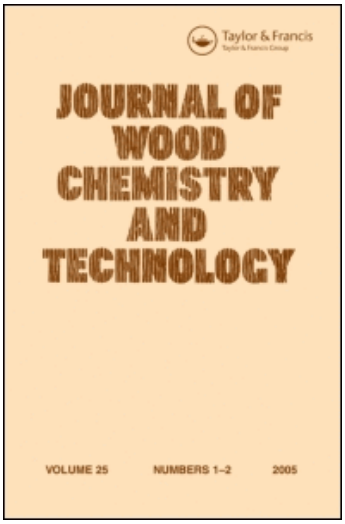

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Vapor Phase Acetylation of Southern Pine, Douglas-Fir, and Aspen Wood Flakes

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VAPOR PHASE ACETYLATION OF SOUTHERN PINE, DOUGLAS-FIR, AND ASPEN WOOD FLAKES

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ABSTRACT

Southern pine, Douglas-fir, and aspen wood flakes were acetylated with acetic anhydride vapor and compared with flakes acetylated with liquid acetic anhydride diluted with xylene. The rate of acetylation was much lower for the vapor than for the liquid phase reaction. Acetylation weight percent gains above 20 were achieved by both methods. Flakeboards made from both types of flakes absorbed much less water, both in water soaking tests and when subjected to humid air, and swelled at a lower rate and to a lower extent than did control boards. At low weight gains of vapor phase acetylation, the rate and extent of swelling were higher than those found for the controls.

Hygroscopicity of the resulting flakeboards decreased with increased level of wood acetylation. The equilibrium moisture content for flakeboards made from liquid phase acetylated flakes was the lowest at each relative humidity tested as compared to control boards, and boards made from vapor acetylated flakes at the same weight gain.

INTRODUCTION

Wood is a hygroscopic material which sorbs and desorbs water as the relative humidity that the wood is exposed to increases

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and decreases.[2] The carbohydrate constituents in wood are mainly responsible for moisture uptake since they are more hygroscopic than lignin. It has been shown, however, that lignin also contributes to the absorption of moisture.[3]

The lack of dimensional stability of wood has restricted its use in some products and is a continuing problem for other products in use. Dimensional instability, especially in the thickness direction, is an even greater problem in reconstituted wood products. In these products, not only normal swelling occurs (reversible swelling) but also swelling due to the release of residual compressive stresses imparted to the board during the pressing process (irreversible swelling).

Chemical modification of wood has been shown to be effective in reducing swelling in water due to a cell wall bulking mechanism.[4] Epoxides, isocyanates, anhydrides, and other chemicals have been reacted with cell wall polymer hydroxyl groups to give solid wood products which are 70 to 80% dimensionally stabilized.

The research reported here was conducted at Chalmers University of Technology in Göteborg, Sweden, and is part of a continuing large-scale research program being conducted in collaboration with several wood research laboratories throughout the world. The first part of this program established the basic chemistry for reacting hardwood and softwood flakes with epoxides and anhydrides. Liquid butylene oxide catalyzed with triethylamine and liquid acetic anhydride diluted with xylene, respectively, were reacted with wood flakes, and the flakes were used to produce flakeboards. These chemical treatments reduced the rate and extent of moisture uptake and reduced thickness swell dramatically.[5] The flakeboards made from acetylated flakes, however, were found to be more effective in reducing swelling than those made from butylene oxide reacted flakes. Various acetylation procedures have been developed and were reviewed in an earlier publication.[5]

Next, research on a liquid acetic anhydride/xylene acetylation procedure to produce dimensionally stable flakeboards was

completed.[6] Following this, a vapor-phase acetic anhydride/xylene acetylation procedure was studied.[7] The acetic anhydride/xylene procedure uses no added catalyst which simplified all previous procedures in this regard.[8]

The research reported here represents a continuation of past work and is aimed at developing a pilot-scale technique for acetylating wood flakes. In this study, we investigated uncatalyzed acetic anhydride vapor alone for acetylating disk-cut flakes from three species. This system eliminated the cosolvent used in the liquid xylene system and greatly simplified the recovery of chemicals after the reaction. Flakeboards made from vapor phase acetylated flakes were compared to those made from liquid phase acetylated flakes for the extent of water sorption and for the rate and extent of thickness swelling when exposed to liquid water as well as to air at various relative humidity levels.

