

## **CHEMICAL MODIFICATION: A NON-TOXIC APPROACH TO WOOD PRESERVATION**

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### **SUMMARY**

Wood can be chemically modified to reduce the moisture content of the cell wall and increases decay resistance. As the level of bonded chemical increases, the cell wall equilibrium moisture content decreases and the resistance to attack by white- and brown-rot fungi increases. There is a direct relationship between the decrease in cell wall moisture Content and resistance to fungal attack.

### **INTRODUCTION**

After millions of years of evolution, wood is designed to perform in a wet environment, and nature is programmed to recycle it, in a timely way, back to the basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradation. The properties of wood are, for the most part, a result of the chemistry of its cell wall components. The polysaccharides (cellulose and hemicelluloses) are mainly responsible for moisture uptake and release in changing environments that results in changes in wood volume (dimensional instability) and in the recognition mechanisms for biological degradation (attack by fungi, termites, etc).

The need to protect wood from decay has been an issue ever since humans first used wood. There are references in the Old Testament to the use of decay resistant wood and the Vikings charred the outside of their ships for preservation.

When wood preservation was in its infancy, the approach for protection was focused only on toxicity. Salts of arsenic, chromium, copper and tin have been used along with toxic organic chemicals such as pentachlorophenol and creosote. The wood was treated with these chemicals at various loading levels using various solvents and most did provide long-term effectiveness against fungal attack. Unfortunately, these chemicals are broad spectra toxins that are so toxic to humans and other life forms.

With a greater awareness of the persistence of some of these toxic wood preservative chemicals in nature and the concern for our ecosystem, less toxic or narrow spectra toxins have been explored and developed into commercial products. Less toxic and narrower toxicity also has resulted in less effectiveness.

Another approach, which was not followed at that time, was to study the mechanisms of fungal attack to determine if preservative methods could be based on metabolic differences between fungi and humans. For example, humans do not possess enzymes capable of breaking down cellulose, a major enzyme system in fungi.

There are several other ways to approach wood preservation without using toxicity as the mechanism of effectiveness. One approach is to interfere with the organisms metabolism. Fungi contain the polysaccharide chitin in their "skin" and interfering with the metabolic formation of chitin would be lethal to fungi and not affect humans. Micro-organisms have enzyme systems that can metabolize cellulose. Since humans do have cellulase enzymes, so blocking cellulose breakdown in fungi would be an effective tool in wood preservation. Chemicals that interfere with the organism's energy or life cycle is another way to achieve the goal of wood preservation without relying on use of toxic chemicals.

There is a very close relationship between the moisture content of wood and its biodegradability. Dry wood does not decay as evidenced by wood found in ancient graves that is still sound after having been underground and dry over thousands of years.

## **CHEMICAL MODIFICATION OF WOOD**

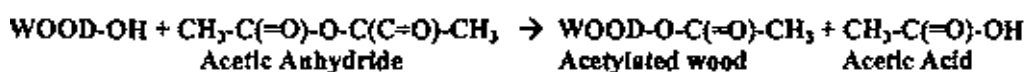
If the chemistry of the wood cell wall polymers is changed, polymer properties change as does the performance of the modified wood. Chemical modification of wood can be defined as a chemical reaction between some reactive part of wood and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two.

Chemical modification of wood has been shown to decrease the amount of moisture wood will pick up from its environment. Chemically modified wood has also been shown to reduce attack by fungi. These two phenomena are interrelated, that is, the decrease in moisture content due to chemical modification is thought to be the reason the modified wood is more decay resistant (Rowell 2005).

Many chemical reaction systems have been published for the modification of wood and the systems have been reviewed in the literature (Jahn 1947; Rowell 1975, 1983, 1991, 2005; Kumar 1994; Hon 1996). The chemicals include anhydrides (such as acetic, butyric, phthalic, succinic, malic, propionic and butyric anhydride), acid chlorides, ketene carboxylic acids, isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthalaldehydic acid, dimethyl sulfate, alkyl chlorides,  $\beta$ -propiolactone, acrylonitrile, and epoxides (such as ethylene, propylene, and butylene oxides, and difunctional epoxides). One of the most studied chemical modification systems is the reaction of wood with acetic anhydride to form acetylated wood. Acetylated wood is a non-toxic approach to wood preservation.

