THERMAL REACTIONS AND INDUSTRIAL USES OF BARK

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ABSTRACT

A kinetic study indicated that the phenolic substances in Douglas-fir and red alder bark can be polymerized by high-temperature heating. Organic extractives that may be leached out by the action of water are condensed to water insolubles. Heat-treated bark is shown to be an appropriate material for the cleaning up of oil spills on water without contributing to high BOD and possible toxicity to fish. The oil absorption of bark, depending on its particle size, is two to seven times its weight.

A vacuum system was developed for hot pressing bark boards, which technique avoids blister formation caused by the evolution of gases from condensation and dehydration reactions in thick boards. Bark boards made under an appropriate time-temperature schedule have both internal bond strength and bending modulus of rupture similar to bark boards made with 4.5% phenolic resin and subsequently pressed at a moderate time-temperature schedule, precluding polymerization of the bark extractives. Hot stacking increased the internal bond strength of boards.

Dimensional stability is the most significant property of these bark boards. Properly made bark boards have a much smaller thickness swelling and linear expansion than bark boards made with 4.5% phenolic resin after soaking in water for 72 hr.

INTRODUCTION

In a previous study (Chow and Pickles 1971), the thermal softening and degradation of wood and bark were examined. Thermal softening was determined by measuring the decrease of column height of packed material under 50 psi pressure and continuous heating from 25 C to 400 C. The oven-dried wood and bark began to soften at about 200 C. An acceleration of this effect was noted at 300 C, with a maximum softening rate occurring at 380 C. In the presence of moisture, an additional softening maximum occurred at 160 C. The extent of softening increased with increased moisture content. From X-ray studies, the crystallinity of the samples was also found to decrease in the range from 200 to 250 C. The possibility of extractive and lignin polymerization at the temperatures causing softening was revealed by infrared spectroscopic analysis.

On the basis of these findings, it was postulated that the thermal softening of moistened wood and bark at temperatures below 200 C was more physical than chemical in nature and was attributed to plasticization by water. This plasticization ef-fect is believed to be important for setting pressing schedules in the manufacture of hardboard and particleboard. The thermal reaction of bark at a temperature greater than 180 C was attributed to the polymerization and partial degradation of bark components.

In the present study, it is not intended to examine moisture plasticization effects at a temperature below 180 C. A kinetic approach was taken to examine further the possibility of polymerization of bark extractive at temperatures greater than 180 C. The derived knowledge was first applied to an exploratory investigation of the potential uses of bark for oil pollution control on water. The information was also used in a preliminary study of the manufacture (on a laboratory scale) of bark board without synthetic resin that would retain its dimensional stability under water-soaking conditions.

MATERIAL AND METHOD

Effect of heating temperatures on the solubility of bark extractives

Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] and red alder [*Alnus rubra* Bong.]

barks, obtained from single trees having a bark thickness of about 2 inches and 0.5 inch respectively, were dried in a forced-draft oven for 10 hr at 105 C and then were ground to pass a 120-mesh screen. The materials were stored in a desiccator over P_2O_5.

To determine the solubility of bark extractives following different heat treatments, samples (0.5 g each) were placed in the furnace of a thermal gravimetric analyzer, one sample only in each run, and were heated over a range of maximum temperatures (room temperature to 420 C) at a rate of 16 C/min. Immediately upon removal from the furnace, samples were cooled in air with dry ice and then stored in a desiccator over P_2O_5.

Ten mg of each sample were extracted with 10 ml of distilled water at room temperature. The mixture was stirred occasionally. After 48 hr, the solution was filtered and an ultraviolet spectrum of the dissolved extractives was recorded.

Kinetics of extractive polymerization

To evaluate the kinetic energy required for extractive polymerization, 1 g each of powdered and homogenized bark samples were separately heated in a static-air oven at 200, 240, 280 and 320 C for 5 to 8 time intervals from 0 (Control) to 120 min. The higher the temperature, the shorter was the heating time. Each sample (10 mg) was extracted with 10 ml of distilled water at room temperature and left for 48 hr with occasional stirring. The ultraviolet spectra for the filtered solutions were recorded and then these data were used to calculate the rate constants for each temperature.