EXPERIMENTAL

Wood Flakes

Southern pine, (mixture of Pinus palustris, P. echinata, P. taeda and P. elliottii) Douglas-fir, and aspen (Populus grandidentata) flakes were used in this study. Different techniques were used for generating flakes for this study; however, there should be no difference between the ring- and disk-cut flakes from a chemical reactivity standpoint. All flakes were retained on a 1/4-inch screen, and were ovendried 24 h at 105°C before use.

Size of flakes (thickness x length x width (cm)):

Southern pine	0.05 x 6.4 x random.
Douglas-fir	0.05 x 5 x random.
Aspen	0.06 x 3.8 x random.

Reaction of Flakes with Acetic Anhydride

The three species of flakes (200 g, o.d.) were separately placed in a stainless steel reactor in a stainless steel mesh

container. A vacuum was applied for 1 h at 105°C, then (under vacuum) 120 ml of acetic anhydride was introduced at the bottom of the reactor. Nitrogen gas was introduced to bring the reactor to atmospheric pressure. The temperature was raised to 120°C and maintained for 4 to 48 h. After the reaction, the excess acetic anhydride, together with the byproduct acetic acid, was drained from the reactor and reduced pressure applied for 1 h at 105°C. The flakes were removed from the reactor and ovendried for 24 h at 105°C. The weight percent gain (WPG) was calculated based on the original flake ovendried (o.d.) weight before reaction.

For comparison, o.d. flakes of all three species were also reacted at atmospheric pressure with refluxing acetic anhydride/xylene (1/1, v/v) in a glass reactor equipped with a condenser. After a reaction time of 0.5 to 48 h, the excess chemicals were drained from the reactor and reduced pressure applied for 1 h at 105°C.

Ovendry southern pine flakes were also reacted with acetic anhydride/xylene (1/1, v/v) at 120°C for 1 to 24 h in a stainless steel reactor pressurized to 150 psi with nitrogen. Removal of excess chemicals and ovendrying were done as given above.

Percent acetyl content was determined as acetic acid by gas chromatography after deacetylation with base of ground and mixed samples.

Flakeboard Preparation

Acetylated and control flakes (180 g, o.d.) were pressed into boards approximately 1.25 by 15 by 15 cm in size. Each board was made to a density of approximately 700 kg/m^3 with a resin solids content of 6% (based on o.d. treated flakes). The adhesive used was a 43.5% aqueous solution of a phenol/formaldehyde resin. No catalyst or wax was added. The mat moisture content was 12 to 13%. Pressing lasted for 10 min at 177°C.

Each flakeboard was lightly sanded, cut into four pieces (5 x 5 cm), ovendried, and weighed. The thickness was measured

at the center point of each specimen, with subsequent measurements taken at the same point.

Water Swelling Rate Tests

Each test specimen was placed in a 10- by 10-cm container, 5 cm deep which was on a flatbed micrometer for the thickness measurements. Water was added to the container and the specimen thickness recorded as a function of time. Measurements were taken every 5 min for the first hour, every hour for the first 6 h, then once a day for 5 days. All water and humidity tests were done in duplicate.

Water Soaking Tests

Cyclic water soaking tests were run as previously described.[9] Each of six cycles consisted of water soaking for 5 days followed by ovendrying at 105°C for 2 days. Thickness swelling was calculated as a percentage of the original thickness (o.d. board). After each cycle, the specimens were reweighed. Weight losses are reported relative to the weight of the o.d. board in the preceding cycle as well as overall weight loss determined by the original and final o.d. weights. Weight gain due to water absorption was determined after each soaking. The specimens were removed from the water, wiped of excess water, and weighed. The percent water absorption was based on the original weight of the o.d. board.

