

# MOISTURE SORPTION ISOTHERMS OF THE WOOD AND INNER BARK OF TEN SOUTHERN U.S. HARDWOODS<sup>1</sup>

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## ABSTRACT

The adsorption isotherms of the woods and inner barks of ten hardwoods, measured at 25 C and atmospheric pressure, were essentially identical, but the desorption isotherms for the barks were consistently lower than those for the woods. Three fundamental constants were required to evaluate the isotherms in terms of the Dent (1977) model, a modification of the classical BET surface model, and of the Hailwood-Horrobin (1946) single-hydrate solution model. Two of these constants are identical for the two models, but the third is somewhat lower for the Dent model. Both models divide the sorbed water into two components, one strongly bonded and the other more weakly bonded to the wood or bark substrate. Also both models predict an identical parabolic relationship giving the ratio of the relative humidity to the moisture content as a function of relative humidity.

*Keywords:* Wood moisture, moisture relationships, moisture models.

## INTRODUCTION

There has been renewed interest in utilizing second-growth hardwoods growing on southern pine sites in the southern United States. This interest culminated in a symposium sponsored by the Southern Forest Experiment Station of the USDA Forest Service, held at Alexandria, Louisiana, on March 10–14, 1975. In preparation for this symposium the authors carried out a research program on the sorption characteristics and electrical resistivities of the twenty-two species of hardwoods of interest to this symposium. Complete adsorption and desorption isotherms were obtained on the woods and inner barks of ten of these hardwoods. These results are reported here.

## THEORIES OF SORPTION

The term *sorption* is used in this paper as a general term including both adsorption and desorption, following the definitions of Stamm (1964).

Many theories have been proposed to explain the sorption of water by hygroscopic polymers such as wood and textile materials. Venkateswaran (1970) lists eighteen sorption isotherm equations and has pointed out that in the derivation of most of these equations, two assumptions are generally made: first, that there are two kinds of sorbed water, primary and secondary; second, that the energy of interaction of the primary sorbed water with the wood is higher than that of the secondary sorbed water.

These sorption theories can be divided into two general categories. In one of these, sorption is treated as a surface phenomenon and in the other as a solution

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phenomenon. Surface sorption theories can be represented by the Brunauer et al. (1938) (BET) theory and solution theories by the Hailwood-Horrobin (1946) theory. These two theories predict different forms for the sorption isotherm, particularly at high moisture contents. However, a recent modification of the BET theory has been proposed by Dent (1977), which predicts a sigmoidal isotherm identical with that of the Hailwood-Horrobin single-hydrate theory. The Dent and single-hydrate form of the Hailwood-Horrobin models will be used to analyze the experimental results presented here.

The equation for the isotherm predicted by both the Dent and Hailwood-Horrobin models is of the form

$$M = \frac{100h}{A + Bh - Ch^2} = \frac{H}{A + Bh - Ch^2}$$

where  $M$  is the percent moisture content (based on oven-dry weight) at equilibrium with the relative vapor pressure  $h$ , or percent relative humidity  $H (=100h)$ , and  $A$ ,  $B$ , and  $C$  are empirical constants. The equation can be written in the form

$$100h/M = H/M = A + Bh - Ch^2$$

which predicts a parabolic relationship between the ratio  $H/M$  and the relative vapor pressure  $h$ . The empirical constants  $A$ ,  $B$ , and  $C$  can be calculated by fitting a parabola to empirical data on the sorption isotherm, plotted as  $H/M$  against  $h$ . These empirical constants are identical for the two models.

Although both the Dent and Hailwood-Horrobin models predict the same sorption isotherm, they differ somewhat in its interpretation.

The Hailwood-Horrobin model treats the sorption process as one of hydration of the polymer (i.e., dry wood) by some of the sorbed water. This hydrate forms a partial solution with the balance of the sorbed water, designated as water of solution.