Oil-pollution control study

To determine the effect of Douglas-fir bark particle size on oil absorption properties, a sample of dried bark was first ground and screened into four particle sizes of 10–20, 20–35, 35–60 and smaller than 60 mesh. These fractions then were heated at a schedule derived from the results of the

aforementioned kinetic work to ensure minimum extractive solubility.

Five g of oil were poured onto the surface of continuously stirred tap water contained in a 1-liter beaker. Ten samples of bark of each mesh size, at weights ranging from 0.5 to 3.0 in 0.25 g increments, were prepared and each sample was added to the surface of the oil-water mixture contained in different beakers. The oil was instantly absorbed by the bark upon contact and the mixture formed into an aggregated body, which then was easily removed from the water by use of a spatula or a screen. The oils used were SAE 30-weight engine oil and light crude oil (Imperial Oil Ltd. B. C. 40 API).

Oil absorptivity of bark was expressed as the weight ratio between oil and bark when oil was completely absorbed by a known weight of bark.

Since previous X-ray work showed a degradation of the wood cellulose crystallinity at temperatures above 200 C (Chow and Pickles 1971), the solubility of the carbohydrates that might have BOD effect in heated bark was examined. The water-soluble substances from 5 g each of air-dried bark and bark heated to 200 and 240 C for 120 and 30 min, respectively, were extracted at room temperature for 48 hr, dried, and imbedded into KBr pellets for infrared spectral analysis.

Bark board formation

Air-dried Douglas-fir bark was obtained from a plywood plant, broken into about one-inch-square chips and dried in a forced-draft oven (air speed 450 ft/min) at 105 C for 72 hr. These chips were further ground to pass a 5-mesh screen and stored in a plastic bag.

To determine the moisture content of the ground bark, three 10-g samples were dried in the same forced-draft oven at 105 C for 10 days. Since the bark samples were ground, the moisture diffusion during drying was probably not impeded by periderm tissues. The moisture content of samples
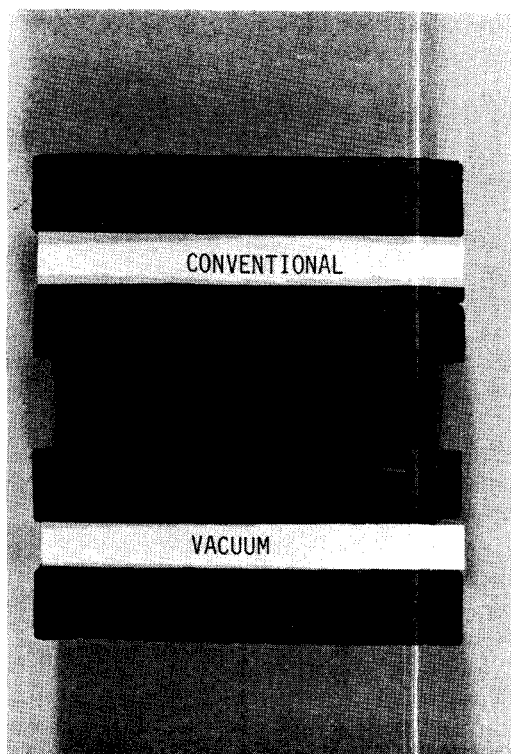
Fig. 1. Comparison of Douglas-fir bark boards made with conventional and vacuum systems.

was found to be 2.5% oven-dry weight basis. The actual moisture content might have been less than 2.5%, since some volatile bark components may have been lost through the long period of heating. A 3000-g sample of ground bark was also heated at the same condition for moisture determination. This material was referred to as "absolutely dry bark," which was later also pressed into bark board.