Humidity Tests

Ovendried specimens were placed in constant humidity rooms at 30, 65, and 90% relative humidity (RH) and 27°C. After 21 days the specimens were weighed, and the equilibrium moisture content (EMC) was determined. Previous work showed that EMC for control and acetylated boards was reached at 14 days.[5]

Separate specimens were placed in a humidity room at 90% RH and 27°C. Thickness and weight were determined after 21 days. The specimens were then placed in a humidity room at 30% RH and

27°C for another 21 days, whereafter thickness and weight were determined. This procedure was repeated for a total of six cycles of 90% to 30% RH. The specimens were then ovendried and thickness and weight determined. Changes in thickness were calculated as a percentage of the original thickness (o.d. board), and the weights were used to determine the EMC after each cycle.

RESULTS AND DISCUSSION

Because of the limited number of specimens per individual test or treatment level, no statistical analysis of the data was possible. The results presented here should be considered as indicative of trends and a larger, statistically valid experiment must be done to confirm them.

Reactivity

WPG as a function of time for the acetylation of flakes with vapor and refluxing liquid acetic anhydride, respectively, is shown in Table 1. For southern pine, very little additional WPG was found in the refluxing liquid after 5 h. The vapor reaction was much slower, and a WPG of over 17 was not achieved until after 24 h. The increase in acetyl content was about the same as the WPG, with the exception of high levels of acetylation in the vapor phase. Pressurizing the liquid system did not result in increased rate of acetylation, which means that the flakes were thin enough to allow penetration of reacting chemical without an increased pressure gradient. The lower reaction rate in the vapor phase treatment was probably due to low concentration of acetic anhydride inside the flakes. Data for Douglas-fir are not given in Table 1 as they were similar to that of southern pine, except the reaction in refluxing liquid was somewhat slower.

For aspen the initial reaction rate in both vapor and refluxing liquid was somewhat higher than for southern pine (Table 1) and Douglas-fir, but the maximum WPG was lower. A WPG of about 15 was obtained in the liquid phase reaction in 4 h and

TABLE 1
Weight Gain Due to Acetylation and Acetyl Content for Southern Pine and Aspen Flakes as a Function of Reaction Time

Time	Liquid phase acetylation		Vapor phase acetylation	
	WPG[1]	Acetyl content	WPG	Acetyl content
h	%		%	
		SOUTHERN PINE		
0	0	1.4	0	1.38
0.5	5.1	8.3	--	--
1	9.8	11.7	--	--
2	11.9	12.3	--	--
3	15.8	17.1	--	--
4	18.2	19.2	--	--
5	19.0	20.1	5.2	6.6
6	20.0	20.3	--	--
7	--	--	7.1	8.3
8	20.7	21.8	--	--
10	22.9	22.0	--	--
12	21.0	22.7	9.4	9.3
20	--	--	11.1	11.8
24	23.0	24.5	17.7	14.3
48	24.5	25.3	23.2	18.5
		ASPEN		
0	0	4.1	0	4.1
0.5	9.3	14.8	--	--
1	--	--	--	--
2	11.9	17.0	--	--
3	12.9	17.9	7.1	11.6
4	14.7	19.4	--	--
5	13.0	19.5	7.7	11.9
6	--	--	--	--
7	13.7	20.6	--	--
8	14.0	20.7	9.7	12.3
10	13.8	21.0	--	--
12	15.4	21.5	12.8	14.5
20	--	--	--	--
24	14.5	21.6	15.7	16.4
48	17.5	24.0	20.0	18.5

[1]Weight percent gain.

in 24 h in the vapor phase reaction. In the liquid phase reaction the increase in acetyl content was higher than the WPG and the acetyl content continued to increase even when WPG stayed constant. Obviously some wood components were dissolved in the mixture of acetic anhydride, acetic acid, and xylene. In the vapor phase reaction the WPG was higher than the acetyl content, which indicates that leachable, highly acetylated components were removed during the vacuum period.

Liquid Water Tests

Water leaching of acetylated flakes for 14 days resulted in a very low weight loss (Table 2). The acetyl content of the flakes at the highest WPG levels increased slightly during the leaching for all three species. The acetyl content of the flakes at the lower WPG levels decreased slightly during the leaching. This shows that at lower WPG's soluble acetylated components were leached. At higher WPG levels the leachable components had a lower acetyl content than the remaining wood.