Acetylation of wood is the reaction of acetic anhydride with the accessible hydroxyl groups on the cell wall polymers of wood (Rowell 1975, 1983, 1984, 2005, Rowell et al. 1986). The acetylation of wood was first performed in Germany in 1928 by Fuchs, using

acetic anhydride and sulfuric acid as a catalyst (Fuchs 1928). Fuchs found an acetyl weight gain of over 40%, which meant that he decrystallized the cellulose in the process. He used the reaction to isolate lignin from pine wood. In the same year, Horn (1928) and Suida and Titsh (1928) acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure. A year later, Suida and Titsch (1929) acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30% to 35% after 15 to 35 days at 100°C. In 1945, Tarkow first demonstrated that acetylated balsa was resistant to decay (Tarkow 1945). In 1946, Tarkow, Stamm and Erickson (Tarkow 1946, Tarkow et al. 1946) first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940s, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources. The most used method of biomaterials acetylation is to use a limited amount of acetic anhydride with no catalyst or co-solvent with a reaction temperature range of 120 to 160 C (Rowell et al. 1986)



## Acetyl Stability

Questions have been raised about the long-term stability of the acetate group in wood. Table 1 shows the stability of acetyl groups in pine and aspen flakes to cyclic exposure to 30% and 90% relative humidity (RH) (3 months at 30% RH, followed by 3 months at 90% RH) (Rowell et al. 1992a,b). Within experimental error, no loss of acetyl occurred over 41 cycles. This experiment has been ongoing for more than 20 years; results continue to show no loss of acetyl from humidity cycling.

Table 1 - Stability of acetyl groups in pine flakes after cyclic exposure between 90% and 30% RH.

| Acetyl content (%)by cycle number |      |      |      |      |
|-----------------------------------|------|------|------|------|
| 0                                 | 13   | 21   | 33   | 41   |
| 18.6                              | 18.2 | 16.2 | 18.0 | 16.5 |
| 17.9                              | 18.1 | 17.1 | 17.8 | 17.1 |

## Reduction in Moisture Content

Table 2 shows the relationship between weight gain due to acetylation and the reduction in equilibrium moisture content and fiber saturation point on pine. The table shows that as the acetyl content increases, the equilibrium moisture content decreases.

The EMC of acetylated wood at 20.4 WPG is reduced approximately 60% at 30, 65 and 90% relative humidity as compared to control pine and the FSP is reduced almost 80%.

Table 2 - Equilibrium moisture content (EMC) at 30, 65 and 90% relative humidity (RH) and fiber saturation point (FSP) of control and acetylated pine.

| WPG <sup>a</sup> | Equilibrium Moisture Content at 27 °C |       |       | Fiber Saturation Point |
|------------------|---------------------------------------|-------|-------|------------------------|
|                  | 30%RH                                 | 65%RH | 90%RH |                        |
| 0                | 5.8                                   | 12.0  | 21.7  | 45                     |
| 6.0              | 4.1                                   | 9.2   | 17.5  | 24                     |
| 10.4             | 3.3                                   | 7.5   | 14.4  | 16                     |
| 14.8             | 2.8                                   | 6.0   | 11.6  | ---                    |
| 18.4             | 2.3                                   | 5.0   | 9.2   | 14                     |
| 20.4             | 2.4                                   | 4.3   | 8.4   | 10                     |

<sup>a</sup>WPG = Weight percent gain of acetyl

Sorption-desorption isotherms for acetylated spruce fibers are shown in Figure 1 (Stromdahl 2000). The 10-min acetylation curve represents a WPG of 13.2 and the 4-h curve a WPG of 19.2. Untreated spruce reached an adsorption-desorption maximum at about 35% moisture content; acetylated spruce at 19.2 WPG reached a maximum of about 10%. Moisture is presumed to be sorbed either as primary or secondary water. Primary water is water sorbed to primary sites with high binding energy, such as the hydroxyl groups. Secondary water is water sorbed to sites with less binding energy; water molecules are sorbed on top of the primary layer. Since some hydroxyl sites are esterified with acetyl groups, there are fewer primary sites to which water sorbs. And since the fiber is more hydrophobic as a result of acetylation, there may also be fewer secondary binding sites.