According to the single-hydrate form of this model, the total sorbed water  $M$  (percent of dry weight) is assumed to exist in two forms. These are (on a percent of dry weight basis), water of hydration  $M_h$  and water of solution  $M_s$ . Thus, the three chemical species that are present in the cell wall are assumed to be unhydrated polymer molecules (or dry wood), hydrated molecules (hydrated wood), and dissolved water. These are considered to behave as an ideal solution, in which the activity of each species is assumed to be proportional to its mole fraction. The total equilibrium results from two sets of individual equilibria. These are, the formation of hydrates between dissolved water and certain units of the polymer molecule with an equilibrium constant  $K_1$ , and the equilibrium between the hydrated water and the water vapor with equilibrium constant  $K_2$ . A third fundamental constant, designated here as  $M_0$ , can be defined as the moisture content (percent of dry weight basis) corresponding to complete polymer hydration (one molecule of water attached to each hydratable polymer unit). This is related to the apparent molecular weight  $W_0$  of the sorbate (dry wood) per mole of sorption sites (Skaar 1972). For water sorption on wood the relationship is  $M_0 = 1800/W_0$ .

Dent (1977) has proposed a multilayer theory for the sorption of gases on polymers which is an extension of the BET surface sorption equations. In terms

TABLE 1. *List of species studied.*

Sweetgum	<i>Liquidambar styraciflua</i> L.
Hickory	<i>Carya</i> sp.
So Red Oak	<i>Quercus falcata</i> Michx.
White Oak	<i>Quercus alba</i> L.
Yellow Poplar	<i>Liriodendron tulipifera</i> L.
Sweetbay	<i>Magnolia virginiana</i> L.
White Ash	<i>Fraxinus americana</i> L.
Green Ash	<i>Fraxinus pennsylvanica</i> Marsh.
Red Maple	<i>Acer rubrum</i> L.
American Elm	<i>Ulmus americana</i> L.

of water vapor sorption by wood, Dent's model, in agreement with the BET model, postulates primary sorption sites and secondary sorption sites. The total moisture content  $M$  is equal to the sum of  $M_1$ , the moisture content on the primary sites or first layer and  $M_2$ , the moisture content on the secondary sites or layers. It also assumes, as does the original BET model, that the binding energy for the water molecules sorbed onto the primary sites or first layer is higher than for those on secondary or multilayer sites. It differs from the BET model, however, in that the water sorbed above the first layer is assumed to be thermodynamically different from ordinary liquid water. Because of this latter assumption, a third constant, additional to the two classical BET constants, is necessary to describe the sorption isotherm.

Two of the three constants  $K_2'$  and  $M_0'$  in the Dent equations are identical with the two corresponding Hailwood-Horrobin constants,  $K_2$  and  $M_0$ . The third constant,  $K_1'$ , although analogous to  $K_1$  of the Hailwood-Horrobin model, has a somewhat lower value for a given isotherm. It is related to the Hailwood-Horrobin constants  $K_1$  and  $K_2$  by,  $K_1' = K_2(K_1 + 1)$ .

The Dent constant  $K_1'$  is equivalent to the saturated water vapor pressure  $p_0$ , multiplied by the ratio of the attachment rate constant of the vapor molecules per unit vapor pressure  $p$  to the escape rate constant for the water molecules at the primary sorption sites (Dent 1977). The Dent constant  $K_2'$  is defined similarly, but for the secondary sorption sites. In the original BET equation  $K_2'$  is taken to be unity, that is, the multilayered or secondary water is assumed to have the same thermodynamic properties as ordinary liquid water. However, in the Dent model it is found to be somewhat lower than unity, indicating a different state than ordinary water.

Table 2 is a convenient summary of the more important equations derived from the Hailwood-Horrobin and Dent models. Equations 2, 3, and 4 in Table 2 show how the Hailwood-Horrobin constants  $K_1$ ,  $K_2$ , and  $M_0$ , and the Dent constants  $K_1'$ ,  $K_2'$ , and  $M_0'$  can be calculated from the empirical constants  $A$ ,  $B$ , and  $C$  of Eq. 1.

Equations 5, 6, 7, and 8 in Table 2 relate the water of hydration ( $M_h$ ), water of solution ( $M_s$ ), and total moisture content  $M$  to the constants  $K_1$ ,  $K_2$ , and  $M_0$ , and the relative vapor pressure  $h$ , for the Hailwood-Horrobin model. They also show the corresponding relationships among the percent primary water ( $M_1$ ),

TABLE 2. Tabulation of analagous equations for the Hailwood-Horrobin and Dent sorption models.