Swelling of southern pine flakeboards in liquid water is shown in Figure 1. The initial rate of swelling was very high for the control and for the boards made from flakes acetylated in the vapor phase to WPG's of 5 to 11. The board made from flakes with 5.2 WPG actually swelled faster than the control during the first hour. The board made from liquid phase reacted flakes with a WPG of 12 swelled less than did the board made from vapor phase reacted flakes of a comparable treatment level. The optimal treatment was the liquid phase acetylation to about 20 WPG. Vapor phase reaction to about the same WPG was not as effective as the liquid phase reaction.

Similar results were obtained for Douglas-fir and aspen. The initial rate of swelling of the aspen control board was somewhat lower than that of both southern pine and Douglas-fir, but the aspen control swelled to a greater extent in 5 days. Acetylation of Douglas-fir and aspen flakes in the liquid phase

TABLE 2
Acetyl Content of Acetylated Southern Pine, Douglas-fir, and Aspen Flakes Before and After Water Leaching for 14 Days[1]

Treatment	WPG[2]	Acetyl content		Weight loss
		Before leaching	After leaching	
		- - - - - - - - % - - - - - - - -		
		SOUTHERN PINE		
None	0	1.4	1.5	1.8
Vapor	5.2	6.6	5.8	.9
Vapor	11.1	11.8	8.8	1.4
Vapor	17.7	14.3	12.8	1.2
Vapor	23.2	18.5	19.3	1.3
Refluxing liquid	23.8	24.1	24.4	1.4
Pressurized liquid	13.3	13.9	13.8	2.1
Pressurized liquid	25.1	23.1	24.7	.6
		DOUGLAS-FIR		
None	0	.5	.6	2.7
Vapor	16.3	15.2	14.5	1.0
Refluxing liquid	18.1	19.7	20.4	1.3
		ASPEN		
None	0	3.8	3.8	.8
Vapor	20.0	18.5	18.9	.9
Refluxing liquid	17.8	21.9	23.0	1.1

[1]The water was removed each day and fresh, distilled water was added.
[2]Weight percent gain.

reduced both the rate and extent of board swelling more effectively than did acetylation to the same WPG in the vapor phase.

Thickness changes in the repeated water soaking tests for southern pine flakeboards are shown in Figure 2. The board made from vapor phase acetylated flakes with a WPG of 5.2 swelled more than the control did. Vapor phase acetylation to 11.1 WPG

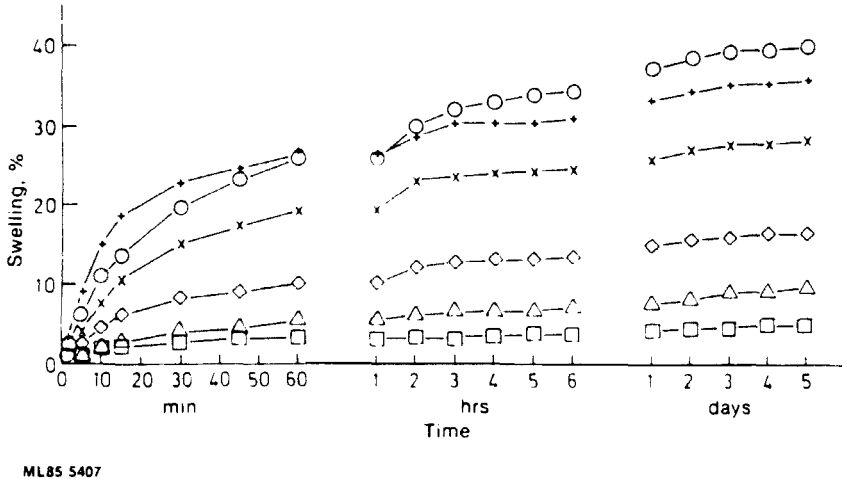

FIGURE 1 Rate of liquid water swelling of southern pine flakeboard made from acetylated flakes. O Control, + Vapor 5.2 WPG, X Vapor 11.1 WPG, Δ Vapor 23.2 WPG, ◇ Liquid 12.4 WPG, □ Liquid 22.6 WPG.

resulted in a board that swelled about the same as the control. Acetylation at WPG's below 10 caused more swelling to occur than in controls, and this trend was not reversed until a WPG of at least 12 was achieved. The board made from vapor phase acetylated flakes at the highest WPG swelled much more than did the board made from liquid phase acetylated flakes at the same WPG. There was no difference, however, between a board made from flakes treated in refluxing liquid acetic anhydride/xylene and one made from flakes treated in the pressurized liquid acetic anhydride/xylene system.