For preparation of bark boards. samples (1180 g) of moisture content less than 2.5% were weighed and spread over a 12 × 12 inch area and pressed to 0.5-inch stops. Because the experiment was primarily designed to study the auto-adhesion properties of bark under the influence of heat, a relatively high pressing pressure of 400 psi was used. This ensured good contact of bark particles during pressing and resulted in a board density of approximately 1.0. Al-

though previous work (Chow and Pickles 1971) indicated that a higher temperature would be optimal and since the maximum temperature of our press is 220 C, experimental boards were pressed at 200 C for time periods of 5, 10, 15, 20, 40, 60, 80 and 120 min. One board each was made in the pressing times of 5 to 20 min, while two boards were made in each schedule of 40 to 120 min pressing time. For purposes of comparison, some boards were made at 180 C with 80 min pressing time, a temperature slightly below the thermal softening temperature of dry bark.

Boards were pressed in the conventional manner with smooth platens using oven-dried bark (moisture content less than 2.5%). Thin boards (¼ inch thick) showed internal bond strengths as high as 150 psi. However, under identical pressing conditions, thicker boards showed blister failures in the middle (Fig. 1). To overcome this difficulty. a vacuum-pressing system was developed. This system made use of two platens having numerous grooves (⅒ inch width and ⅜ inch depth—Fig. 2). Grooves in platens were connected by hoses to a vacuum system. Released water vapor was condensed into a graduated cylinder before it reached the vacuum pump. To prevent bark particles from plugging the platen grooves, 16 × 16 inch metal screens (Fig. 2) were used to cover the platens, which were further covered with a thin tissue paper before accepting a board mat. This technique proved to be successful in preventing blistering.

Strength test. The boards were sanded to obtain a smooth surface for testing. Bending strength (MOR) and internal bond (IB) strength were then determined in accordance with ASTM D-1037. Two bending samples and four samples for IB strength testing were cut from each board after trimming a half inch from the edges. Two of the samples for IB strength testing were hot stacked at 105 C for 72 hr and tested after the samples were cooled to room temperature.
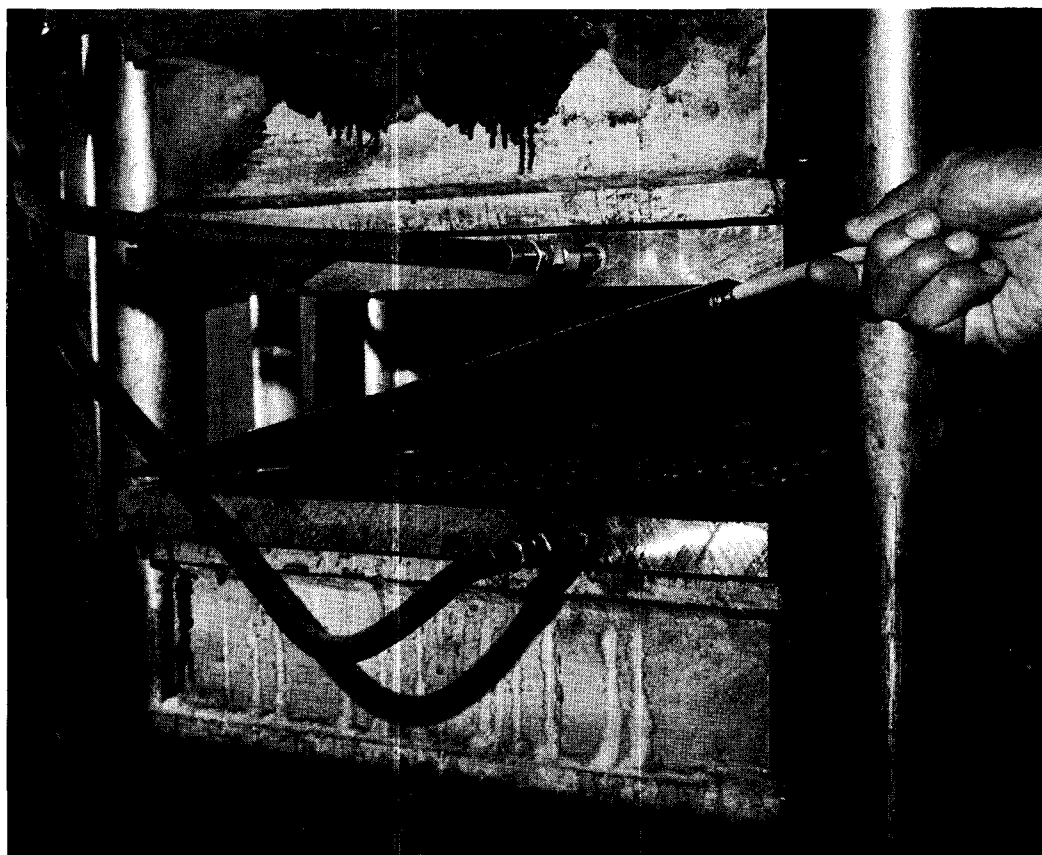
FIG. 2.   The vacuum-pressing system and metal screen.