HAILWOOD-HORROBIN	EQU. NO.	DENT
$\frac{H}{M} = A + Bh - Ch^2$	(1)	$\frac{H}{M} = A + Bh - Ch^2$
$K_2 = \frac{-B + \sqrt{B^2 + 4AC}}{2A}$	(2)	$K_2' = K_2$
$K_1 = \frac{1}{1 - K_2(B/C)}$	(3)	$K_1' = K_2(K_1 + 1)$
$M_0 = \frac{100}{AK_2(K_1 + 1)}$	(4)	$M_0' = M_0$
$M_h = \frac{M_0 K_1 K_2 h}{1 + K_1 K_2 h}$	(5)	$M_1 = \frac{M_0' K_1' h}{1 + (K_1' - K_2') h}$
$M_s = \frac{M_0 K_2 h}{1 - K_2 h}$	(6)	$M_2 = \frac{M_0' K_1' K_2' h^2}{(1 - K_2' h)(1 + (K_1' - K_2') h)}$
$M = M_h + M_s$	(7)	$M = M_1 + M_2$
$M = \frac{M_0 K_2 (K_1 + 1) h}{(1 + K_1 K_2 h)(1 - K_2 h)}$	(8)	$M = \frac{M_0' K_1' h}{(1 - K_2' h)(1 + (K_1' - K_2') h)}$
$\Delta G_1 = -RT \ln K_1$	(9)	$\Delta G_1' = -RT \ln K_1'$
$\Delta G_2 = -RT \ln K_2$	(10)	$\Delta G_2' = -RT \ln K_2'$

secondary water ( $M_2$ ) and total water contents  $M$ ; and the Dent constants  $K_1'$ ,  $K_2'$ , and  $M_0'$ .

Finally Table 2 also shows how the free energy changes  $\Delta G_1$  and  $\Delta G_2$  associated with sorption according to the Hailwood-Horrobin model can be calculated from  $K_1$  and  $K_2$  using Eq. 9 and 10. The corresponding Dent equations can be used to calculate  $\Delta G_1'$  and  $\Delta G_2'$ , based on the values of  $K_1'$  and  $K_2'$ .

As mentioned above, the Hailwood-Horrobin constants  $M_0$  and  $K_2$  are identical with  $M_0'$  and  $K_2'$  of the Dent model. Also since  $K_1' = K_2(K_1 + 1)$ , it can be shown that certain simple relationships exist between  $M_1$  and  $M_2$  of the Dent model and  $M_h$  and  $M_s$  of the Hailwood-Horrobin model. These can be expressed in the form

$$M_1 = M_h(1 + (1/K_1)) \quad (11)$$

and

$$M_2 = M_s(M_1/M_0) \quad (12)$$

Dent (1977) has pointed out that Eq. 8 reduces to the BET equation when the constant  $K_2'$  is taken to be unity. Thus, the BET equation is obtained in the form,

$$M = \frac{M_0 K_1' h}{(1-h)(1+K_1' h - h)} \quad (13)$$

When  $K_2'$  is zero, Dent also shows that Eq. 8 reduces to the Langmuir equation, or

$$M = \frac{M_0 h}{(1/K_1') + h} \quad (14)$$

#### EXPERIMENTAL MATERIALS AND PROCEDURES

The material used in this study came from ten different hardwoods (Table 1) supplied by the U.S. Forest Service Experiment Station in Pineville, La. The wood was received in the form of short round bolts, from 5 to 8 inches in diameter and 12 to 15 inches in length. The barks had previously been removed from the same bolts. Both wood and bark had been air-dried before being received in Syracuse.

A single wood sample was cut from each bolt, so there was only one test sample per species. The samples were three millimeters thick along the grain. The cross-section was irregular in shape, approximately 30 square centimeters in area.

It was not practical to obtain such large samples of the inner bark. Therefore, the bark samples were shaved or scraped from the cambial side of the last-formed periderm. The particles ranged in size from fragments to about 2- × 2- × 5-mm splinters. The total sample weight was approximately two grams for each species, with one sample per species. They were kept in weighing bottles during the entire experiment, with the cap removed during time of exposure to the appropriate humidity conditions.

The samples were conditioned in an Aminco Climate-Lab (American Instrument Co., Inc.) modified such that the dry-bulb and the dew-point temperatures were each controlled by means of thermistor bridges. The dry-bulb temperature was maintained at  $25.0 \pm 0.2$  C. The dew-point temperature was controlled within  $\pm 0.1$  C, to give the required relative humidity at constant dry-bulb temperature for each condition.

