

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

### Flakeboards Made From Aspen and Southern Pine Wood Flakes Reacted with Gaseous Ketene

Roger M. Rowell<sup>a</sup>; Richard H. S. Wang<sup>b</sup>; John A. Hyatt<sup>b</sup>

<sup>a</sup> Forest Products Laboratory, Forest Service U.S. Department of Agriculture, Madison, WI <sup>b</sup> Research Laboratories, Eastman Chemicals Division, Eastman Kodak Company, Kingsport, TN

**To cite this Article** Rowell, Roger M. , Wang, Richard H. S. and Hyatt, John A.(1986) 'Flakeboards Made From Aspen and Southern Pine Wood Flakes Reacted with Gaseous Ketene', *Journal of Wood Chemistry and Technology*, 6: 3, 449 – 471

**To link to this Article:** DOI: 10.1080/02773818608085237

**URL:** <http://dx.doi.org/10.1080/02773818608085237>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

FLAKEBOARDS MADE FROM ASPEN AND SOUTHERN PINE  
WOOD FLAKES REACTED WITH GASEOUS KETENE

Roger M. Rowell  
Forest Products Laboratory,<sup>1</sup> Forest Service  
U.S. Department of Agriculture  
Madison, WI 53705-2398

and

Richard H.S. Wang and John A. Hyatt  
Research Laboratories, Eastman Chemicals Division  
Eastman Kodak Company  
Kingsport, TN 37662

Keywords: Ketene, chemical modification, flakeboards, dimensional stability, acetylation

ABSTRACT

Southern pine and aspen wood flakes were chemically modified by reaction at ca. 55°C with ketene in the absence of solvent. Reactions were relatively slow, with weight gains of up to 17% and 20%, respectively, obtained. Acetyl content correlated with weight gain only up to the 12% level. Water and solvent extraction of ketene-modified southern pine and aspen flakes showed very little loss in acetyl.

Flakeboards made from southern pine and aspen flakes treated with ketene showed a greatly reduced rate and extent of swelling resulting from liquid water sorption as compared to control boards. Similar results were obtained in swelling tests done in water vapor. Ketene modification had a much greater effect on improving dimensional stability properties of aspen flakeboards than on southern pine flakeboards.

## INTRODUCTION

Acetylation of wood flakes prior to flakeboard production has been shown to greatly improve dimensional stability of the resulting boards.<sup>2</sup> Various techniques of acetylation have been reviewed in earlier publications.<sup>2,3</sup> Flakeboard made from flakes acetylated with refluxing liquid acetic anhydride diluted with xylene and made into flakeboards showed a greatly reduced rate and extent of moisture uptake and reduced thickness swelling in both liquid water and water vapor tests.<sup>2,4,5</sup> Boards made from flakes acetylated with gaseous acetic anhydride also had improved the dimensional stability properties.<sup>6,7</sup>

In both of the above procedures, acetic anhydride was used as the acetylating agent. For every mole of acetylation that occurs in one of the cell wall polymers, one mole of byproduct acetic acid is generated. This acetic acid is difficult to remove completely from the flakes and also increases the cost of the process since only half of the reagent is added to the wood structure.

The use of ketene to acetylate wood has intrigued chemists for many years. Tarkow, in 1945, tried to acetylate spruce with ketene gas but achieved only a 2% to 5% weight gain.<sup>8</sup> He concluded that the limiting factor in the reaction is the inability of ketene to swell wood.

Later, however, Karlson and Shvalbe reported the acetylation of several species of wood with gaseous ketene, achieving chemical weight gains up to 25%.<sup>9,10</sup> The optimum reaction conditions found were 55° to 60°C with gaseous ketene for 6 to 8 h. The modified wood was found to have improved dimensional stability and was resistant to attack by the wood-destroying fungus Coniophora cerebella.

The purpose of the research reported here was to investigate the modification of southern pine and aspen flakes with gaseous ketene. We anticipated that the small dimensions of the flakes used would result in faster and more complete penetration by

ketene. This would shorten the reaction time needed to achieve the weight gain necessary for improving the dimensional stability of flakeboards made from these modified flakes. Thus, the reaction of wood with ketene would be faster and easier than reaction with liquid acetylating agents.

## EXPERIMENTAL

### Wood Flakes

Southern pine and aspen flakes were used in this study. Different techniques were used for generating flakes; however, there should be no difference between ring- and disk-cut flakes from a chemical reactivity standpoint. All flakes were retained on a 0.6-cm screen. They were oven-dried (o.d.) for 24 hours at 105°C before use.

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

Southern pine: 0.05 x 6.4 x random.

Aspen: 0.06 x 3.8 x random.

### Acetylation with Ketene

#### Ketene Preparation

The method used was essentially that of Andreades and Carlson.<sup>11</sup> A vertical 3- x 40-cm quartz-chip packed quartz tube was electrically heated to 550-570°C (controlled by an Omega controller using a thermocouple placed in the center of the pyrolysis tube) and subjected to a flow of 3-5 ml/min of dry nitrogen. Pure diketene (50-60 g) was added dropwise at 0.5 ml/min to the top of the tube and the product ketene was collected in a drying tube vented two-neck flask attached to the exit end of the pyrolysis tube and cooled in a dry ice-acetone bath. Quantities of 20-30 g of ketene were thus produced in ~2 h; after completion of the pyrolysis the cooled receiving flask was closed with stoppers and stored in a -78°C dry ice-acetone bath until needed (usually <1 h).