Similar results were obtained for Douglas-fir and aspen boards. The extent of swelling was not as great for Douglas-fir controls as it was for both southern pine and aspen controls. For all three species, liquid phase acetylation to WPG's above about 18 resulted in boards with about 10% thickness swelling after six o.d./wet cycles.

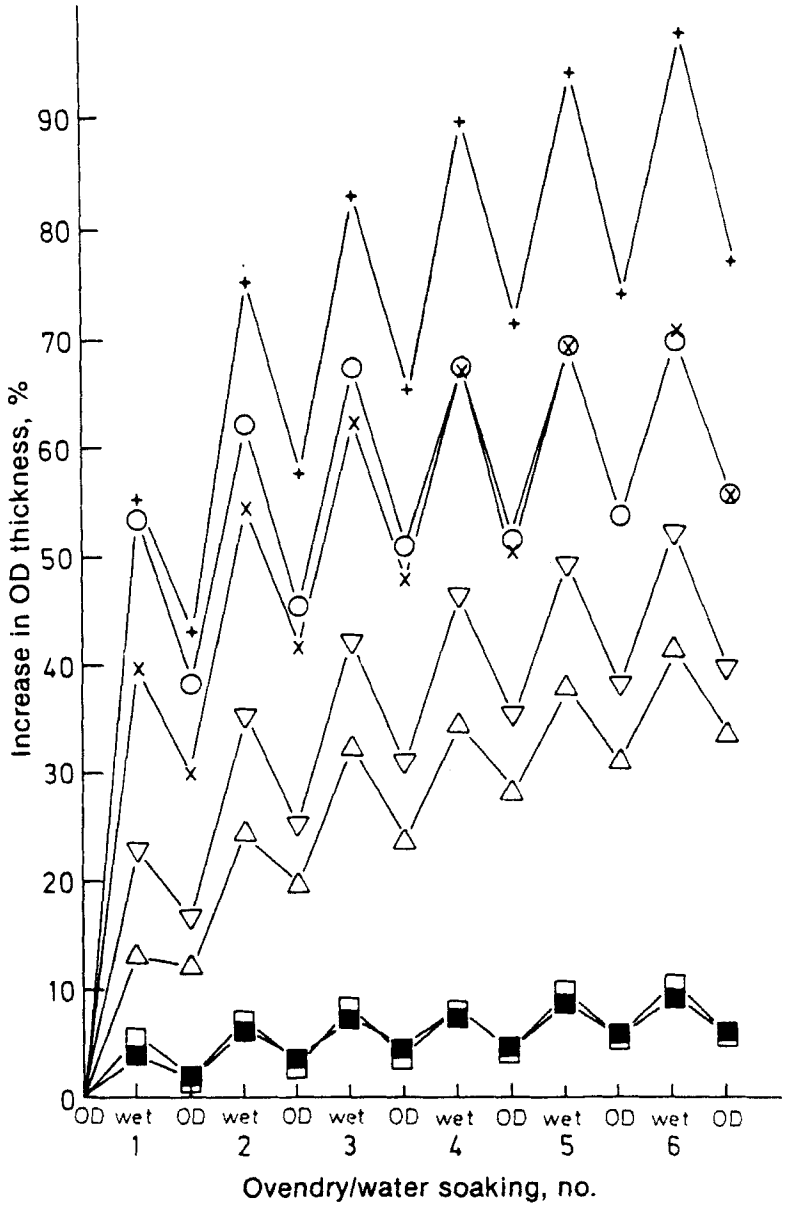

FIGURE 2 Change in ovendry thickness in liquid water of southern pine flakeboard made from acetylated flakes. O Control, + Vapor 5.2 WPG, X Vapor 11.1 WPG, ∇ Vapor 17.7 WPG, Δ Vapor 23.2 WPG, □ Liquid reflux 22.6 WPG, ■ Liquid pressure 24.4 WPG.