Dimensional stability. Two samples from each board having the dimensions 3 × 3 × 0.5 inch were prepared and soaked in water for 72 hr. The moisture absorption (M), thickness swelling (T) and linear expansion (L) were measured.

A similar test was conducted to compare the performance of the above boards with bark boards containing 4.5% phenol-formaldehyde resin pressed at 200 C for 20 min.

RESULTS AND DISCUSSION
Effect of heating temperature on solubility of bark extractives

A graph comparing the absorbance of water-soluble extractives at 280 nm, the only absorption maximum of the ultraviolet spectrum, with the heating temperature is shown in Fig. 3. Between room temperature and 200 C, the extractive absorbance remains constant. However, over 200 C, which coincides with the thermal softening temperature (Chow and Pickles 1971), the absorbance decreases markedly. At 420 C, samples have almost zero absorbance. These results indicate that the softening of bark and the loss in solubility of water-soluble extractives follow the same temperature trend.

The infrared spectra of the recovered water-soluble extractives from air-dry and heated bark samples showed that the carbohydrate absorbance (1020 cm^{-1}) of the heated samples is only 30 to 50% of the air-dried bark. Low water solubility is most likely due to the effect of dehydration and possibly the cross-linking during heat treatment.
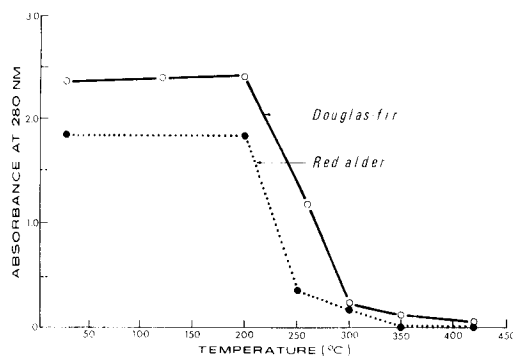
Fig. 3. Relationship between heating temperature and solubility of Douglas-fir and red alder barks expressed as the absorbance at 280 nm.

Kinetics of extractive polymerization

The loss of ultraviolet absorbance of water-soluble extractives in the course of heating follows first-order kinetics. Calculated rate constants at different temperatures are shown in Table 1. Activation energies obtained using the Arrhenius equation were 13 and 16 Kcal/mole for Douglas-fir and red alder bark, respectively. In calculating the rate constants, it was assumed that the decrease in absorbance was due to condensation reactions of the extractives, but some of this decrease might also arise from the loss of more volatile components.

The heating schedules required to reach a point of minimum solubility of bark extractives are shown in Table 2.

These kinetic results indicate the existence of polymerization of phenolic substances in barks. This is consistent with the finding of Levin and co-workers (1971), who studied the heating of Siberian larch bark by electron paramagnetic resonance (EPR) in air and in vacuum. EPR signals

were recorded from 130 to 700 C. The intensity of the signal depends on the heating temperature. At temperatures above 200 C, increased EPR signal intensity and increased condensation products were apparently related to formation of free radicals.

Oil-pollution control study

When bark is heated at an appropriate time-temperature combination (Table 2), leaching of organic extractives by water may be prevented. After this treatment, contamination of water by extractives (compounds high in BOD and possibly toxic to fish) is minimized and the bark can then be used without further treatment to control oil pollution of water. In view of the wide availability of low-cost bark, this treatment makes bark an obvious candidate for absorbing marine oil spills.