## Wood Acetylation

The reaction vessel used for all acetylations was a 3-L, wide-mouthed Pyrex resin flask equipped with a heating mantle, thermometer, stopcock-controlled gas inlet and outlet tubes (the inlet was at the top of the flask; the outlet was placed at the bottom), and a manometer. The gas outlet was attached to a vacuum pump via KOH pellet and cold traps. The reactor was charged with a weighed quantity of oven-dried wood flakes (usually ~50 or 100 g).

### A. Batchwise Addition of Ketene

The reactor was heated to 50-60°C under nitrogen flow; the gas inlet was then closed and the reactor evacuated to 1-5 mm Hg for 30 min. The vacuum stopcock was closed, the gas inlet connected to a flask of ketene, and the inlet stopcock carefully opened. The -70°C cooling bath on the ketene flask was slowly removed and ketene was allowed to fill the system to 1 atm. The reaction flask was then sealed by closing the inlet stopcock and the ketene supply returned to -78°C. After 1 h at 50-60°C in the ketene atmosphere, the reactor was again evacuated to 2-5 mm Hg for 10 min and then refilled with ketene. This cycle was repeated up to four to five times; after the final reaction stage, the system was purged with N<sub>2</sub> for ~2 h and the acetylated wood stored in a 110°C oven overnight. The product was then cooled in a dessicator, weighed, and the weight percent gain (WPG) recorded.

The WPG was calculated based on the original flake o.d. weight before reaction. In general, WPG values of 5-7% were obtained for ~100-g batches exposed to a 20- to 30-g total of ketene; 10-15% levels were achieved when the wood charge was ~50 g. Higher levels (to 20%-22%) were obtained by subjecting partially acetylated wood to a second series of evacuations and exposures to ketene.

### B. Continuous Acetylation with Ketene

The reactor was charged with wood flakes, heated to 50-60°C under N<sub>2</sub> and evacuated as above. The gas inlet tube was then con-

ected to the outlet of the ketene generator via a trap maintained at +20°C (to remove any unreacted diketene or polymeric material from the ketene/nitrogen stream), and ketene was continuously swept through the reactor vessel by the N<sub>2</sub> stream (the reactor exit tube was disconnected from the vacuum system and vented to the hood via a solid KOH scrubber). After the addition of ketene was complete, the system was nitrogen purged and the wood flakes stored at 110°C overnight before weighing as for flakes prepared using the batchwise method.

#### Leaching and Acetyl Content of Acetylated Flakes

Weighed oven-dry acetylated and unreacted flakes were leached under three conditions: (1) 14 days in distilled water at 24°C (changing water every 24 h, (2) 2 h in a Soxhlet extractor with refluxing water, or (3) 2 h in a Soxhlet extractor with refluxing toluene/ethanol (1/1, v/v). After redrying, oven-dry weight loss was determined.

Percent acetyl content was obtained by deacetylation with sodium hydroxide of ground and mixed samples and determining the acetic acid concentration by gas chromatography.

#### Flakeboard Preparation

Acetylated or control wood flakes (180 g, o.d.) were pressed into boards approximately 1.25 x 15 x 15 cm in size. Each board was made to a density of approximately 700 kg/m<sup>3</sup> 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), oven-dried, and weighed. The thickness was measured at the center point of each specimen, and subsequent measurements were taken at the same point.

### Water Swelling Rate Tests

Each test specimen was placed in a 10- x 10-cm container, 5 cm deep. The container was on a flatbed micrometer for the thickness measurements. Water was added to the container and the 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.<sup>12</sup> Each of the six cycles run consisted of water soaking for 5 days followed by oven drying 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 as overall weight loss determined by the original and final oven dry weights. Weight increase due to water absorption was determined after each soaking. The specimens were removed from the water, wiped of excess water, and weighed. The percent weight increase due to water absorption was based on the original weight of the o.d. board.

### Humidity Tests

Oven dried 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.

Separate specimens were placed in a humidity room at 30% RH and 27°C. Thickness was measured after 21 days. The specimens were then placed in a humidity room at 90% RH and 27°C for another 21 days, whereafter thickness was determined. This procedure was repeated for a total of four cycles of 30% to 90% RH. The speci-

mens were then oven-dried and thickness determined. Changes in thickness were calculated as a percentage of the original thickness (o.d. board).

### 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 that a larger, statistically valid experiment should confirm.

#### Reactivity

Ketene is difficult to handle in the laboratory, being both toxic and unstable relative to dimerization. It is poorly soluble in inert solvents, cannot be used under pressure (the dimerization rate merely increases), and is difficult to analyze. In view of these difficulties, we chose to modify the wood flakes by exposure to ketene vapor at atmospheric pressure until a desired weight gain value was obtained, and no attempt was made to assay the efficiency of ketene utilization in these early studies.

