

WOOD PROPIONYLATION IN THE PRESENCE OF CATALYSTS

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ABSTRACT

Effects of potassium and sodium salts as catalysts on propionylation of wood and on the color change of propionylated wood have been investigated. It was found that potassium acetate, sodium acetate, sodium propionate, and sodium thiosulfate as catalysts were effective for propionylation of wood, and the catalyst loadings (CLs) of them had an effect on weight percent gains. The color of propionylated wood catalyzed with potassium acetate, sodium acetate, or sodium propionate changed very slightly, while sodium thiosulfate-catalyzed wood changed greatly with the increase of CL. Otherwise, potassium sulfate and sodium sulfate showed little or no catalytic effect, and sodium tetraborate decahydrate showed a negative catalytic effect on propionylation of wood.

Keywords: Propionylation, catalyst, catalytic effect, catalyst loading, color difference.

INTRODUCTION

Acetylation of wood has been being studied for several decades to improve its dimensional stability (Goldstein et al. 1961; Rowell et al. 1986; Sadachi 1989; Beckers and Militz 1994), to increase its resistance to degradation (Goldstein et al. 1961; Peterson and Thomas 1978; Kumar et al. 1979; Imamura and Nishimoto 1987), and to enhance other properties of wood (Yano et al. 1986), while propionylation of wood has made little progress until recent years (Hill and Jones 1996a, 1996b, 1999; Li et al. 2000).

It is important to retain its inherent advantages when wood is chemically modified to improve performance characteristics. Generally, the reaction conditions must be mild enough that the modified wood still possesses the desirable properties of wood. That is, the

temperature should be low and the reaction time should be as short as possible. For this reason, many catalysts have been tried, and it has been found that potassium acetate, sodium acetate, and some other chemical compounds are very effective for catalyzing the acetylation of wood (Clermont and Bender 1957; Tarkow 1959; Arni et al. 1961; Baird 1969; Rowell et al. 1986).

Studies on uncatalyzed propionylation of wood have established that propionylation of wood plus propionic anhydride at high temperature can endow wood with great dimensional stability (Li et al. 2000). On the other hand, chemical reaction at high temperature always leads wood to degradation and color change. We think it is important to try to find effective catalysts for propionylation of wood to reduce the reaction temperature. Few studies have been done on catalyzed reaction be-

tween wood and propionic anhydride; much more study is needed for a better understanding of catalyzed propionylation of wood.

In order to protect wood from degradation or color change during the reaction, the most favorable catalysts are weak alkaline chemicals or neutral chemicals. In addition, from the standpoint of keeping the reaction system as simple as possible and reducing the cost, it would be best to eliminate organic solvent from the reaction system.

In this study, several weak alkaline or neutral potassium salts and sodium salts were used for propionylation as catalysts without solvents to try to improve the reactivity between wood and propionic anhydride. For evaluating the catalytic efficiency of catalysts used, the weight percent gain (WPG) and the antismelling efficiency (ASE) of modified wood were calculated. The effect of catalysts on the color change of wood was also observed. The experiment of catalyzed acetylation at the same reaction conditions was also done to determine whether the catalysts give a similar catalysis on both propionylation and acetylation of wood.

MATERIALS AND METHODS

Wood specimens

Sapwood specimens of hinoki (*Chamaecyparis obtusa* Endl.) and yellow-poplar (*Liriodendron tulipifera* L.) with a size of 30(R) × 30(T) × 5(L) mm were used. The wood specimens were initially extracted with a solution of ethanol and benzene (vol/vol = 1/2) for 12 h, and with acetone for another 12 h using a Soxhlet extractor. Extracted specimens were then dried at 105°C for 24 h. Subsequently, their weights and sizes were measured. Three specimens were used for each condition.

Chemical agents

Acetic anhydride [(CH₃CO)₂O], propionic anhydride [(CH₃CH₂CO)₂O], potassium acetate (CH₃COOK), sodium acetate (CH₃COONa), sodium propionate (CH₃CH₂COONa), sodium thiosulfate (Na₂S₂O₃·5H₂O), potassium sulfate

(KSO₄), sodium sulfate (NaSO₄), sodium tetraborate decahydrate (Na₂B₄O₇·10H₂O), and all the other chemical agents used were of chemical grade from Wako Pure Chemical Industries, Ltd, Japan.