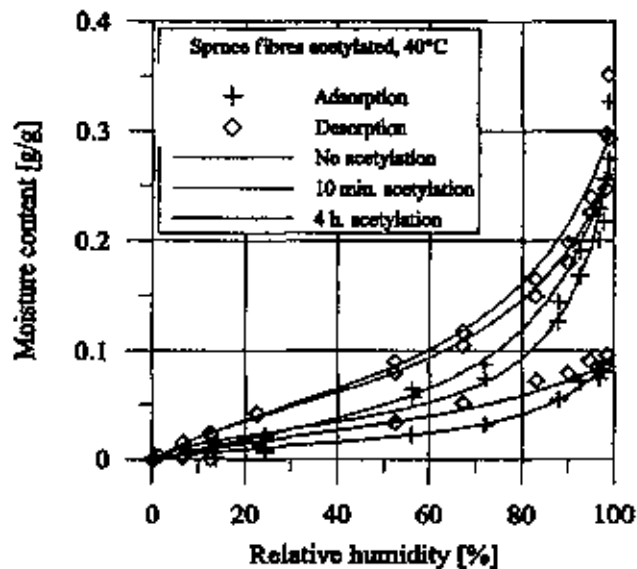


Figure 1 -Sorption isotherm for control and acetylated spruce.

## Resistance to Attack by Fungi

Table 3 shows the resistance of acetylated particleboards to attack by the brown-rot fungus *Gloeophyllum trabeum* or the white-rot fungus *Trametes versicolor* as a function of the weight gain due to acetylation in a Standard ASTM 12 week soil bottle test. As the weight gain of acetyl increases, weight loss due to fungal attack decreases. Acetylated pine becomes resistant to attack by white-rot fungi at about 11 WPG and to brown-rot fungi at about 15 WPG.

Table 3 - Resistance of control and acetylated pine against attack by the brown-rot fungus *Gloeophyllum trabeum* or the white-rot fungus *Trametes versicolor* in a 12-week ASTM Standard soil block test.

| WPG  | Weigh Loss After 12 Weeks |           |
|------|---------------------------|-----------|
|      | Brown-rot                 | White-rot |
|      | Fungus                    | Fungus    |
|      | (%)                       | (%)       |
| 0    | 61.3                      | 7.8       |
| 6.0  | 34.6                      | 4.2       |
| 10.4 | 6.7                       | 2.6       |
| 14.8 | 3.4                       | <2        |
| 17.8 | <2                        | <2        |

In a bending creep test of aspen flakeboards, control boards made with phenol-formaldehyde adhesive failed in an average of 71 days when exposed to the brown-rot fungus *Tyromyces palustris* and in 212 days when exposed to the white-rot fungus *Traetes versicolor* (Imamura et al. 1988, Rowell et al. 1988). At failure, weight loss averaged 7.8% for *T. palustris* and

bonded acetylated flakeboards showed surface mycelium colonization during the test, but since the fungus did not attack the acetylated flakes, little strength was lost.

In similar bending creep tests, both control and acetylated pine particleboards made using melamine–urea-formaldehyde adhesive failed because *T. palustris* attacked the adhesive in the glue line (Imamura et al. 1988). Mycelium invaded the inner part of all boards, colonizing in both the wood and glue line in control boards but only in the glue line in acetylated boards. These results show that the glue line is also important in protecting composites from biological attack.