Experimental results of the laboratory test to scavenge light crude and 30-weight engine oil from a water surface using Douglas-fir bark indicate that the amount of oil absorbed by heat-treated, pulverized bark depends on its particle size. The smaller the particle size, the greater is the amount of oil absorbed. The average oil absorption of bark with particle size smaller than that passing a 35-mesh screen was about seven times its weight, while bark of particle size greater than 20 mesh absorbed about twice its weight. Both types of oil behaved in a similar fashion.

Particles that absorbed oil floated almost indefinitely, while those that did not contact oil ultimately became waterlogged and slowly sank. These laboratory results indicate the necessity for tests comparing the efficiency of heat-treated bark with presently used materials for recovering oil from

TABLE 1. Kinetic data for the thermal polymerization of water-soluble bark extractives

Species	Rate constant (min⁻¹)				Activation energy (Kcal/mole)
	200 C	240 C	280 C	320 C	
Douglas-fir	0.0055	0.0163	0.0376	0.0891	13
Red alder	0.0095	0.0304	0.1220	0.2230	16

TABLE 2. The time-temperature schedules for heating barks for minimum extractive solubility in water

	Douglas-fir bark			
Temperature (C)	200	240	280	320
Time (min)	120	30	10	5
	Red alder bark			
Temperature (C)	200	240	280	320
Time (min)	80	20	7	4

water surfaces. If the results are promising, finely divided, heat-treated bark particles might be produced and stored in quantity at critical port locations as a means of cleaning up oil spills.

Bark board formation

Strength properties. Because extractives and possibly also lignin of bark can polymerize in the course of thermal treatment, they should be able to serve as an adhesive to bind bark particles into a board. The strengths of boards made with and without phenolic resin are given in Table 3.

Average strength of unmodified boards

without hot stacking increases with pressing time. After 80 min, both IB and MOR reach maximum values (IB, 135 psi; MOR, 1270 psi); but when pressing time is greater than 80 min, both decrease slightly. This indicates that either the polymerization of bark components is complete or that thermal degradation has become a dominant factor.

The strength properties of boards hot stacked at 105 C for 72 hr are also shown in Table 3. With the exception of boards pressed for 120 min, which showed no change, the IB strengths of boards increased with hot stacking. The percentage increase in strength, depending on the pressing time, ranged from 10 to 250%, with greater benefits associated with longer pressing times. The average IB strength for boards made with 80 min pressing time increased to 195 psi after hot stacking, the maximum value attained. Bending strength, on the other hand, showed no change with hot stacking.

As shown in Table 3, under pressing conditions of 200 C for 20 min, the strength of a bark board fortified with phenolic resin was greater than a comparable board made

TABLE 3. Comparison of average strengths and dimensional stability of Douglas-fir bark boards made with and without the addition of phenol-formaldehyde resin

	Pressing		Strength (psi)				Dimensional stability† (boards without hot stacking)		
			Internal bond		Modulus of rupture in bending				
Sample	Temp. (C)	Time (min)	without hot stacking	with hot stacking	without hot stacking	with hot stacking	M (%)	T (%)	L (%)
Bark only	*200	5	0(2)	6(2)	104(2)		38	21	3.5
	* ,,	10	24(2)	35(2)	486(2)		25	16	2.2
	* ,,	15	34(2)	37(2)	653(2)		22	13	2.0
	* ,,	20	36(4)	97(4)	730(2)	714(2)	20	11	1.5
	** ,,	40	61(4)	99(4)	818(2)	855(2)	15	8	0.8
	** ,,	60	80(4)	120(4)	1190(2)	1010(2)	12	7	0.8
	** ,,	80	135(4)	195(4)	1270(2)	1260(2)	11	4	0.7
	** ,,	120	112(4)	110(4)	1140(2)	895(2)	12	5	0.6
	**180	80	62(4)	95(4)	865(2)	735(2)	20	10	1.5
Bark + 4.5% PF resin	*200	20	94(2)		1350(2)		18	10	1.1
	*200	80	124(2)		1471(2)		8	4	0.4