Preparation of propionylated wood and acetylated wood

Impregnation of catalysts into wood.—The specimens, whose sizes were mentioned previously, were immersed in different aqueous catalyst solutions with several different concentrations of catalyst (0.1–12.0%), and placed in a desiccator. After being placed under vacuum (2–6 kPa) for 30 min, the interior of the desiccator was returned to atmospheric pressure for 24 h. Then the specimens were oven-dried at 105°C for 24 h. Subsequently, their weights were measured and the catalyst loadings (CLs) were calculated.

Preparation of acetylated wood and propionylated wood.—The specimens impregnated with catalysts were immersed in propionic anhydride or acetic anhydride at reduced pressure for 30 min and at atmospheric pressure for 24 h. Then the specimens were wrapped with polyvinylidene chloride film and aluminum foil and heated at 90°C or 110°C for different periods (2, 4, or 8 h). After immersing in water at reduced pressure for 30 min and leaching in flowing water for 48 h, the specimens were extracted with acetone for 12 h. Afterwards they were oven-dried at 105°C for 24 h, and their sizes (tangential, radial, and longitudinal directions) and weights were measured. The weight percent gain (WPG) of the treated specimens was calculated on the oven-dried weight basis.

Evaluation of propionylated wood

Dimensional stability measurement.—The specimens were immersed in distilled water and put in a vacuum desiccator, and the pressure was reduced to 2–6 kPa for 30 min; then it returned to atmospheric pressure for 24 h at room temperature. After this operation, the sizes of the water-swollen specimens were

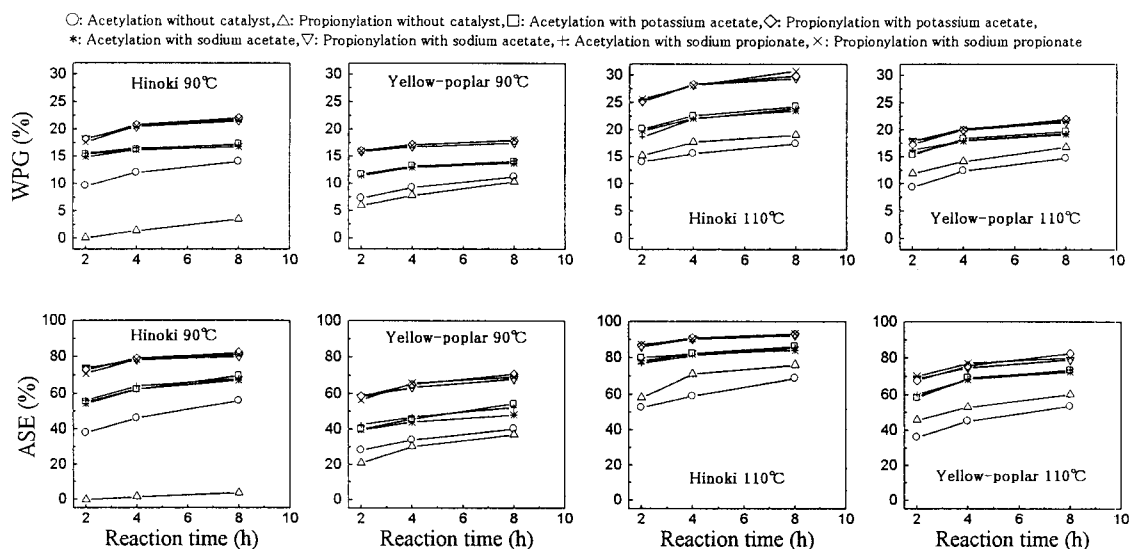


FIG. 1. Effects of potassium acetate, sodium acetate, and sodium propionate as catalysts on propionylation and acetylation of hinoki and yellow-poplar. WPG = weight percent gain. ASE = antiswelling efficiency. Catalyst loading of hinoki (from 3.5% aqueous solution) is 5.6–6.0% and that of yellow-poplar (from 5.0% aqueous solution) is 5.6–6.2%.

measured. From the changes in volumetric dimensions, the antiswelling efficiency (ASE) during water absorption was calculated.