The dry-bulb, wet-bulb, and dew-point temperatures were all measured and recorded on a multipoint chart recorder, using copper-constantan thermocouples as sensing elements, referred to a water-ice mixture. The wet-bulb depression was also measured directly with similar thermocouples, using the wet-bulb temperature as the reference junction. The relative humidity was calculated from the dry-bulb temperature and wet-bulb depression, using standard equations. The estimated maximum errors in temperature and relative humidity were  $\pm 0.2$  C and  $\pm 1.5\%$ , respectively.

Single-step adsorption isotherms were determined for both the wood and bark samples at 25 C. This was accomplished by vacuum-drying the samples overnight at a pressure of one mm Hg, or less, prior to exposure to each adsorption humidity condition. The sequence of humidities for the wood samples were 37.0, 51.4,

TABLE 3. Mean values with standard deviations of the experimentally determined adsorption and desorption equilibrium moisture contents  $M$  at various relative humidities  $H$  for the woods and barks of the ten species studied.

Wood-adsorption		Bark-adsorption		Wood-desorption		Bark-desorption	
H(%)	M(%)	H(%)	M(%)	H(%)	M(%)	H(%)	M(%)
37.0	7.01 ± 0.33	32.3	6.59 ± 0.51	35.0	8.20 ± 0.38	38.5	8.47 ± 0.51
51.4	8.95 ± 0.34	50.6	8.91 ± 0.59	56.4	12.15 ± 0.43	49.8	10.17 ± 0.48
71.2	12.55 ± 0.40	65.9	11.61 ± 0.79	72.8	15.95 ± 0.47	63.3	12.46 ± 0.53
86.2	17.13 ± 0.51	73.3	13.31 ± 0.96	81.8	19.11 ± 0.62	71.1	14.13 ± 0.65
94.1	21.74 ± 0.74	81.8	15.90 ± 1.14			80.0	16.97 ± 0.95
		87.3	18.53 ± 1.40				
		95.0	23.02 ± 2.00				

71.2, 86.2, and 94.1%. Those for the bark samples were 32.3, 50.6, 65.9, 73.3, 81.8, 87.3, and 95.0%. The samples were considered to have reached equilibrium at any given humidity when the daily weight changes were less than 0.1 mg. This corresponded to  $\pm 0.01\%$  moisture content or less for all samples. Equilibrium generally required about two weeks for each exposure condition, for both adsorption and desorption measurements.

Desorption measurements were made in sequential steps and were therefore multi-step isotherms, unlike the single-step adsorption isotherms. The sequence