Gain in weight due to liquid water absorption for southern pine is shown in Figure 3. After six o.d./wet cycles, the board made from southern pine flakes acetylated to 5.2 WPG sorbed more water than the control did. As in other tests, boards made from vapor phase reacted flakes were not as effective as liquid phase reacted boards to the same WPG. The boards made from liquid phase acetylated flakes absorbed about 50% of the amount absorbed by the controls of the same species. Similar results were found for Douglas-fir and aspen.

Weight loss determined after each water soaking cycle is shown in Table 3. The largest weight loss occurred, for all species and treatments, after the first soaking cycle. In all cases the control boards lost more weight than any of the boards made from acetylated flakes. The weight loss after the third soaking cycle was negligible and probably within experimental error. The total weight loss of the boards after six o.d./wet cycles (a total of 30 d water soaking) was slightly larger than the weight the flakes alone lost in soaking for 14 days (Table 2). This means that there is not a significant loss of adhesive during the water soaking tests.

Humidity Tests

Table 4 shows that for all three species the EMC at each RH decreased as the acetylation level increased. The lowest EMC was obtained for the boards made from flakes acetylated to high WPG's in the liquid phase reaction system. The largest reduction in board EMC, about 50% at all three relative humidities, was obtained for the southern pine boards made from liquid phase acetylated flakes at the highest WPG.

Figure 4 shows the thickness changes at 30% and 90% RH of boards made from southern pine control and acetylated flakes. As in the repeated water soaking test, the boards made from vapor phase acetylated southern pine flakes at low WPG's swelled more than controls. The extent of swelling decreased as WPG increased for all three species. The most dramatic swelling

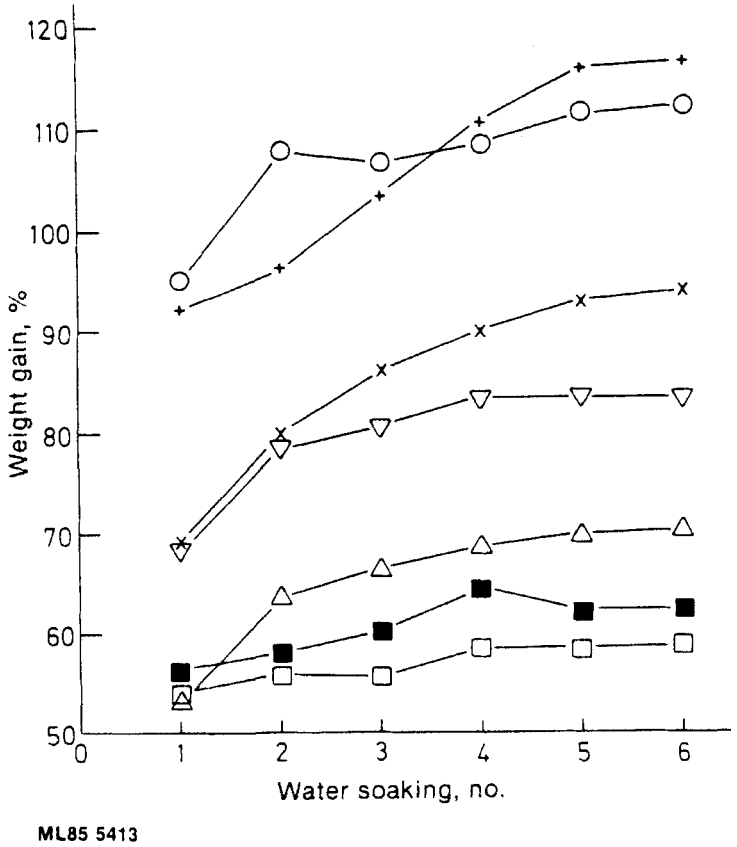

FIGURE 3 Weight gain due to liquid water pickup of southern pine flakeboard made from acetylated flakes. O Control, + Vapor 5.2 WPG, X Vapor 11.1 WPG, ▽ Vapor 17.7 WPG, Δ Vapor 23.2 WPG, □ Liquid reflux 22.6 WPG, ■ Liquid pressure 24.4 WPG.

reduction in humid air was found for southern pine and aspen boards made from liquid phase acetylated flakes at 17 to 22 WPG, while the effect for Douglas-fir was not as great since that control did not swell as much.