Values within parentheses are the numbers of samples tested.
* One board was made with each of these pressing schedules.
** Two boards were made with each of these pressing schedules. Each board contributed two samples for each class of internal bond tests and one sample each for each class of bending tests.
† M, moisture absorption; T, thickness swelling; and L, linear expansion, all after 72 hours soaking.
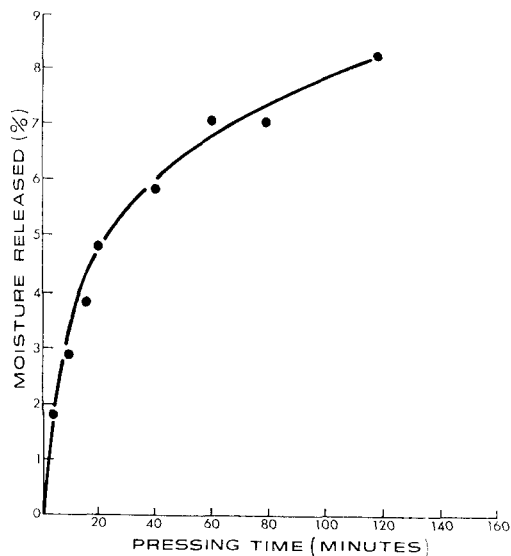
Fig. 4. Release of moisture (% of o.d. bark) from bark boards during pressing at 200 C. Each point after 20 min pressing time is the average of two values.

Fig. 5. Relationship between the moisture released (% of o.d. bark) and internal bond strength of bark without hot stacking.

from bark alone. This was expected, since the bark extractives are only partially polymerized at 20 min (Table 2), while the phenolic resin should be cured under these experimental conditions. However, at 200 C for 80 min pressing, at which point most bark extractives are polymerized (Table 2), both the IB and bending strengths of unmodified bark boards were similar to those of the boards containing 4.5% phenolic resin.

Since the MOR of the board made with 4.5% phenolic resin is 1350 psi, it may suggest that the maximum MOR for Douglas-fir board at density of approximately 1.0 could only be about 1300 psi. In comparison with the MOR of wood particleboard (about 6000 psi at density 1.0—Johnson 1956), the strength of the bark board is much less. This could be influenced by anatomical characteristics of tree species, such as the length and proportion of fibers in bark.

Moisture release. One interesting observation from these experiments is the continuous release of clear liquid solution
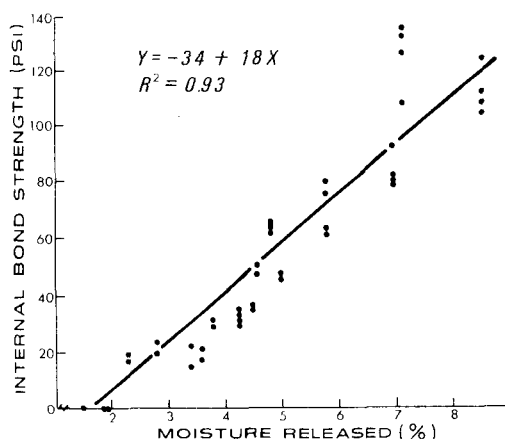
during pressing from bark with an original moisture content of less than 2.5% (Fig. 4). Fractional distillation analysis of the liquid obtained after 80 min pressing at 200 C shows that it contains more than 95% water (bp 85 to 105 C). The quantity of the solution released will hereafter be referred to as the percentage moisture released. The IB strength is linearly related to the percentage moisture released (from 2 to 9%) as shown in Fig. 5. The study using absolutely dry bark gave 4.1% released moisture at 200 C for 80 min pressing. Since the original moisture content of bark used in the main experiment was less than 2.5%, the water released after 2% moisture content must be mainly from condensation and dehydration reactions occurring in the bark. These chemical reactions would contribute to the strength of bark boards.