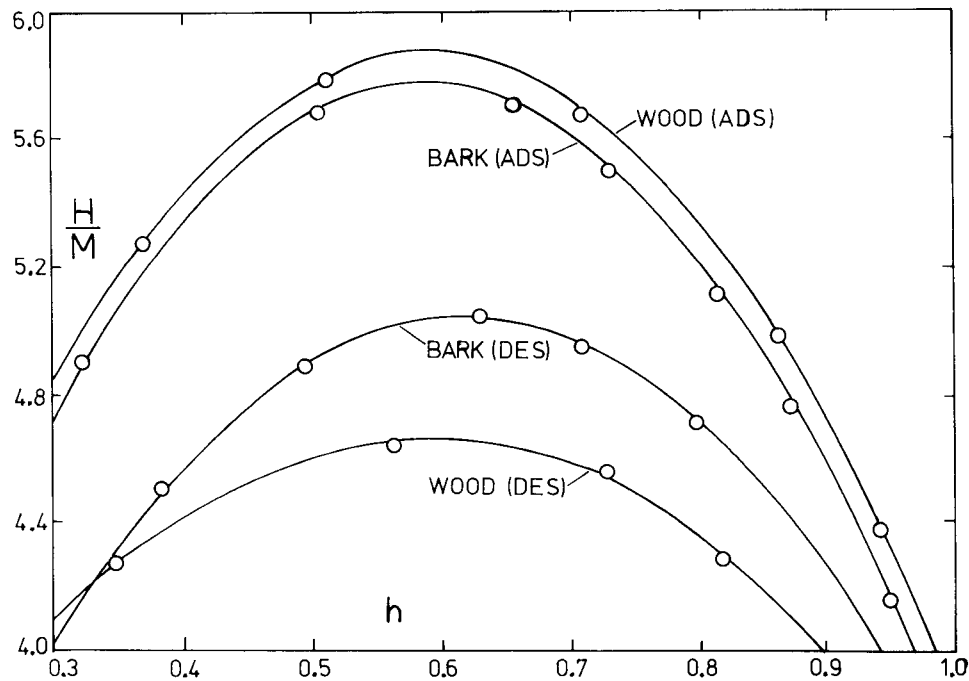


FIG. 1. Plotted points and fitted curves of the ratio  $H/M$  against relative vapor pressure  $h$  for adsorption and desorption based on the mean values for the woods and barks of the ten selected species.

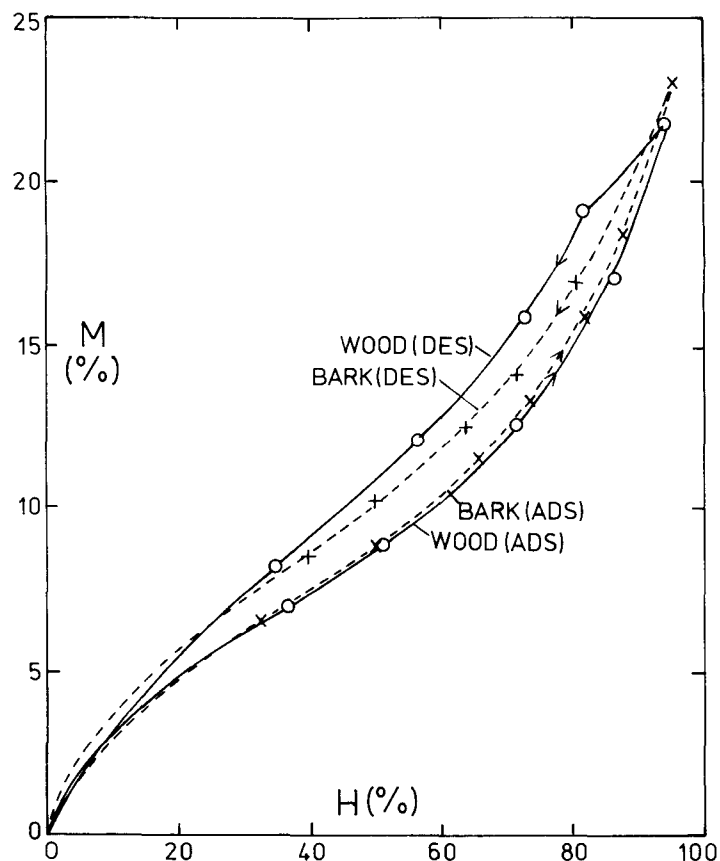


FIG. 2. Plotted points and fitted adsorption and desorption isotherm curves based on the mean values for the woods and barks of the ten selected species.

of humidities for the wood samples were 81.8, 72.8, 56.4, and 35.0%, following attainment of equilibrium at the last adsorption step at 94.1% humidity. For the bark samples they were 80.0, 71.1, 63.3, 49.8, and 38.5%, following the last adsorption step at 95.0% humidity.

Following the last desorption step, the samples were oven-dried at  $103 \pm 2$  C for 24 h, and dry weights were determined prior to calculating the equilibrium moisture contents at each humidity condition.

#### ANALYSIS OF DATA

Table 3 summarizes the sorption data used in the analysis. Although individual sorption isotherms were obtained for the wood and bark of each species measured (Okoh 1976), these are not reported here because there was no replication of wood or bark samples within a species. Therefore, the analysis, which was intended to compare adsorption and desorption isotherms of wood and inner bark, used pooled data for the ten species. Table 3 gives the mean values of the equilibrium moisture contents at each humidity, as well as the standard deviation of the measurements in each case.