Measurement for the color changes of specimens.—The color on the cross section of specimens before and after treatment was measured by a spectrophotometer (MINOLTA CM-3700d) according to the CIE $L^*a^*b^*$ color system. Three specimens were used for each treatment and three areas (3×5 mm) were measured for each specimen. The color difference of specimens was calculated by the following formula (1):

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where ΔE^* is the color difference, ΔL^* is the lightness difference, and Δa^* and Δb^* are the chroma differences.

RESULTS AND DISCUSSION

Effects of catalysts on propionylation of wood

Potassium acetate, sodium acetate, and sodium propionate as catalysts.—Figure 1 shows the effects of potassium acetate, sodium

acetate, and sodium propionate as catalysts on propionylation of hinoki and yellow-poplar specimens at 90°C and 110°C, and the results of uncatalyzed propionylation and catalyzed and uncatalyzed acetylation from the same reaction conditions are also shown in Fig. 1.

At 90°C without a catalyst, acetic anhydride could react with both hinoki and yellow-poplar, and it showed a higher reactivity with hinoki. On the other hand, propionic anhydride showed little or no reactivity with hinoki. But propionic anhydride showed a fair reactivity with yellow-poplar. Even in 8-h reaction, the propionylated hinoki developed a very small WPG value revealing no dimensional stability ($ASE \approx 5\%$), while the propionylated yellow-poplar had about 10% WPG and 37% ASE. Otherwise, the acetylated hinoki showed about 14% WPG and 55% ASE, higher values than those of the propionylated yellow-poplar.

In the presence of potassium acetate, sodium acetate, and sodium propionate, propionylation as well as acetylation of both hinoki and yellow-poplar was accelerated markedly, and the three catalysts showed a similar cata-

lytic effect. Compared with acetylated wood, the propionylated wood showed a considerably greater increase in WPG and ASE, and the increase in those values for propionylated hinoki was greater than that for propionylated yellow-poplar. In 8-h reaction, ASE values of propionylated yellow-poplar and hinoki were about 68% (about 17% WPG) and about 80% (about 22% WPG), respectively. This indicated that propionylation at 90°C with catalysts could endow wood with a high dimensional stability.

At 110°C, it was obvious that the reaction rates of propionylation as well as acetylation of wood without catalyst were generally higher than those at 90°C. The propionylated wood showed slightly greater WPG and ASE values than the acetylated wood. This was also recognized in our previous study (Li et al. 2000).

A similar catalysis tendency of potassium acetate, sodium acetate, and sodium propionate on propionylation as well as acetylation of wood was also recognized at 110°C as compared with that at 90°C, indicating a great increase in WPG and ASE. It was found that the modified hinoki showed higher WPG and ASE values than the modified yellow-poplar, and the propionylated wood displayed higher WPG and ASE values than the acetylated wood. In the reaction of 4 h with catalysts at 110°C, the propionylated hinoki could attain about 90% ASE (about 28% WPG), showing a supereminent dimensional stability.

From the above experiments, we found that hinoki and yellow-poplar showed a different result on propionylation or acetylation with or without a catalyst. This may be due to the different reactivity of the different chemical composition of wood according to Ohkoshi's studies (Ohkoshi et al. 1997): Xylan is reactive in comparison with cellulose during acetylation of wood, producing the substitutions of hydroxyl groups at small WPGs. But what makes xylans so special is not clear. It is likely that xylans are more accessible. Similarly, during propionylation of wood, yellow-poplar having much more xylan (about 20%) may show a higher reactivity with propionic anhydride

than hinoki (xylan, about 10%) at low temperature without a catalysts. At high temperature or with catalysts, the reactivity of all the chemical composition (cellulose, hemicellulose, and lignin) is raised, and hinoki (softwood) shows a much greater accessibility to the reaction sites owing to a much lower density than yellow-poplar (hardwood), resulting in more access of chemicals to reactive sites.