Dimensional stability. Water released from condensation and dehydration reactions during pressing results from the loss of hydroxyl groups of bark components. This loss will decrease the hygroscopicity of bark. Figure 6 shows the dimensional changes of bark boards produced with various pressing times. Moisture absorption (M), thickness swelling (T), and linear expansion (L) of the boards decrease in a

curvilinear fashion with increase in pressing time.

The values for M, T, and L are also given in Table 3 for bark boards pressed under the different conditions. Using these values as criteria for dimensional stability, bark boards pressed for 20 min at 200 C showed a similar stability to bark boards containing 4.5% phenolic resin pressed under the same conditions. Dimensional changes reached a minimum for board pressed for 80 min. The increase in the values M and T for bark boards pressed for 120 min is associated with a decrease in MOR and IB strengths, which is most likely attributable to thermal degradation reactions taking place in the boards.

The effect of temperature was examined by pressing boards at 180 and 200 C for the same period of time (80 min). The dimensional changes for boards pressed at 180 C are about twice as great as those for boards made at 200 C (Table 3). This finding is in agreement with the faster polymerization reaction rates at increased temperatures.

Although the press used was incapable of attaining the optimum high temperatures required, the above results indicate that the auto-adhesion properties of bark developed by high-temperature pressing can be used to produce good bark boards.

As indicated in Tables 2 and 3, the pressing schedule is critical to the development of bond strength. The need for a high-temperature press and vacuum system to produce bark boards with good strength properties using a short pressing time is a limitation of the present work.

CONCLUSIONS AND SUMMARY

Thermal polymerization of bark extractive components offers an important key to the greater utilization of bark. The potential uses of bark, after thermal treatment, for composite products and oil absorption could help to increase the utilization of bark.

Bark board made using high-temperature pressing conditions without the addition of adhesive gave internal bond strength com-
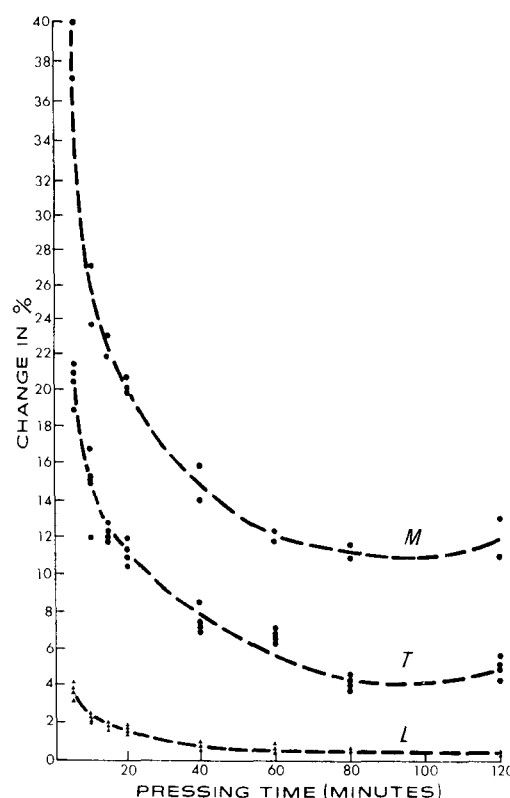

Fig. 6. Pressing time and stability (change in % of dry dimension) relationship of bark boards after soaking in water for 72 hr; moisture absorption (M), thickness swelling (T), and linear expansion (L).

parable to bark board containing 4.5% phenolic resin, as well as excellent dimensional stability. It appears that the application of the auto-adhesion principle may be an economical means for board production, if further work to determine the optimum high temperature is capable of reducing the pressing time.

Since heat-treated bark particles absorbed up to seven times their weight of oil and the modified bark itself apparently does not constitute a water pollution problem, the efficiency of this bark compared to presently accepted scavenging materials should be investigated. If the results are promising, finely divided, heat-treated bark particles might be produced and stored in quantity at

critical port locations as a means for reducing the harmful environmental effects of oil spills.

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