After 16-week exposure to *T. palustris*, the internal bond strength (IBS) of control aspen flakeboards made using a phenol-formaldehyde resin was reduced more than 90%; IBS of flakeboards made using an isocyanate resin was reduced 85% (Imamura et al. 1987). After 6-month exposure in moist unsterile soil, the same control flakeboards made using a phenol-formaldehyde resin lost 65% IBS and those made using an isocyanate resin lost 64% IBS. Failure was due mainly to strength reduction in the wood resulting from fungal attack. Acetylated aspen flakeboards lost much less IBS during the 16-week exposure to *T. palustris* or 6-month soil exposure.

A fungal cellar was set up using unsterile soil that contained white-, brown- and soft-rot fungi and tunneling bacteria (Nilsson et al. 1988). Particleboards made using control and acetylated particles, at various levels of bonded acetyl groups were tested over a 144 month period (12 years). Table 4 shows the results of a long-term fungal cellar test. Control particleboards were swollen at the first 2 month inspection, some fungal attack was observed and the boards failed at 6 months. Swelling was detected in the 7.3 WPG acetylated particleboards at 2 months but no fungal attack was observed until 3 months and failure occurred at 12 months. Swelling was observed in the 11.5 WPG acetylated particleboards at 4 months but no decay was detected until 5 months and the boards failed at 24 months. Swelling was observed in the 13.6 WPG acetylated particleboards at 6 months but no fungal attack was detected until 12 months and failure was at 36 months. Particleboards acetylated above 16 WPG did not swell or decay in the 144 month test.

Acetylated solid wood and flakeboards have been subjected to in-ground tests (Hadi et al. 1996, Rowell et al. 1997, Larsson-Brelid et al. 2000) throughout the world. In the United States, Sweden, and New Zealand, specimens showed little or no attack after 10 years of exposure. In Indonesia, specimens failed in less than 3 years (Hadi et al. 1996), mainly as a result of termite attack. In Sweden, acetylated pine at a WPG of 21.2 has been outperforming wood treated with copper chromium arsenic at 10.3 kp/m<sup>3</sup> after 8 years of exposure (Larsson-Brelid et al. 2000).

Table 4–Fungal cellar test on control and acetylated pine particleboards.

| WPG   | Rating <sup>1</sup> at intervals (Months) |     |     |     |     |     |       |     |    |     |
|-------|-------------------------------------------|-----|-----|-----|-----|-----|-------|-----|----|-----|
|       | 2                                         | 3   | 4   | 5   | 6   | 12  | 24    | 36  | 72 | 144 |
| ----- |                                           |     |     |     |     |     |       |     |    |     |
| 0     | S/2                                       | S/3 | S/3 | S/3 | S/4 | --  | --    | --  | -- | --  |
| 7.3   | S/0                                       | S/1 | S/1 | S/2 | S/3 | S/4 | --    | --  | -- | --  |
| 11.5  | 0                                         | 0   | S/0 | S/1 | S/2 | S/3 | S/4-- | --  | -- | --  |
| 13.6  | 0                                         | 0   | 0   | 0   | S/0 | S/1 | S/2   | S/4 | -- | --  |
| 16.3  | 0                                         | 0   | 0   | 0   | 0   | 0   | 0     | 0   | 0  | 0   |
| 17.9  | 0                                         | 0   | 0   | 0   | 0   | 0   | 0     | 0   | 0  | 0   |

Combining data from Tables 2, 3 and 4, Table 5 shows the relationship between equilibrium moisture content at 90% relative humidity and the performance of the equivalent control or acetylated particleboard in the soil block and fungal cellar tests. The data suggests that the mechanism of resistance of acetylated wood to attack by fungi is closely connected to the moisture content of the wood. The mechanism may also involve blocking of specific enzymatic reactions as a result of changes in configuration and conformation of the polymers in the cell wall of the modified wood. In the case of brown-rot fungal attack, authors have suggested that the reduced moisture content of acetylated wood prevents the fungus from initiating the breakdown of hemicelluloses as an energy source (Winandy and Rowell 2005; Nilsson, personal communication, 1986). This mechanism is consistent with the data from soil block weight loss tests and strength loss tests.