Oven-dried aspen and southern pine wood flakes were reacted with ketene under both static and flow conditions (see Experimental). We could detect no differences between the modified flakes (at a given weight-gain value) prepared by the two procedures; for reasons of operational convenience the batchwise method was used to prepare the modified flakes, whose properties are described below. As noted in the Experimental Section, ca. 7% weight gain was obtained on 100 to 110 g batches of wood exposed to 25-30 g of ketene over 4-5 h. In order to obtain higher WPG values, samples were resubjected to the reaction conditions on subsequent days. In this way we prepared 200 to 300 g batches of southern pine having 8.5% and 17.0% weight gain, and aspen at 12.0% and 20.0% gain.



It should be noted that the wood flake-ketene reactions were relatively slow. Although analytical problems made direct measurement of ketene consumption rates unavailable, we are confident that the flakes were exposed to an excess of ketene throughout the reaction periods. Therefore the need to use 10- to 15-h reaction times to achieve 20 WPG can be compared to the 1 to 3 h needed to achieve similar WPG values using acetic anhydride as the acetylating agent.<sup>6,7</sup> The absence of a liquid phase capable of swelling the wood may account for the rate reduction observed for the ketene reactions.

We found that southern pine reacted slightly more slowly with ketene than did aspen; furthermore, we were unable to get as high a WPG value for pine as we could with aspen. Thus a pine WPG value of 17 was not exceeded even upon very prolonged exposure to ketene, whereas aspen could be forced to 23-25% levels under the same conditions.

Our reactions were carried out at 50-60°C. While the rate of acetylation clearly increased with temperature, we observed a very marked degree of discoloration of the flakes exposed to ketene at temperatures much above 65°C. Since flakes acetylated with acetic anhydride show very little color change, we presume that this darkening arises from nonacetylation side reactions of the ketene (vide infra). Reactions at 23°C gave little darkening, but the rate of weight gain was very slow. The choice of ca. 55°C for our preparations was therefore a compromise between unacceptably low reaction rates and high discoloration levels.

#### Infrared Spectroscopic Analysis

Fourier transform infrared (FTIR) analysis was used to establish the presence of acetate groups in the modified flakes. Figures 1 and 2 show FTIR spectra of aspen flakes acetylated with acetic anhydride and ketene, respectively. The spectra are virtually superimposable and suggest that the anhydride and ketene do essentially the same chemistry at these acetylation levels. The strong absorption at 5750 nm is characteristic of acetate groups in wood.

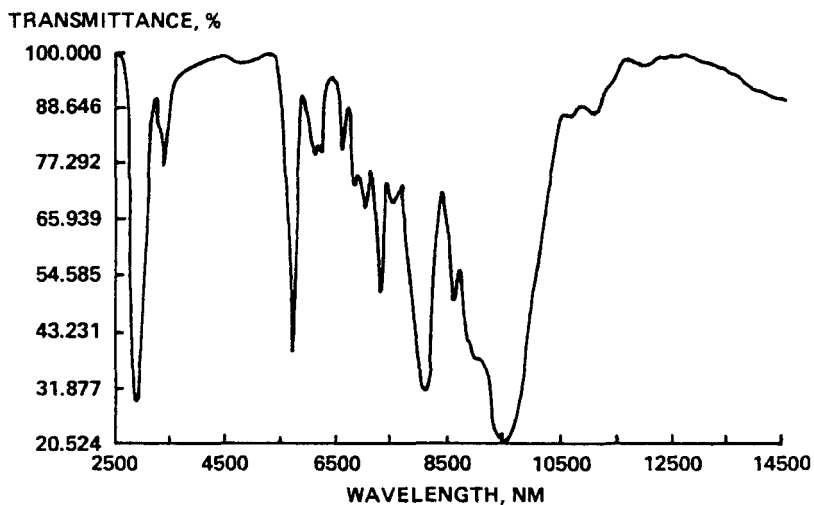


FIGURE 1.--Infrared spectrum of aspen modified to 15.7 WPG with acetic anhydride vapor. ML85 5548

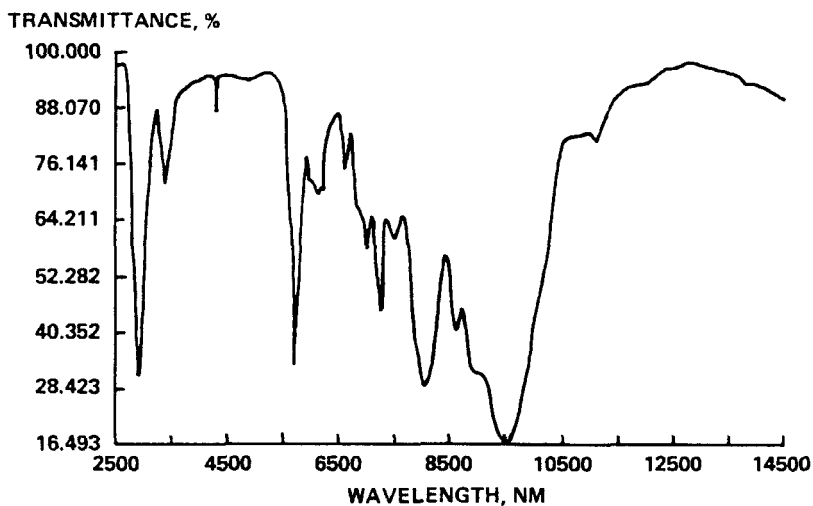


FIGURE 2.--Infrared spectrum of aspen modified to 22.8 WPG with ketene. ML85 5549