It can be concluded that potassium acetate, sodium acetate, and sodium propionate were all effective catalysts for propionylation as well as acetylation of wood and they showed a similar catalytic effect. The result of potassium acetate and sodium acetate catalyzing acetylation is in agreement with Conant, Tarkow, and others' results (Clermont and Bender 1957; Tarkow 1959).

Sodium thiosulfate as a catalyst.—Figure 2 shows the effects of sodium thiosulfate as a catalyst on propionylation as well as acetylation of hinoki and yellow-poplar specimens at 90°C and 110°C.

At 90°C, sodium thiosulfate accelerated propionylation of hinoki more greatly than that of acetylation. It also displayed a catalytic effect on propionylation as well as acetylation of yellow-poplar.

At 110°C, the catalytic effect of sodium thiosulfate on propionylation as well as acetylation of hinoki and yellow-poplar was also apparent. Propionylation catalyzed with sodium thiosulfate in 4-h reaction could endow hinoki with about 85% ASE (about 24% WPG), and yellow-poplar with about 70% ASE (about 20% WPG).

Potassium sulfate and sodium sulfate as catalysts.—Figure 3 shows the results of propionylation of hinoki and yellow-poplar with and without the presence of potassium sulfate and sodium sulfate.

Propionylation as well as acetylation in the presence of potassium sulfate and sodium sulfate at reaction temperatures of both 90°C and 110°C did not show any distinct differences from those without catalysts. This means that potassium sulfate and sodium sulfate possess

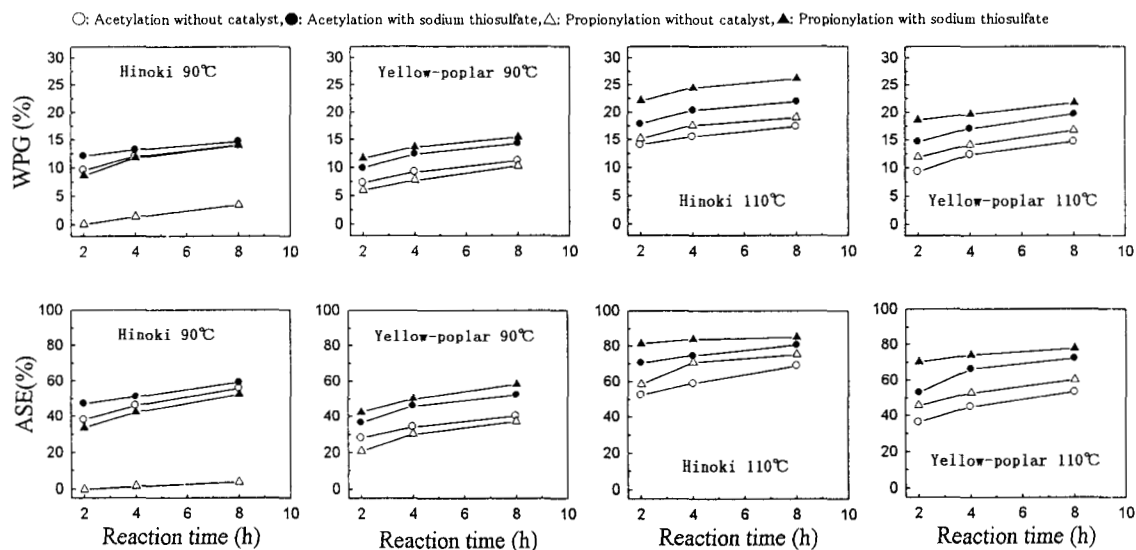


FIG. 2. Effects of sodium thiosulfate as a catalyst on propionylation and acetylation of hinoki and yellow-poplar. WPG = weight percent gain, ASE = antiswelling efficiency. Catalyst loadings of hinoki (from 4.5% aqueous solution) and yellow-poplar (from 7.5% aqueous solution) are 5.5–6.0%.

little or no catalytic effect on propionylation and acetylation of wood.

