	30.5	0.9	0.0	1.4 (1.0)	9.0 (1.4)
Control						30.6 (3.4)

<sup>&</sup>lt;sup>a</sup> Chemical retention based on weight at 27°C, 30% RH for 3 wk before and after silicate treatments.

acid. Most of polysilicic acids formed by acidification with 2.5 and 5% phosphoric acid were high-molecular-weight polymers, which may not contribute to the fungal decay resistance. However, a small amount of low-molecular-weight polysilicicacid, including dimer, trimer, and tetramer, reported in the literature (Svensson et al 1986; McComick et al 1987; Weber and Hunt 2003) may play an important role in decay resistance through membrane permeability disruption. Surfactants such as alkyl quaternary ammonium compounds are effective germicides (Domagk 1935) and have been used as commercial wood preservatives since 1980 (Nicholas and Preston 1980). The mechanism of fungi inhibition by alkyl quaternary ammonium compounds is attributed to disruption of permeability of fungal cell membranes (Eaton and Hale 1993). Progress in membrane disruption of fungal cell walls by silicate derivatives from sodium silicate for fungal decay protection has made in our laboratory. In the future, we will report on this area of research.

#### CONCLUSIONS

High loadings (21 - 24%) weight gain) of polysilicic acid in leached wood were needed to prevent or decrease fungal decay. Polysilicic acid (silica)

in wood is safe to the environment. Sodium silicate after impregnation in wood may rapidly polymerize in the cell lumens from acidity of wood and was deposited mainly on the surface layers as evidenced by EDXA. Polysilicic acid prepared by this method did not have desiccant properties as evidenced by moisture sorption. The increase in MC and other properties of this product needs to be assessed for certain applications. Research is needed to prepare small pore sizes (2.2 – 2.6 nm) of polysilicic acid in wood that have desiccant properties. Research is also needed to prepare silicates or organosilicates from water glass that have surfactant properties.

### ACKNOWLEDGMENT

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#### REFERENCES

ASTM (2000) Standard method of testing wood preservatives by laboratory soil-block cultures D1413-99. Volume 4.10. American Society of Testing and Materials, West Conshohocken, PA. Pages 218 – 224.

b Based on 12 wk in growth chamber at 27°C and 70% RH and conditioned for 3 wk at 27°C and 30% RH before and after test, average of three replicates.

c Average of five replicates; numbers in parentheses are SDs, based on weights of blocks conditioned at 27°C and 30% RH for 3 wk before and after decay tests.

- Colthup NB, Daley LH, Wiberley SE (1964) Chapter 10. Ethers, alcohols, and phenols. Pages 269 277; Chapter 12. Compounds containing boron, silicon, phosphorus, sulfur, or halogen. Pages 291 318. *In* Introduction to infrared and raman spectroscopy. Academic Press, New York, NY.
- Domagk G (1935) Ein beittrag zur chemotherapie der bakteriellen infektionen. Deut Med Wochschr 61:250 253.
- Eaton RA, Hale MDC (1993) Wood: Decay, pests and protection. Chapman & Hall, New York, NY. Pages 319 343.
- Eitel W (1954) The physical chemistry of the silicates. The University of Chicago Press, Chicago, IL. 1592 pp.
- Furuno TK, Shimada T, Uehara T, Jodai S (1992) Combinations of wood and silicate II. Wood–mineral composites using water glass and reactants of barium chloride, boric acid and borax, and their properties. Mokuzai Gakkaishi 38(5):448 457.
- Gezer ED, Yalinkilic MK, Kizilkaya K, Michael JH (1999) Estimation of preservative toxic threshold retention from laboratory decay tests: A new method. Wood Sci Technol 33:63 – 71.
- Goodwine W (1990) Suitability of propiconazole as a new generation wood preserving fungicide. *In* Proc American Wood-Preserver's Association. 86:206 214.
- Green F III, Henry W, Schultz TP (2002) Mechanisms of protection by NHA against fungal decay. The International Research Group on Wood Preservation. IGR/WP 02-10429.
- Greenley DE (1986) Laboratory and field evaluation of a substituted isothiazolone as a potential wood preservative. *In* Proc American Wood-Preserver's Association. 82:1 10.
- Hubard SS (1954) Silica and silicates. Encyclopedia of chemical technology. Vol. 12. Encyclopedia, Inc., New York, NY. 955 pp.
- Lee HL (1998) Evaluation of phosphoramides to improve thermal and fungal resistance of wood. University of Wisconsin–Madison, Madison, WI. PhD Diss. 280 pp.
- Los Angeles Times (2002) Wood with arsenic to be phased out. 13 Feb. 2002. Pages 1 4.

- Marchessault RH (1962) Application of infra-red spectroscopy to cellulose and wood polysaccharides. Pure Appl Chem 5:107 129.
- McComick AV, Bell AT, Radke CJ (1987) Quantitative demonstration of siliceous species in sodium silicate solutions by silicone-29 NMR spectroscopy. Zeolites 7(3):183 190.
- Nance WN, Amburgey TL (1976) Statistical analysis of data from laboratory decay tests. *In* Proc American Wood-Preserver's Association 72:161 171.
- Nicholas DD, Preston AF (1980) Evaluation of alkyl ammonium compounds as potential wood preservatives. *In* Proc American Wood-Preserver's Association 76: 13 21.
- Reisch M (2002) Getting arsenic out of wood. Chemical and Engineering News. 11 Feb 2002. Page 9.
- Schultz TP, Nicholas DD (2002) Development of environmentally-benign wood preservatives based on the combination of organic biocides with antioxidants and metal chelators. Phytochemistry 61:555 560.
- Steel RGD, Torrie JH (1960) Principles and procedures of statistics. Pages 332 – 345 in Non-linear regression analysis. (Steel and Torrie, eds). McGraw-Hill Book Company, Inc., New York, NY. 666 pp.
- Svensson IL, Sjoberg S, Ohman LO (1986) Polysilicate equilibria in concentrated sodium silicate solutions. J Chem Soc, Faraday Trans 182:3635 3646.
- Valcke AR, Goodwine WR (1985) Azaconazole, A new wood preservative. In Proc American Wood-Preserver's Association 81:196 – 202.
- Weber CF, Hunt RD (2003) Modeling alkaline silicate solutions at 25°C. Ind Eng Chem Res 42:6970 6976.
- Willis JH (1954) Soluble silicates and synthetic insoluble silicates, Encyclopedia of chemical technology. Vol 12. The Interscience, Inc., New York, NY. 955 pp.
- Woods T, Bell J (1990) Development of chlorothalonil as a wood preservative. *In Proc American Wood-Preserver's* Association 86:190 – 196.