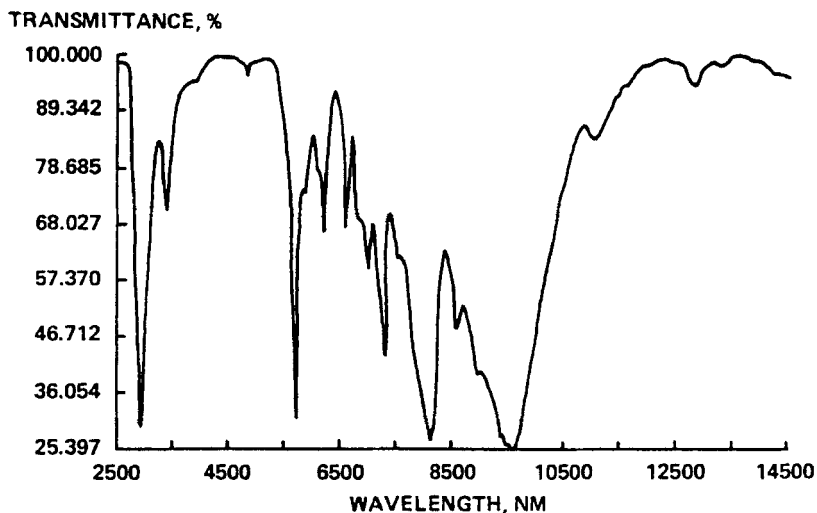


FIGURE 3.--Infrared spectrum of southern pine modified to 18.3 WPG with acetic anhydride vapor. ML85 5550

Figures 3 and 4 give FTIR spectra of southern pine after reaction with acetic anhydride and with ketene, respectively. In this case the anhydride-modified sample exhibits the expected 5750 nm acetate bond, but the ketene-modified material has a very complex group of carbonyl absorption bands. It thus appears that while the aspen-ketene reaction parallels that of aspen with acetic anhydride, southern pine undergoes reactions leading to product structures quite different from those obtained with anhydride. We considered the possibility that the ketene might be dimerizing to diketene before reacting with the wood flakes; such a process would lead to acetoacetylated, rather than acetylated, wood. This mechanism would account for the low percent acetyl analyses of samples at high WPG (see below). This possibility was tested by reacting both aspen and southern pine with diketene; the resulting acetoacetylated flakes were found to have FTIR spectra quite different from those of the ketene-modified flakes, and this pathway

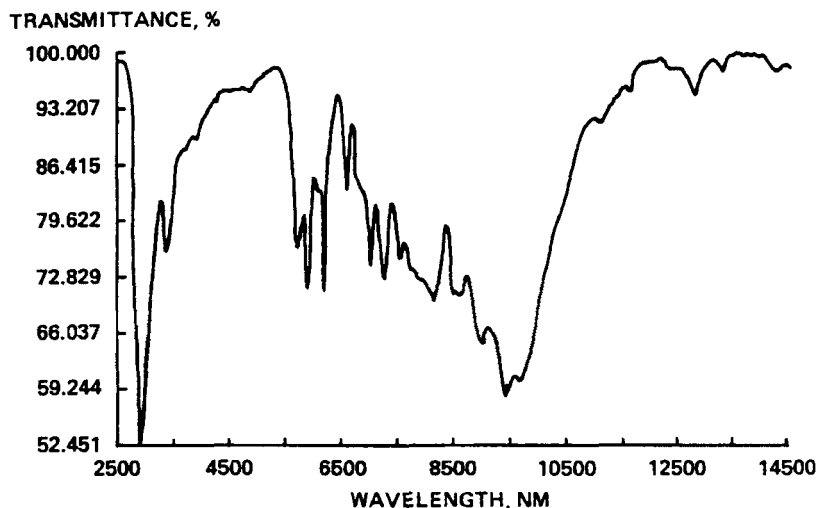
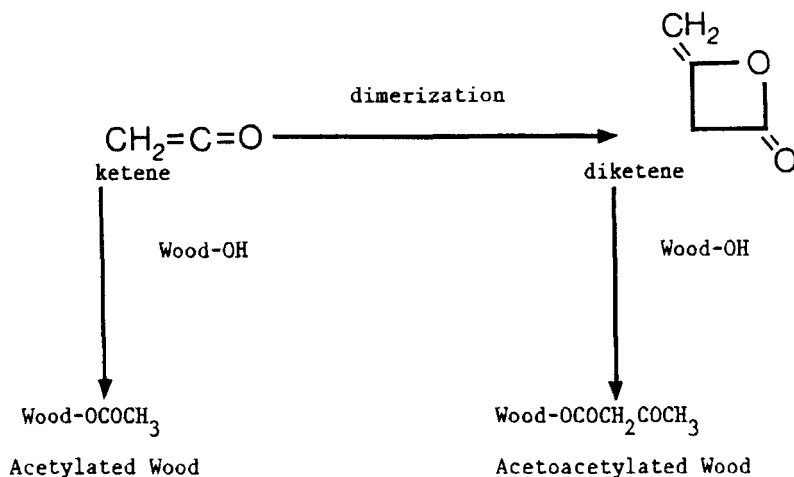


FIGURE 4.--Infrared spectrum of southern pine modified to 19.2 WPG with ketene. ML85 5551

was therefore judged unimportant under our reaction conditions. The preparation, characterization, and properties of acetoacetylated wood flakes will be reported elsewhere.