Sodium tetraborate decahydrate as a catalyst.—The experimental results of propionylation of hinoki and yellow-poplar with and

without sodium tetraborate decahydrate as a catalyst are shown in Fig. 4.

Compared to the reaction without a catalyst, propionylation and acetylation of hinoki and yellow-poplar in the presence of sodium tet-

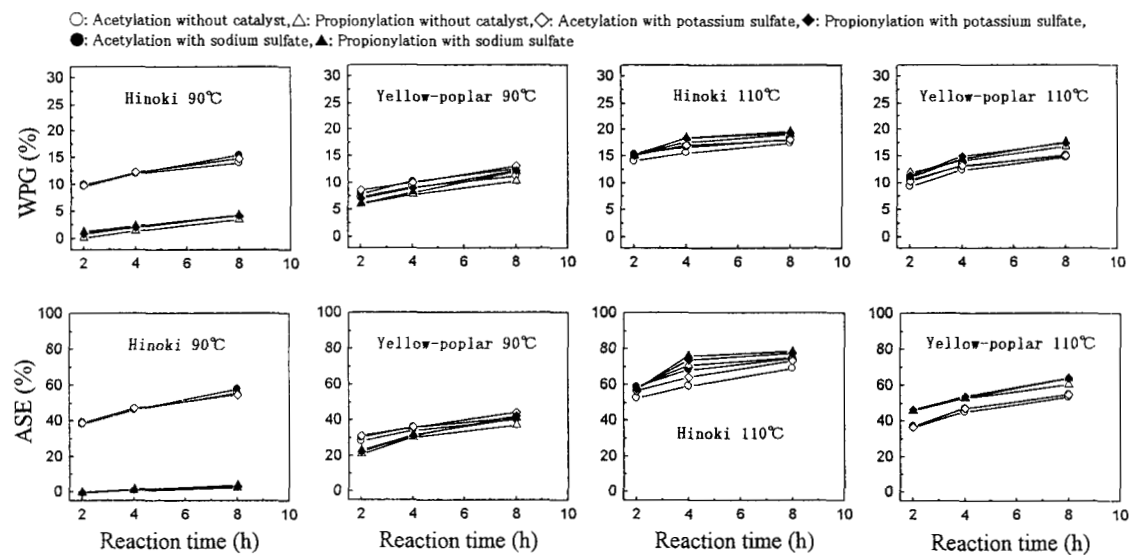


FIG. 3. Effects of potassium sulfate and sodium sulfate as catalysts on propionylation and acetylation of hinoki and yellow-poplar. WPG = weight percent gain, ASE = antiswelling efficiency. Catalyst loadings of hinoki (from 4.0% aqueous solution) and yellow-poplar (from 6.0% aqueous solution) are 5.8–6.6%.

