

DIMENSIONAL STABILIZATION OF WOOD BY CHLOROSILANATION

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Nominal 100 micron thick, 1 cm wide and 10 cm long radial/longitudinal *Pinus nigra* microtome sections were dried and treated with dimethyl dichlorosilane in the vapour phase. The same experiment was repeated with previously water-leached specimens. The chlorosilane readily reacted with wood hydroxyl groups to form silyl cellulose. The silanation product was quite resistant to the effects of prolonged water leaching and is quite durable too.

2 x 2 cm radial-tangential 6 mm thick transverse wafer specimens of the same species were treated in both vapour and liquid phases. Water repelling effectiveness of the specimens were measured by time to half swell ($T_{\frac{1}{2}}$).

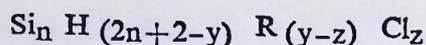
Silanation by both vapour and liquid phases slows down the sorption process by over 70 times the normal process. The maximum equilibrium swelling is also brought down to 72.5% in the case of liquid phase and 75.0% in the liquid and vapour phase respectively. Conventional water repellents slow down the rate of water uptake but do not change the total sorption. This establishes the superiority of silanation over conventional water repellents in decreasing the maximum equilibrium swelling of wood in contact with moisture.

INTRODUCTION

Silicon and carbon both belonging to the fourth group in the Periodic Table show similar chemical reactivity in many respects. Both are able to form a series of covalently bonded compounds, the bonds being directed towards the corners of a regular tetrahedron.

Silanes, corresponding to alkanes in organic chemistry, have an empirical formula, $Si_n H_{2n+2}$. Each of the hydrogens in the silane molecule may be substituted by an electrophilic group, e. g., halogen or by methyl groups. The properties of the organochlorosilanes are dependent on the

effects of silicon atoms, alkyl groups and halogen groups. Alkylchlorosilanes may be represented by the following general formula :

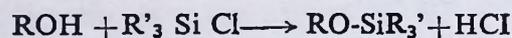


where R=alkyl group i. e. $\text{C}_n \text{H}_{2n+1}$

'y' is an integer having values between 2 and $2n+2$, and

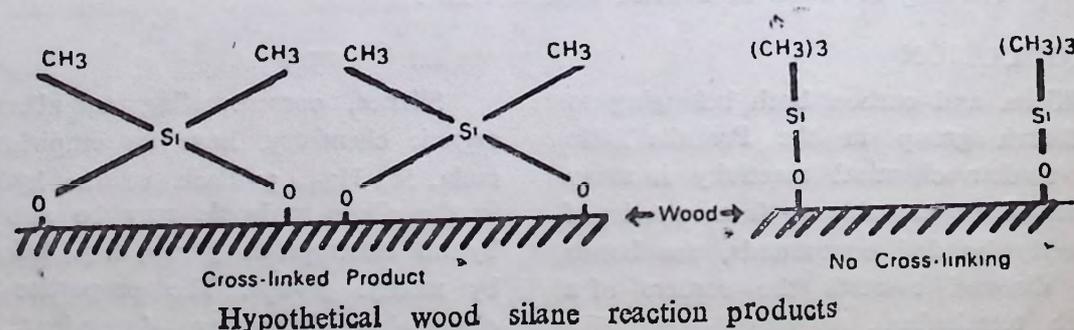
'z' is an integer having values between 1 and $2n+1$

The reactivity of this series of compounds with wood varies with the length of the silicon chain, the nature of the alkyl group, the number of alkyl and chloro groups present and their position along the silicon chain. Generally, however, they react with hydroxyl groups in wood with the elimination of a proton :



where R is a polysaccharide residue and R' is an alkyl group

Preliminary experiments have shown that wood treated with the bifunctional substituted silane, dimethyl dichloro silane (DMDCS) has better water repellent properties than that treated with trimethylchlorosilane (TMCS). This may be due to the cross-linking obtained with bifunctional groups :