Table 5 - Comparison of equilibrium moisture content at 90% relative humidity and swelling, decay and failure of control and acetylated pine particleboards.

| WPG         | EMC at 90% RH Months to board: |                       |                    |                      |
|-------------|--------------------------------|-----------------------|--------------------|----------------------|
|             |                                | swelling <sup>1</sup> | Decay <sup>2</sup> | Failure <sup>3</sup> |
| 0           | 22                             | <7                    | 2                  | 6                    |
| 6 - 7.3     | 17                             | 2                     | 3                  | 12                   |
| 10.4 - 11.5 | 14                             | 4                     | 5                  | 24                   |
| 13.6–14.8   | 12                             | 6                     | 12                 | 36                   |
| 16.3 - 20.4 | 9                              | >144                  | >144               | >144                 |

<sup>1</sup>Swelling first observed, <sup>2</sup>Start of decay; <sup>3</sup>Reached a rating of 4

### Resistance to Attack by Termites

Table 6 shows the results of a 2-week termite test using *Reticulitermes flavipes* (subterranean termites) on several types of chemically modified pine (Rowell et al. 1988). The lack of complete resistance to attack may be attributed to the severity of the test. However, termites can live on acetic acid and decompose cellulose to mainly acetate.

Termite survival was quite high at the end of the tests, which indicates that the modified wood was not toxic to these insects.

Table 6. Resistance of acetylated pine to *Reticulitermes flavipes*.

| WPG (%) | Weight loss (%) |
|---------|-----------------|
| 0       | 31              |
| 10.4    | 9               |
| 17.8    | 6               |
| 21.6    | 5               |

### Resistance to Attack by Marine Organisms

Acetylated wood is resistant to attack by marine organisms. In Florida, control specimens were destroyed in 6 months to 1 year, mainly because of attack by *Limnoria tripunctata*, while acetylated wood showed good resistance (Johnson and Rowell 1988, Table 7). In similar tests in Sweden, acetylated wood failed after 2 years of exposure and control specimens failed in less than 1 year (Larsson-Brelid et al. 2000). For both control and acetylated specimens, failure was due to attack by crustaceans and molluscs.

Table 7. Resistance of acetylated pine to marine organisms<sup>a</sup>

| WPG (%) | Exposure (years) | Mean rating of attack by various organisms <sup>b</sup> |                              |
|---------|------------------|---------------------------------------------------------|------------------------------|
|         |                  | <i>Limnoriid</i> and <i>terebrans</i> <sup>c</sup>      | <i>Shaeroma</i> <sup>d</sup> |
| 0       | 1                | 2-4                                                     | 3.4                          |
| 22.0    | 3                | 8                                                       | 8.8                          |

<sup>a</sup> *Teredinid* borers

<sup>b</sup> Rating system: 10 = no attack; 9 = slight attack; 7 = some attack  
4 = heavy attack; 0 = destroyed.

<sup>c</sup> Installed in Key West, FL.

<sup>d</sup> Installed in Tarpon Springs, FL.

## CONCLUSIONS

Reaction of wood with acetic anhydrides is effective in reducing the equilibrium moisture content of the modified wood.

As the weight gain due to reaction with acetic anhydride increases, equilibrium moisture content decreases and resistance to attack by white- and brown-rot fungi increases.



As the weight gain due to acetylation increases, the resistance to attack by white- and brown-rot fungi increases.

Acetylated pine particleboards above a weight gain of approximately 16% show the lowest equilibrium moisture content and are very resistant to attack by white-, brown-, and soft-rot fungi and tunneling bacteria.

Finally, the data suggests that the mechanism of resistance to attack by fungi by chemical modification is due to a reduction in the cell wall moisture content.

Acetylation of wood provides protection from fungal attack of wood without the use of toxic chemicals.

Acetylation of wood is now a commercial process in Japan and soon will be in the United States and Europe. Its first application is likely to be in wood used for residential decking. While acetylated wood is more expensive than CCA treated wood, it provides an alternative to the use of toxic chemicals in the environment.

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