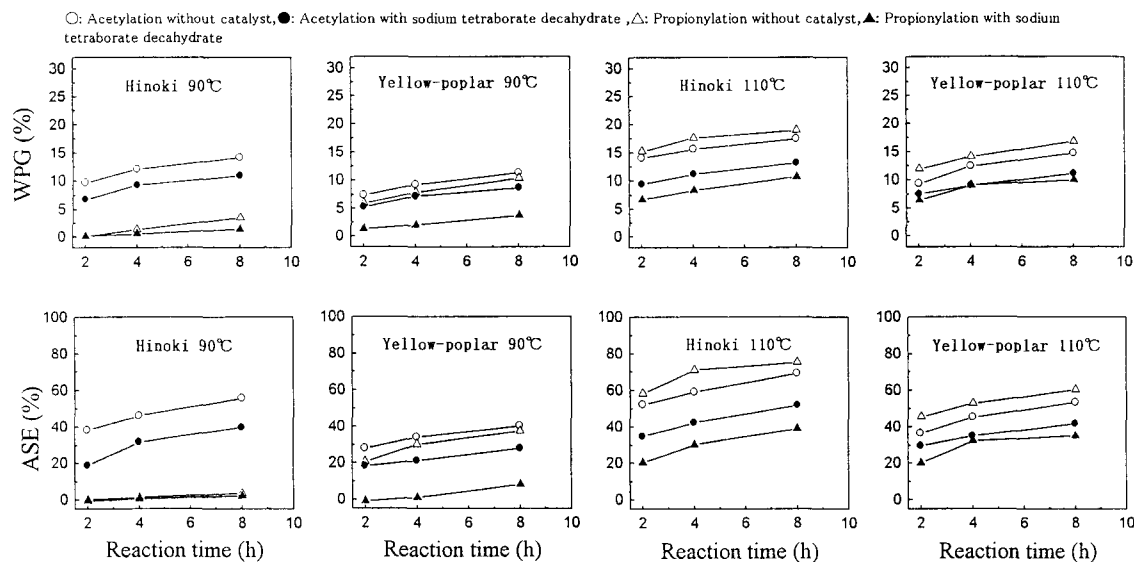


FIG. 4. Effects of sodium tetraborate decahydrate as a catalyst on propionylation and acetylation of hinoki and yellow-poplar. WPG = weight percent gain, ASE = antiswelling efficiency. Catalyst loadings of hinoki (from 7.0% aqueous solution) and yellow-poplar (from 12.0% aqueous solution at 50°C) are 5.8–6.5%.

rorate decahydrate were decelerated at both 90°C and 110°C, and the treated wood displayed much lower WPG and ASE values. This implies that sodium tetraborate decahydrate has a negative catalysis effect on propionylation and acetylation of wood. This may be due to the fact that borates form complexes with adjacent diols, which could prevent propionylation and acetylation from occurring.

Catalysis of acidic compounds for acetylation using acetic anhydride was considered to be due to generation of acetoxy ion (CH_3CO^+), which possesses higher reactivity than acetic anhydride. It was suggested that the catalytic efficiency of potassium acetate for acetylation was due to some characteristics

of the acetate (Tarkow 1959), but the rationale for weak alkaline or neutral compounds acting as catalysts for propionylation as well as acetylation still remains unclear. Consequently, we aimed in this study to investigate the catalytic effect of weak alkaline or neutral compounds for esterification, especially for propionylation and acetylation. Our long-term aim is to explore the catalysis mechanism and the regularity of the catalysts. This may lead to finding the optimum catalyst and may improve the productivity of wood propionylation or acetylation. Our initial experimental results showed that the catalysts used in this study had different bulking capability in wood (Table 1). Wood specimens bulked when impreg-

TABLE 1. Bulking coefficients of specimens impregnated with catalysts.

Wood species	Catalysts													
	CH_3COOK		CH_3COONa		$\text{CH}_3\text{CH}_2\text{COONa}$		$\text{Na}_2\text{S}_2\text{O}_3$		K_2SO_4		Na_2SO_4		$\text{Na}_2\text{B}_4\text{O}_7$	
	B* (%)	CL** (%)	B (%)	CL (%)	B (%)	CL (%)	B (%)	CL (%)	B (%)	CL (%)	B (%)	CL (%)	B (%)	CL (%)
Hinoki	1.28	5.8	1.25	5.9	1.27	5.8	0.98	6.0	0.06	6.1	0.08	6.6	-0.67	6.5
Yellow-poplar	1.52	6.1	1.48	6.1	1.50	5.9	1.03	6.0	0.01	6.2	-0.03	6.6	-0.97	6.5

* B = bulking coefficient of specimens impregnated with a catalyst.

** CL = catalyst loading of specimens.

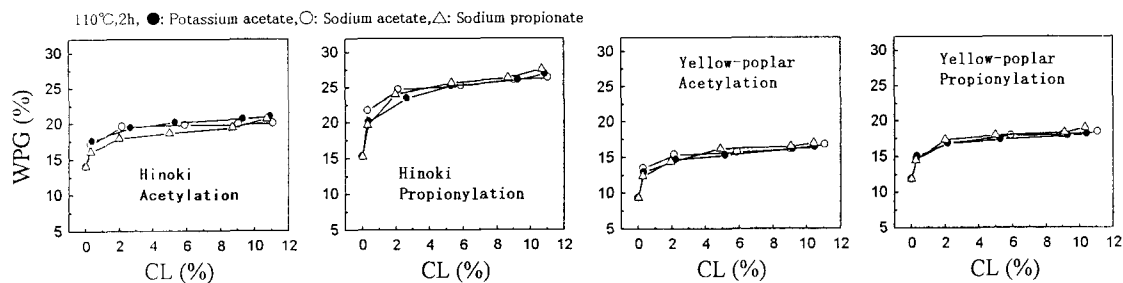


FIG. 5. Effects of catalyst loadings (CLs) of potassium acetate, sodium acetate, and sodium propionate on weight percent gains (WPGs) of treated specimens.