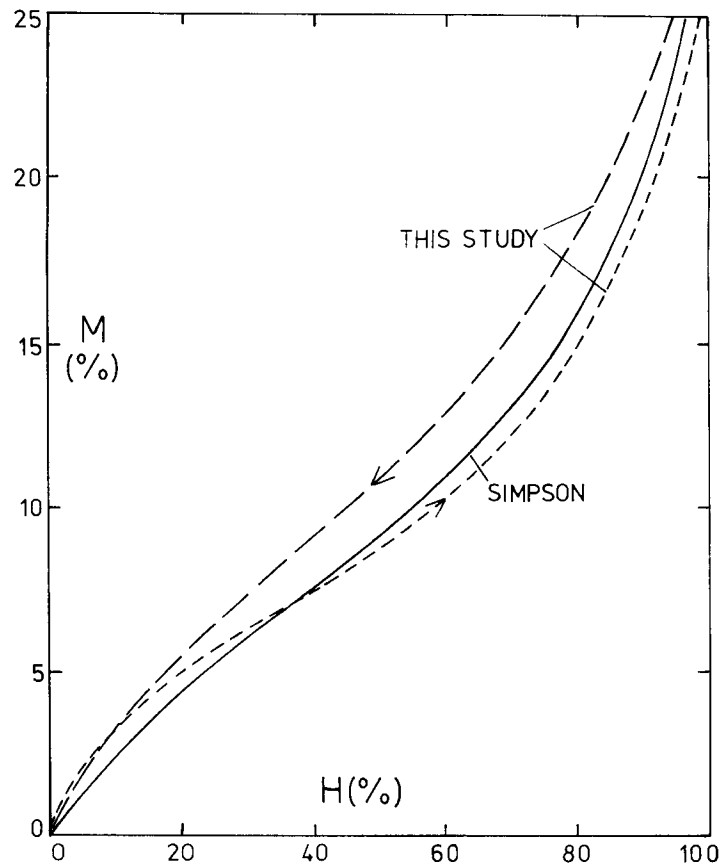


FIG. 3. Comparison of the sorption isotherm for wood at 77 F (25 C) as given by Simpson (1971) with the mean isotherms obtained in this study for the ten selected woods at 25 C.

The empirical constants A, B, and C were evaluated by fitting Eq. 1 to the data by a least squares technique for each set of sorption isotherms. Figure 1 shows a plot of the ratio  $H/M$  against relative vapor pressure  $h$ , using the parabolic equation for the adsorption and desorption isotherms for the woods and barks fitted to the mean data for the ten species. Also shown are the mean values of  $H/M$  measured at each relative vapor pressure. Figure 2 shows the corresponding sorption isotherms obtained by use of the calculated values of A, B, and C. Also plotted are the mean moisture content points as measured.

Figure 3 shows a plot of the sorption isotherm for wood at 77 F (25 C) obtained from equations given by Simpson (1973), based on Hailwood and Horrobin parameters fitted to data in the Wood Handbook (1955). These equations form the basis of the revised sorption isotherms published in the most recent Wood Handbook (1974). Also shown in the same figure are the mean adsorption and desorption isotherms for the woods of the ten selected species.

The sorption hysteresis effect may be defined in terms of the ratio ( $M_a/M_d$ ) of the adsorption ( $M_a$ ) to desorption ( $M_d$ ) equilibrium moisture contents at any given