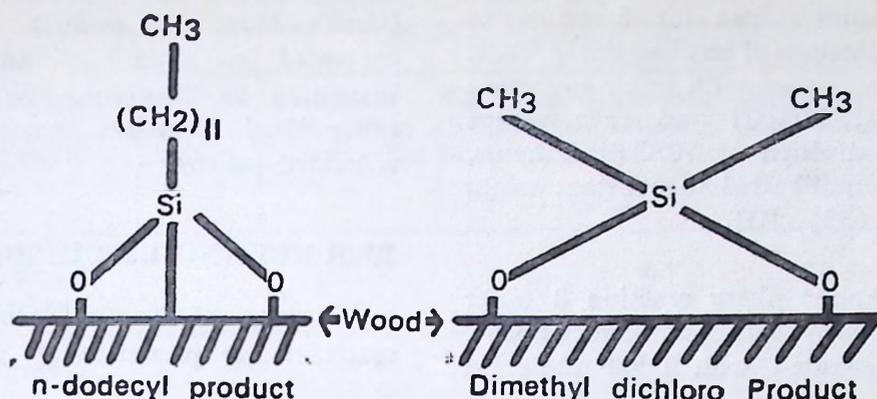


Reactions with n-dodecyl trichlorosilane (DDTCS) gave rise to a product slightly more water repellent than that formed with DMDCS. The effect may be due to the greater cross-linking as well as the presence of a more hydrophobic longer chain hydrocarbon, which surpasses the benefit of the greater number of alkyl groups per substituted hydroxyl group in wood (Schuyten *et al* 1948) :

Thus a reasonably broad range of silane characteristics has been investigated in the preliminary experiments. Considering the effects produced and the economic aspects of the reaction media, DMDCS only has been investigated in this study.

Apart from the reactions between wood hydroxyl groups and chlorosilanes outlined (Schuyten *et al* 1948) it is believed that resistance to water uptake by silane treatment may result from two alternative mechanisms.

- (i) Silanes may react with moisture in wood to form siloxanes which remain as a coating on cell surfaces. Such coatings are insoluble in water and common organic solvents (Rochow 1951).



- (ii) In addition to attaching hydrophobic alkyl groups to wood polymer surfaces, the silyl groups replace hydroxyl groups and hence reduce the tendency for wood-water hydrogen bonds to be formed.

MATERIALS AND METHODS

(i) **Durability of chloro-silanation in wood** : Nominal 100 micron thick, 1 cm wide and 10 cm long radial/longitudinal microtome sections were cut from pre-soaked Corsican pine blocks. The specimens were conditioned at 20°C and 65% RH under light pressure for 7 days and were then dried over P_2O_5 . The weighed specimens were treated with DMDCS (i) in the vapour phase and (ii) in the liquid phase. In the vapour phase reactions the microtome sections were kept in the vertical position in a desiccator reaction vessel with the help of a perforated porcelain platform. The silane was vaporized at 70°C in a round bottomed flask, fitted with nitrogen tube, thermometer and a side outlet tube, over an oil bath. The vapour was blown in the reaction vessel by nitrogen gas through a bent tube fitted to the ground glass connectors of the flask and the vessel.

The liquid phase treatments were carried out using 5 ml DMDCS dissolved in 50 ml CCl_4 to treat 20 microtomed specimens. Nitrogen gas was bubbled through the liquid in the reaction vessel to carry away HCl gas. The reaction was allowed to proceed for 10 minutes.

Separate sets of weighed specimens were leached in running deionized water for 24 hours. These were then manipulated and treated in the same way as the unleached specimens. After silane treatment all the specimens were leached with flowing deionized water for 24 hours at ambient temperature.

(ii) **Treatment of water specimens** : Experiments were designed to treat 6 mm thick transverse wafer specimens (2 x 2 cm in the radial and tangential directions) of *pinus nigra* wood with DMDCS in both the vapour and liquid phases.

In the liquid phase reaction 8 wafer specimens dried to constant weight over P_2O_5 were treated for 15 minutes in a solution of 5 ml DMDCS in 15 ml dimethyl formamide (DMF) as acid acceptor and 100 ml CCl_4 solvent. The specimens were kept immersed and the solution was swirled at room temperature.

After the reaction the specimens were kept in ammonia atmosphere for 5 minutes to ensure neutralization of any remaining HCl. They were then rinsed with water to remove any superficial NH_4Cl and then washed in acetone and dried at 70°C for 2 hours, before being equilibrated to constant weight at 20°C and 65% RH.

In the vapour phase reaction 8 wafer specimens, similar to those described above, were first pretreated with DMF and dried at 70°C for 4 hours. Some weight gain occurred due to retention of DMF. The specimens were then put in a desiccator reaction vessel and connected to a source of DMDCS vapour. The chlorosilane was vaporized at 70°C over an oil bath. Dry N_2 gas was bubbled through the silane at a rate of approximately 5 bubbles per second. The vaporized silane was carried by the N_2 gas into the reaction vessel through the side tube. Another tube fitted to the ground glass stopper of the reaction vessel allowed the escape of excess gas. The reaction was allowed to continue for 10 minutes. After reaction the specimens were manipulated in the same way as in the case of those treated by liquid phase reaction.