nated with potassium acetate, sodium acetate, sodium propionate, or sodium thiosulfate, which acted as an effective catalyst for propionylation or acetylation. On the other hand, the specimens shrank when impregnated with sodium tetraborate decahydrate, which showed a negative catalytic effect. It is possible that bulked wood possessed a much greater accessibility to the reaction sites, resulting in a higher reactivity while shrank wood possessed a much lower accessibility to the reaction sites, resulting in a lower reactivity.

Effect of catalyst loading of potassium acetate, sodium acetate, sodium propionate, and sodium thiosulfate on propionylation and acetylation

Effect of catalyst loading (CL) of potassium acetate, sodium acetate, and sodium propionate.—Figure 5 shows the relationship between CL of potassium acetate, sodium acetate, and sodium propionate and weight per-

cent gains (WPGs) of propionylated wood specimens which were reacted at 110°C.

The WPGs of both hinoki and yellow-poplar increased with an increase in CL. It was observed that potassium acetate, sodium acetate, and sodium propionate as catalysts were very effective for propionylation as well as acetylation even at a quite small CL, based on the fact that the WPGs increased abruptly at the initial increment in CL. This increase of WPGs ceased when the CL exceeded 3–4%.

Effect of CL of sodium thiosulfate.—Figure 6 shows the relationship between CL of sodium thiosulfate and WPGs of propionylated and acetylated wood specimens.

Sodium thiosulfate as a catalyst in propionylation as well as acetylation of wood specimens reacted at 110°C showed an accelerating tendency similar to that of potassium acetate, sodium acetate or sodium propionate (Fig. 5). The WPGs of specimens increased with an increase in CL. Specially, the increase was

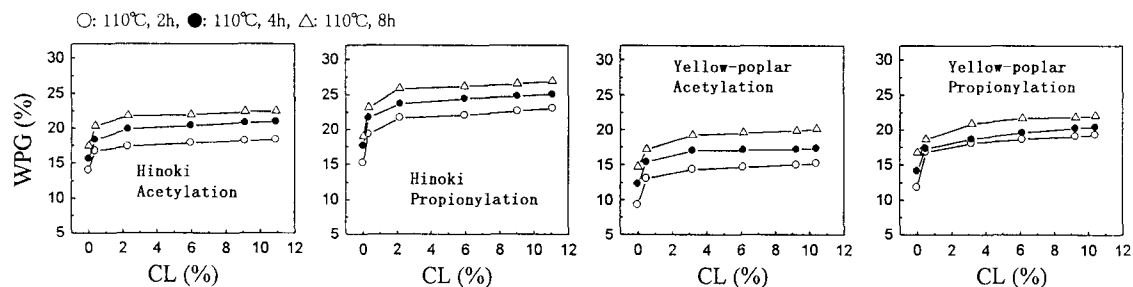


FIG. 6. Effects of catalyst loadings (CLs) of sodium thiosulfate on weight percent gains (WPGs) of treated specimens.