### Acetyl Analysis

The acetyl content of ketene-reacted flakes was determined before and after extraction under various conditions (Table 1). Southern pine flakes at 8.5 WPG and aspen flakes at 12.0 WPG gave an acetyl content close to the expected value based on weight gain. Both sets of flakes modified at the highest levels (southern pine of 17.0 WPG and aspen at 20.0) showed an acetyl content far below the expected value based on weight gain.

Leaching treated wood flakes in water at 24°C for 14 days or refluxing them for 2 h in either water or toluene/ethanol (2/1, v/v) showed only small losses in acetyl content. This shows that the weight gain is due to a bonded chemical and not due to the addition of a ketene homopolymer which is leachable under these conditions.

We are presently unable to propose exact chemical structures for the moieties responsible for weight gain beyond the 12% level attributable to acetylation. The most reasonable explanation is that the ketene undergoes polymerization reactions which lead to tightly bound organic material near the wood surface. The unusual FTIR spectra and surface darkening of the southern pine flakes support this view, and further studies, including solid-state  $^{13}\text{C}$  NMR spectroscopy, are being directed toward clarifying this point.

### Liquid Water Tests

The rate of swelling due to liquid water of southern pine flakeboards is shown in Figure 5. Both boards made from ketene-modified flakes show a reduced rate of swelling, with the 17 WPG specimen showing the slowest rate. Much more dramatic effects on the rate of swelling can be seen in ketene-modified aspen flakeboards (Fig. 6). In this case the control sample swelled many times faster than modified boards, and there was not as much difference in swelling rate of the two levels of chemical loadings.

Thickness changes in the repeated water-soaking tests for southern pine flakeboards are shown in Figure 7. There is little

TABLE 1  
 Acetyl Content of Ketene-Modified Southern Pine and Aspen Flakes  
 After Leaching in Various Solvents

Sample	Weight percent gain	Acetyl before leaching	Leaching in:					
			Water 14 days 24°C		Water reflux 2 h		Toluene/ethanol 2/1, v/v 2 h	
			Weight loss	Acetyl	Weight loss	Acetyl	Weight loss	Acetyl
----- % -----								
Southern pine								
Control	0	1.4	1.1	1.3	1.3	1.4	2.2	1.3
Ketene modified	8.5	6.7	2.1	5.7	2.0	5.6	1.8	5.6
Ketene modified	17.0	10.3	2.3	9.4	1.8	9.5	4.4	8.5
Aspen								
Control	0	3.9	0	3.9	1.2	3.8	2.6	3.8
Ketene modified	12.0	11.3	2.1	11.3	1.6	10.2	3.5	10.9
Ketene modified	20.0	12.4	2.6	12.9	5.1	11.7	7.5	12.5

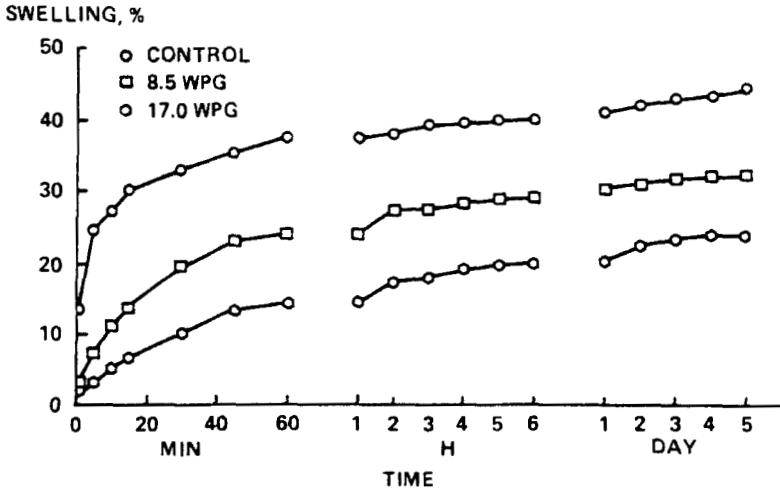


FIGURE 5.--Rate of swelling in liquid water of southern pine flakeboard made from ketene-modified flakes. ML85 5552