(iii) **Assessment of water repellency using-wafer specimens:** The rate of tangential swelling is directly related to the rate of water uptake in wood (Stamm 1964). The rate of tangential swelling was thus adopted as the criterion for monitoring water repellent effectiveness in these wafer specimens.

Swelling was measured during immersion in deionized water at 20°C using either dial gauze micrometers fitted to jigs allowing specimens to remain submerged in water during measurement or displacement

transducers giving a potentiometric output (Banks 1971, Banks 1973). Results were expressed as time to attain half the maximum swelling, time to half swell $T_{\frac{1}{2}}$, interpolated from the maximum swell in untreated control.

RESULTS AND DISCUSSION

Results of the persistence of silanation reactions are presented in Table 1.

Prior to any treatment the specimens were dried over P_2O_5 , hence it is unlikely that significant quantities of siloxane polymer could be formed. Neither the silylcellulose formed by the reactions nor minor quantities of any siloxanes formed are likely to be leached by the cold water wash.

Nearly 30% weight gain was reached with both leached and unleached specimens. A very high degree leach resistance indicate that the silane is chemically bonded to the wood hydroxyl groups. Of the weight loss which does occur, a proportion is probably wood breakdown products produced by the action of HCl released as a byproduct of the silanation reaction.

The degree of silanation achieved and water repellent effectiveness data for these initial liquid and vapour phase reactions with wafer specimens are given in Tables 2 and 3 respectively.

From the data of Tables 2 and 3 it can be seen that the degree of substitution (weight gain) achieved by the two types of reaction are broadly similar. The initial water repellent effectiveness expressed as time to half swell ($T_{\frac{1}{2}}$) and the degree

Table 1. Persistence of silanation in Corsican pine strips

Pretreatment leaching	Mode of silanation (DMDCS)	Weight loss/gain, percent*					
		Loss on initial leaching	Gain on silanation over initial wt.	Gain over 1st leached wt.	Loss on leaching based on silanated wt.	Retention after leaching over initial wt.	Retention based on 1st leached wt.
No	Vapour phase	-	31.7 (4.5)	-	4.7 (1.9)	25.5	-
No	Liquid phase	-	2.4 (0.5)	-	0.7 (0.3)	1.7	-
Yes	Vapour phase	3.8 (0.2)	27.9 (2.1)	34.1 (2.0)	4.0 (0.6)	22.8	27.6
Yes	Liquid phase	3.4 (0.2)	1.1 (0.3)	4.6 (0.4)	1.9 (0.2)	-0.9	2.6

*Mean of 20 specimens ± standard deviation

Table 2. Liquid phase silanation

Specimens	Wt. gain on silanation, % of dry unreacted wt.	T _{1/2} , min.	Maximum equilibrium swelling, (mm)
Control	-	1.0	1.20
Treated	2.2(0.2)*	71.4(3.4)	0.87 (72.5% of control)

*Figures in parentheses indicate ± standard deviation

Table 3. Vapour phase silanation

Specimens	Wt. increase on DMF treatment %	Wt. increase on silanation over pretreated wt. %	T _{1/2} , min.	Maximum swelling, mm.
Control	-	-	1.1	1.31
Treated	2.3(0.03)*	3.6(0.3)	75.7 (1.8)	0.98 (75% of Control)

*Figures in parentheses indicate ± standard deviation

of stabilization achieved are also similar for specimens treated in the two ways. The $T_{\frac{1}{2}}$ value for the liquid phase silanation was 71.4 and that for the vapour phase reaction was 75.7.

Over 70 times increase in the rate of water repellency was achieved. Conventional water repellents only slow down the rate of sorption, they do not decrease the maximum equilibrium swelling (Borgin 1961, Borgin 1965, Borgin 1968). Silanation reaction not only slows down the rate of water uptake in wood but also substantially decreases the maximum equilibrium swelling of wood (27.5 and 25 percent respectively in cases of liquid phase and vapour phase reactions).

CONCLUSION

Silanes chemically modify wood by reacting with wood hydroxyl groups. The reaction product is quite stable. The reaction decreases the hydrogen bonding capacity of wood and thus imparts water repellency in the treated specimens. The maximum equilibrium swelling of the specimens are also reduced substantially, making wood dimensionally stable.

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