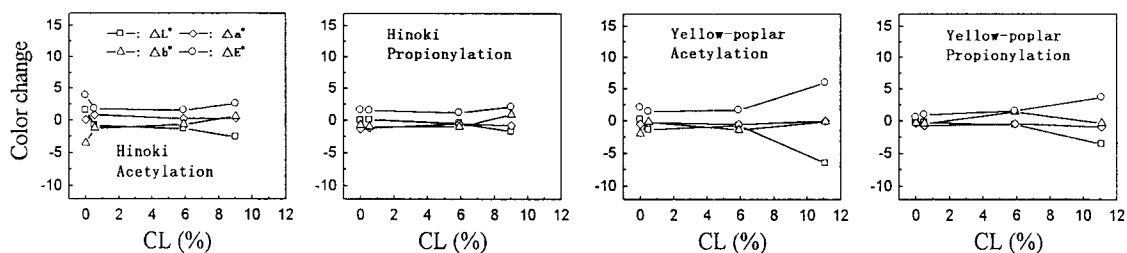


FIG. 7. Color changes of hinoki and yellow-poplar specimens after propionylation and acetylation with sodium acetate as a catalyst (110°C, 8 h). ΔL^* = lightness difference, Δa^* and Δb^* = chroma differences, and ΔE^* = color difference.

abrupt at smaller CL, and slow when the CL was more than 3%.

The catalyzed propionylated hinoki showed the highest WPG among treated woods. This is because hinoki possesses a greater accessibility to the reaction sites than yellow-poplar and propionyl has a higher molar weight than acetyl.

Effects of catalysts on the color changes of wood

Effects of CL of sodium acetate on the color changes of propionylated and acetylated wood specimens are shown in Fig. 7. When the CL value was small, the propionylated wood or acetylated wood showed little color change. With the increase of CL, the lightness of treated specimens decreased gradually and the color difference increased slightly, changing to a dull color. However, the a^* and b^* values showed little or no change with the increase of CL.

The potassium acetate and sodium propionate as catalysts achieved the same results,

that is, the propionylated wood or acetylated wood showed little or no color change.

Figure 8 shows the color changes of hinoki and yellow-poplar specimens after propionylation or acetylation using sodium thiosulfate as a catalyst.

The color difference increased very remarkably with the increase of CL. The lightness obviously decreased and the wood specimens became dull. The a^* increased somewhat and the b^* increased greatly, resulting in the specimens becoming slightly red and much more yellow.

The great color changes of propionylated or acetylated wood catalyzed by sodium thiosulfate, which is a reducing agent and used in determination of pulp lignin contents (kappa numbers), are probably associated with structural changes in the lignin.

CONCLUSIONS

The results indicated that:

1. Potassium acetate, sodium acetate, and so-

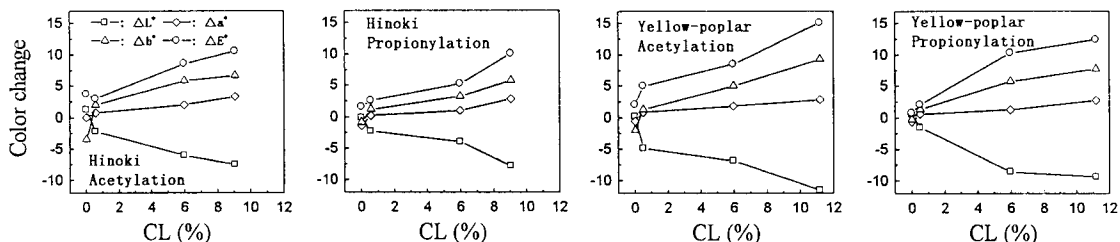


FIG. 8. Color changes of hinoki and yellow-poplar specimens after propionylation and acetylation with sodium thiosulfate as a catalyst (110°C, 8 h). ΔL^* , Δa^* , Δb^* , and ΔE^* are the same as shown in Fig. 7.

- dium propionate were all very effective as catalysts for propionylation as well as acetylation, and they had a very slight effect on the color change of propionylated and acetylated woods.
- Sodium thiosulfate showed an obvious catalytic effect on propionylation as well as acetylation of wood, but it had an unfavorable effect on the color change of treated woods.
 - Catalyst loading (CL) of potassium acetate, sodium acetate, sodium propionate, and sodium thiosulfate had an effect on the weight percent gains in propionylated and acetylated woods.
 - Potassium sulfate and sodium sulfate had little or no accelerating effect on propionylation as well as acetylation of wood. Sodium tetraborate decahydrate had a negative catalytic effect on propionylation as well as acetylation of wood.
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