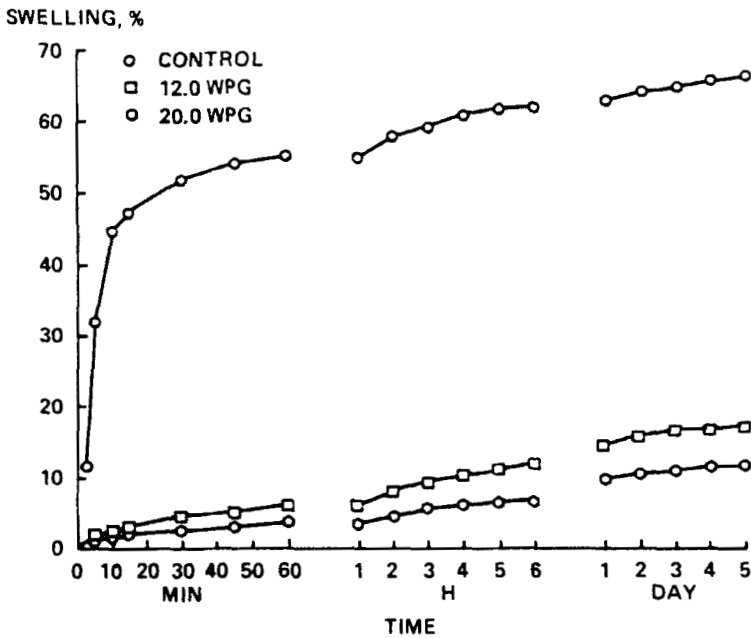


FIGURE 6.--Rate of swelling in liquid water of aspen flakeboard made from ketene-modified flakes. ML85 5553

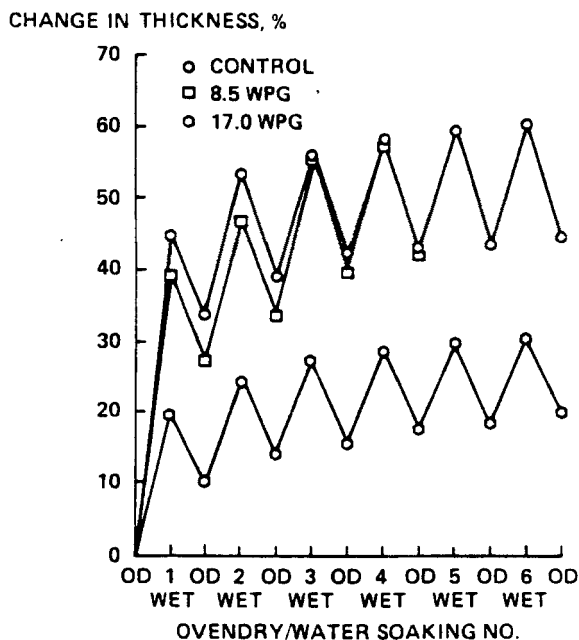


FIGURE 7.--Change in thickness during six oven-dry/liquid water sorption cycles of southern pine flakeboard made from ketene-modified flakes. ML85 5554

difference between the control and the flakeboard made from ketene-modified flakes at 8.5 WPG. The 8.5-WPG board broke apart after four swelling cycles and was taken out of test. The board at 17.0 WPG reduced thickness swelling by 50% as compared to the control board.

In the case of aspen flakeboards (Fig. 8), the control boards swelled over 75% in thickness during the cycle tests, while the board made from ketene-modified flakes at 20.0 WPG swelled only 15% in thickness. While the ketene-modified southern pine board continued to swell after each liquid water cycle, modified aspen flakeboards showed very little change in thickness swelling after four cycles.



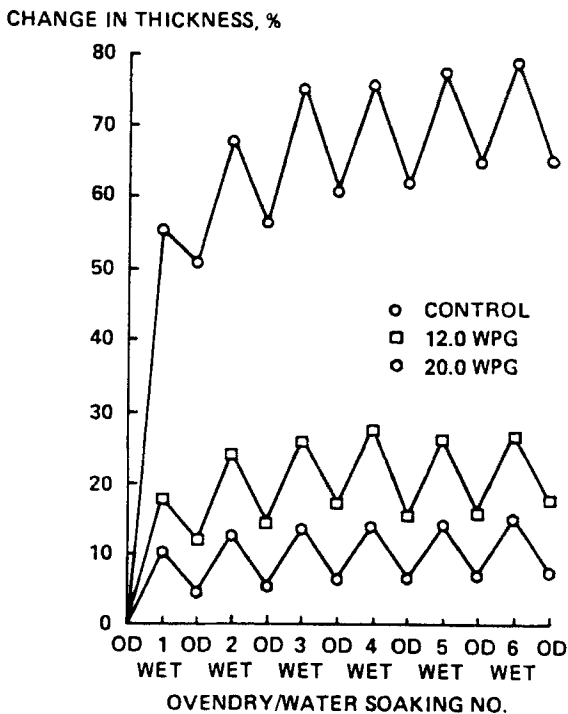


FIGURE 8.--Change in thickness during six oven-dry/liquid water sorption cycles of aspen flakeboard made from ketene-modified flakes. ML85 5555

Gain in weight due to liquid water sorption is shown in Figures 9 and 10. Southern pine control boards gained about 120% in weight during the first four wettings, then decreased slightly. The ketene-modified board at 8.5 WPG gained considerable weight in the water cycle in which it failed. Swelling forces were great enough to break the adhesive bonds holding the board together. The aspen control board gained over 130% in weight during the six cycles of wetting. Ketene-modified southern pine flakeboard at 17.0 WPG and both ketene-modified aspen boards gained 75% to 80% in weight and remained about constant during the entire test.