The water soaking and the humidity test results show that irreversible swelling was evident in the early cycles. There was an increase in permanent swelling, however, even during later

TABLE 3
Weight Loss After Each Water Soaking and Ovendrying Cycle of Flakeboards Made from Acetylated Southern Pine, Douglas-fir, and Aspen Flakes

Treatment	WPG[1]	Weight loss in cycle						Total weight loss[2]
		1	2	3	4	5	6	
		- - - - - - - - - % - - - - - - - - -						
SOUTHERN PINE								
None	0	2.0	0.5	0.3	0.1	0.3	<0.1	3.1
Vapor	5.2	1.8	.6	.3	.2	.3	<.1	3.1
Vapor	11.1	1.5	.5	.3	.3	.1	<.1	2.6
Vapor	17.7	1.3	.4	.2	.2	>.1	.1	2.2
Vapor	23.2	1.2	.7	>.1	.1	>.1	<.1	2.2
Refluxing liquid	22.6	1.2	.3	.2	.1	.1	<.1	1.7
Pressurized liquid	13.3	1.5	.5	.3	.1	.2	<.1	2.5
Pressurized liquid	24.4	1.3	.3	.1	.1	>.1	.1	1.9
DOUGLAS-FIR								
None	0	1.6	.6	.5	.1	.2	>.1	3.0
Vapor	16.3	.8	.3	.5	.3	.3	.1	2.2
Refluxing liquid	18.1	1.0	.4	.3	.2	.2	>.1	3.0
ASPEN								
None	0	1.6	.7	.3	.2	.1	>.1	3.0
Vapor	20.6	.8	.3	.4	.3	.2	.2	2.0
Refluxing liquid	17.8	.9	.4	.2	.2	.2	>.1	1.9

[1]Weight percent gain.
[2]Based on original and final ovendried weights.

cycles which was more prominent for boards at low WPG's. This was probably partly due to adhesive and wood failures resulting from the harsh test conditions.

SUMMARY AND CONCLUSIONS

Both liquid acetic anhydride/xylene and acetic anhydride vapor alone acetylate southern pine, Douglas-fir, and aspen flakes. Flakeboards made from the three species and from both

TABLE 4
Equilibrium Moisture Content (EMC) of Flakeboards Made from Acetylated Southern Pine, Douglas-fir, and Aspen Flakes

Treatment	WPG[1]	EMC at 30% relative humidity	EMC at 65% relative humidity	EMC at 90% relative humidity
		SOUTHERN PINE		
None	0	6.6	10.4	22.4
Vapor	5.2	5.8	9.3	17.3
Vapor	7.9	5.3	8.8	16.8
Vapor	11.1	4.7	8.1	15.6
Vapor	17.7	3.6	6.9	14.1
Vapor	19.1	3.5	6.6	13.9
Vapor	23.2	2.9	5.9	13.2
Liquid	13.3	3.4	6.9	14.5
Liquid	24.4	2.0	5.2	11.9
		DOUGLAS-FIR		
None	0	6.5	9.4	17.7
Vapor	16.3	3.7	6.8	13.7
Liquid	18.1	2.6	6.0	13.3
		ASPEN		
None	0	5.8	8.8	18.4
Vapor	20.0	3.0	6.2	14.5
Liquid	17.4	2.1	5.5	13.3

[1]Weight percent gain.

types of acetylated flakes showed a greatly reduced rate and extent of swelling due to liquid water sorption as compared to control boards. Similar results were obtained in swelling tests done in water vapor. Liquid phase acetylation of flakes was more effective in reducing board swelling in both liquid and water vapor tests than was the vapor phase acetylated flakes. Acetylation by both procedures improved board properties for all three species,