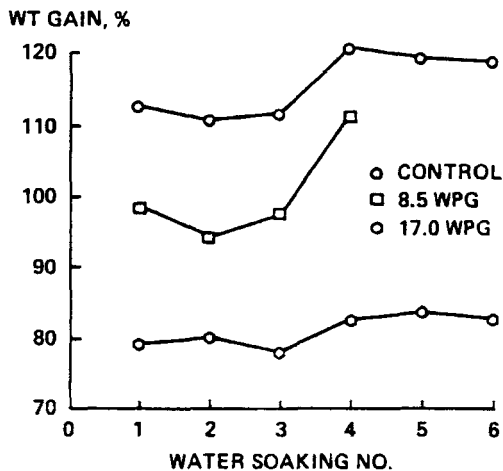


FIGURE 9.--Weight gain during six oventdry/liquid water sorption cycles of southern pine flakeboard made from ketene-modified flakes. ML85 5556

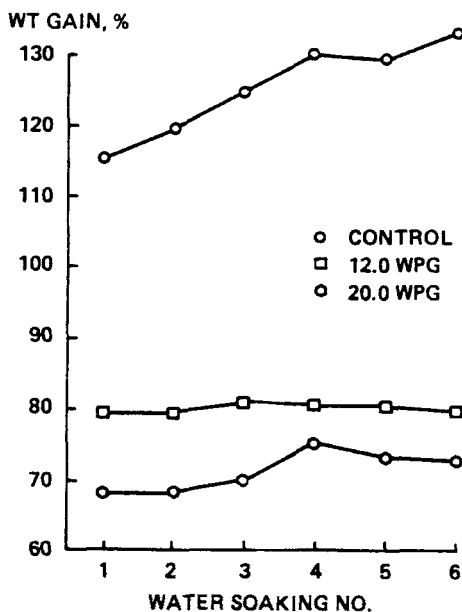


FIGURE 10.--Weight gain during six oventdry/liquid water sorption cycles of aspen flakeboard made from ketene-modified flakes. ML85 5557

TABLE 2

Ovendry Weight Loss After Water Soaking of Flakeboards Made From Ketene-Modified Flakes

Sample	Weight percent gain	Weight loss after two weeks continuous water soaking (25°C)	Six cycle water soaking/ovendried tests
Southern pine			
Control	0	2.3	3.7
Ketene modified	8.5	2.7	<sup>a</sup> 2.8
Ketene modified	17.0	2.5	2.9
Aspen			
Control	0	2.8	3.2
Ketene modified	12.0	2.6	3.1
Ketene modified	20.0	2.9	3.2

<sup>a</sup>After four cycles.

Ovendry weight loss determined after the six cycles in the liquid water test as well as weight loss in a 2-week water-soaking test is shown in Table 2. The total weight loss in the boards after six o.d./wet cycles (a total of 30 days' water soaking) was slightly larger than the weight the boards lost in two 2-week water-soaking tests on flakes (Table 1) and boards (Table 2). The losses are about the same for ketene-modified flakes and boards (between 2% and 3%), while the control boards lost two to three times more weight than control flakes.

#### Humidity Tests

Table 3 shows that for both species, the EMC at each RH decreases as the level of ketene modification increased.

Figures 11 and 12 show the thickness changes at 30% and 90% RH of boards made from control and ketene-modified flakes. As in the repeated water-soaking tests, the greatest effect is seen in ketene-modified aspen flakeboards as compared to aspen control boards. In this case the control board swells over 32%, while the

TABLE 3  
 Equilibrium Moisture Content of Southern Pine and Aspen Flakeboards  
 Made From Ketene-Modified Flakes (27°C)

Sample	Weight percent gain	Equilibrium moisture content (EMC) at:				
		30 percent relative humidity	65 percent relative humidity	80 percent relative humidity	90 percent relative humidity	
Southern pine						
Control	0	4.5	10.3	14.5	20.1	
Ketene modified	8.5	3.7	8.7	13.0	17.4	
Ketene modified	17.0	2.8	7.3	11.0	15.1	
Aspen						
Control	0	3.8	8.6	13.2	19.0	
Ketene modified	12.0	2.7	7.0	11.1	15.8	
Ketene modified	20.0	2.6	5.9	9.5	14.1	

## CHANGE IN OD THICKNESS, %

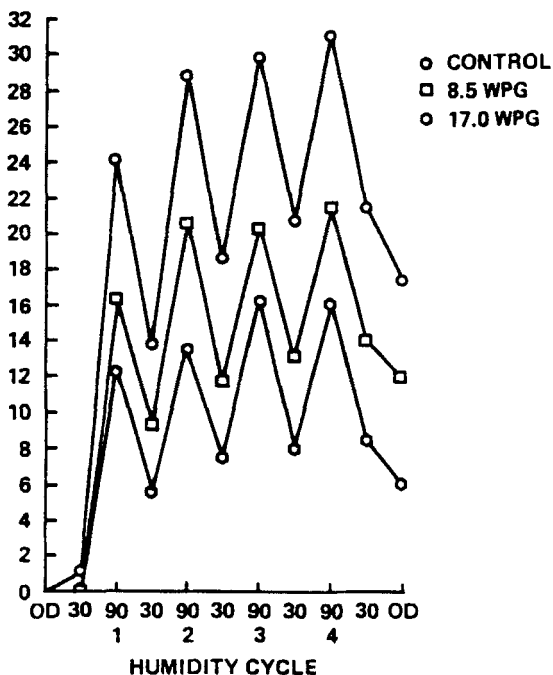


FIGURE 11.--Changes in thickness at 30% and 90% relative humidity of southern pine flakeboard made from ketene-modified flakes (27°C). OD = oven-dry. ML85 5558

ketene-modified board at 20.0-WPG swells less than 8%. The southern pine control board swells about the same as the aspen control board but the ketene-modified southern pine board at 17.0 WPG shows a swelling of 16%.