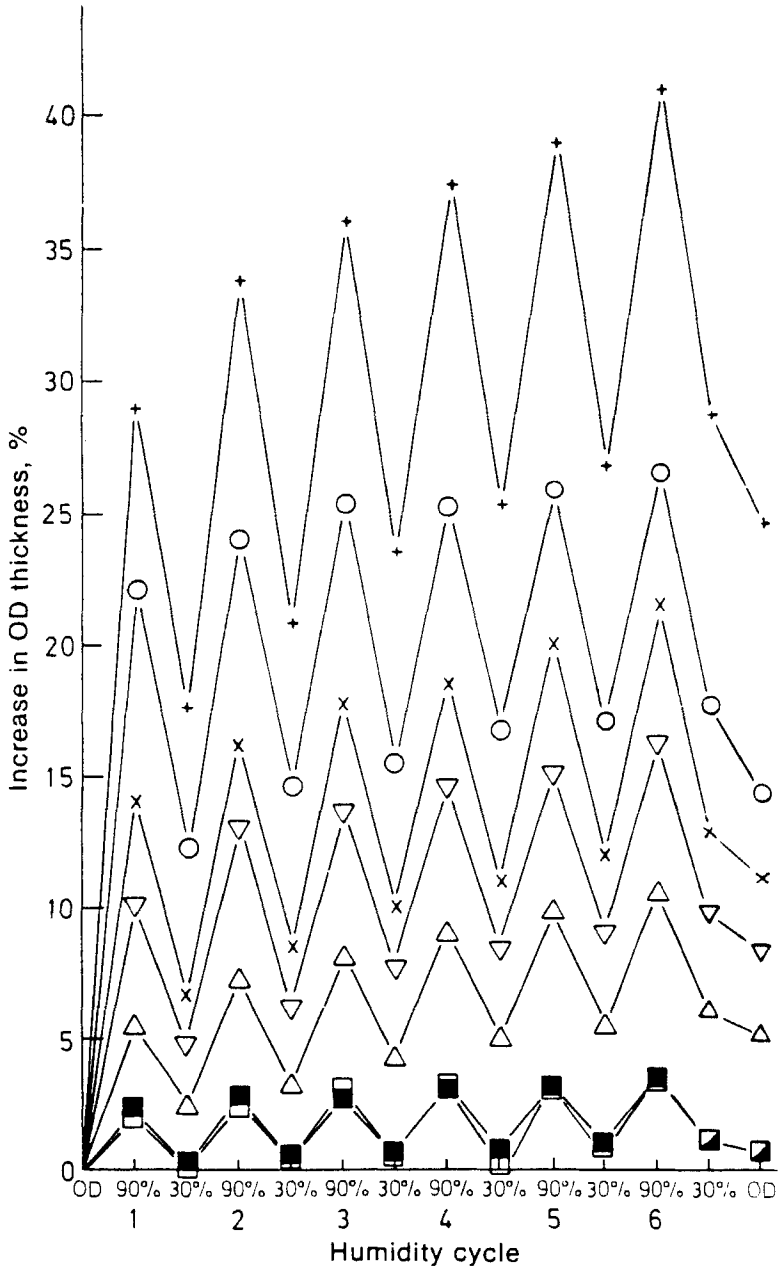

FIGURE 4 Change in ovendry thickness at 30% and 90% relative humidity of southern pine flakeboard made from acetylated flakes. O Control, + Vapor 5.2 WPG, X Vapor 11.1 WPG, ∇ Vapor 17.7 WPG, Δ Vapor 23.2 WPG, □ Liquid reflux 22.6 WPG, ■ Liquid pressure 24.4 WPG.

southern pine, Douglas-fir, and aspen, but the effect was greatest for southern pine.

Boards made from flakes acetylated to low levels by vapor phase acetylation swelled faster and to a greater extent than control boards.

The vapor phase acetylation procedure was much slower than the liquid phase reaction system. The results showed, however, that the xylene cosolvent is not needed in the reaction system. Increasing the concentration of uncatalyzed acetic anhydride in the flakes without cosolvent should lead to a much faster acetylation system with greatly reduced chemical recovery problems. This is presently under further study.

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