#### SUMMARY AND CONCLUSIONS

Flakeboards made from ketene-modified southern pine and aspen 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. The

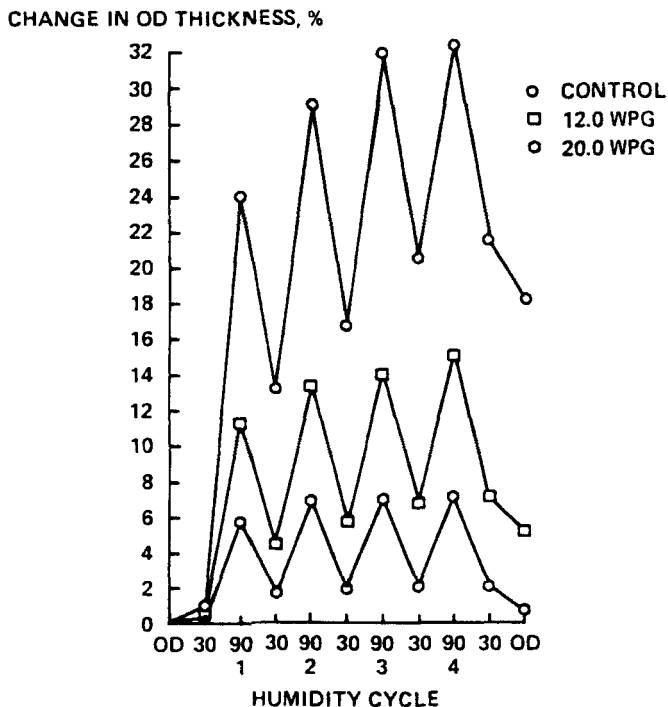


FIGURE 12.--Changes in thickness at 30% and 90% relative humidity of aspen flakeboards made from ketene-modified flakes (27°C).

OD = ovoidry. ML85 5559

ketene modification had a much greater effect on improving dimensional stability properties on aspen boards than on southern pine boards.

Ketene modification of wood is not as effective in improving dimensional stability properties as was found for acetylation with liquid acetic anhydride<sup>2,4,5</sup> or acetic anhydride vapor.<sup>6,7</sup> This may be due to the fact that weight gains above 10% did not correlate with the acetyl content. Ketene-modified boards at 20.0 WPG are not the same as boards made from liquid acetic anhydride modification at 20.0 WPG. The acetic anhydride-modified flakes at 20.0 WPG analyze for 20% acetyl while the ketene modified flakes

at 20.0 WPG showed only 12% acetyl. This discrepancy is presently under investigation.

It can be concluded from this research that it is possible to modify wood flakes with gaseous ketene. The rate of reaction is slow, and attempts to increase the rate by increasing the reaction temperature only results in increased reagent polymerization and darkening of the wood. The advantages of ketene for flake modification is that it eliminates the need for catalyst, and no by-product acetic acid is generated. The fact that ketene does not swell the wood may be the reason the reaction is slow. Future research in this area will look at the addition of a swelling agent (gas or liquid) to facilitate penetration.

#### REFERENCES

1. Maintained at Madison, WI, in cooperation with the University of Wisconsin.
2. R. M. Rowell, A.-M. Tillman, and Z. Liu, Wood Science and Technology, (in press).
3. R. M. Rowell, In The Chemistry of Solid Wood, Chap. 4, R. M. Rowell (ed.), Advances in Chemistry Series No. 207, American Chemical Society, Washington, DC, 1984.
4. J. A. Youngquist, A. Krzysik, and R. M. Rowell, Wood and Fiber Science, (in press).
5. J. A. Youngquist, A. Krzysik, and R. M. Rowell, Holz als Roh-und Werkstoff, (in press).
6. R. M. Rowell, A.-M. Tillman, and T. Simonson, Journal of Wood Chemistry and Technology, (in press).
7. R. M. Rowell, R. Simonson, and A.-M. Tillman, Svensk Papperstidning, (in press).
8. H. Tarkow, Record Report, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, 1945.
9. I. M. Karlson, and K. P. Shvalbe, Uchen. Zap. Latv. Univ., 166:89-94, 98-104, 1972.

10. I. M. Karlson, and K. P. Shvalbe, LLA Latvijas Lauksaimniecības Akadēmija, Rakst. No. 130, 10-21, 1977.
11. S. Andreades, and H. D. Carlson, Organic Syntheses, Coll. Vol. V, p. 679, J. Wiley, New York, 1973.
12. R. M. Rowell, and W. D. Ellis, Wood and Fiber 10, 104 (1978).