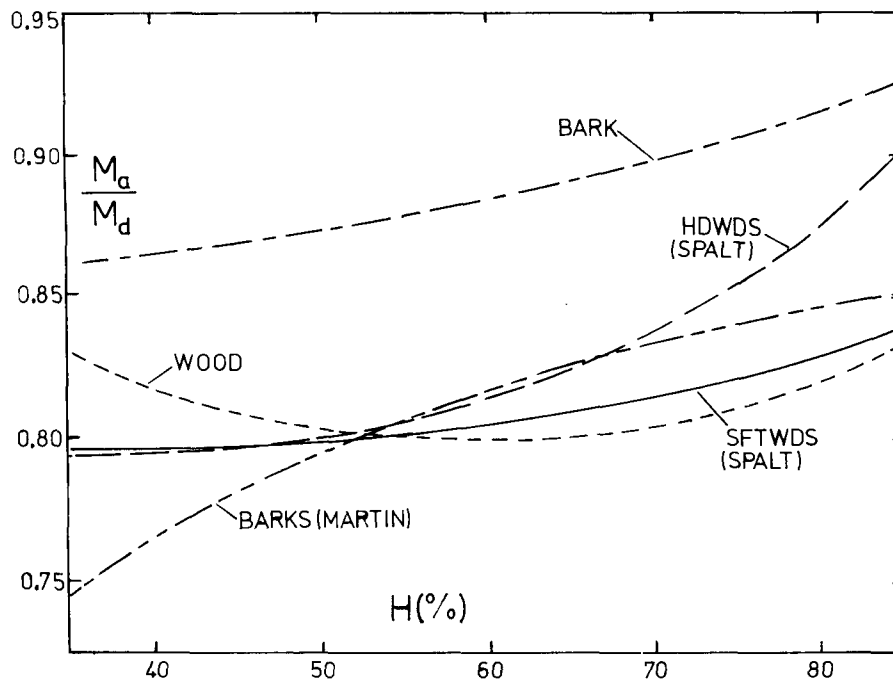


FIG. 4. Comparison of the  $M_a/M_d$  ratios as functions of  $H$  obtained in this study with those obtained by other workers.

relative humidity. These ratios are plotted as functions of relative humidity for the means of the ten woods and barks in Fig. 4, over the humidity range from 35 to 85%. Also shown are similar curves calculated from the data of Spalt (1958) on wood of both softwoods and hardwoods, and of Martin (1967) on barks.

The constants  $K_1'$ ,  $K_1$ ,  $K_2$  ( $K_2'$ ), and  $M_0$  ( $M_0'$ ) were evaluated from the previously calculated values of  $A$ ,  $B$ , and  $C$  using Eq. 2, 3, and 4 of Table 2. They are listed in Table 4, together with similar parameters calculated from data of Spalt (1958) on wood, of Martin (1967) on bark, and of Simpson (1973) on wood. Also shown are the same parameters calculated from mean desorption data given by Choong and Manwiller (1976) for twenty-two hardwoods, including the ten used in this study, but measured at 105 F (40.5 C).

Figures 5 and 6 show the mean adsorption isotherms for wood and bark, in addition to the curves of  $M_h$ ,  $M_s$ ,  $M_1$ , and  $M_2$ , calculated by means of Eq. 5 and 6. Figures 7 and 8 show similar curves for the desorption isotherms.

#### DISCUSSION OF RESULTS

The adsorption isotherms for the wood and bark samples (Figs. 2 and 3) were essentially similar. However, the desorption isotherms for the woods were consistently higher than those for the barks over the entire humidity range covered.

For convenience in comparing the sorption isotherms, the individual curves were calculated for each species for adsorption and desorption of wood and bark,

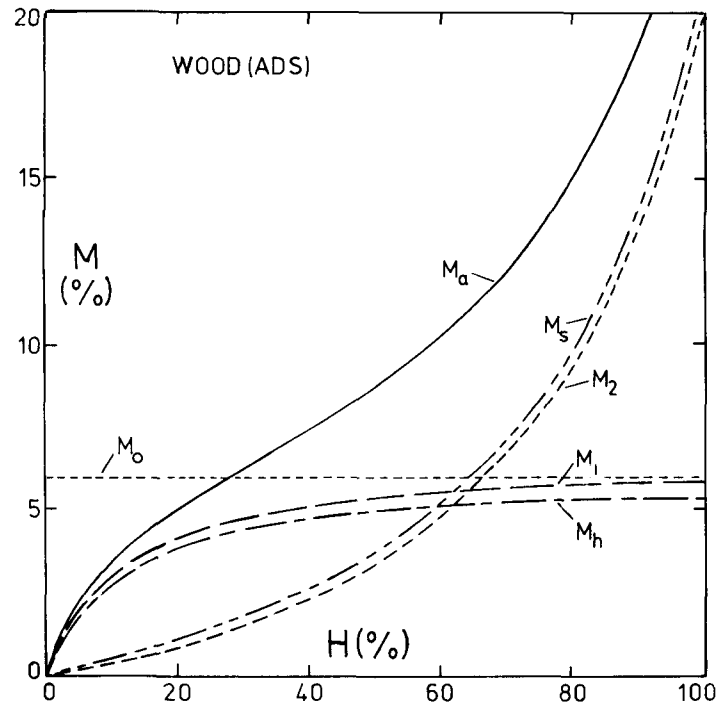


FIG. 5. Mean adsorption isotherms for the woods of the ten selected species and of the curves of  $M_h$ ,  $M_s$ ,  $M_1$ , and  $M_2$ , as functions of  $H$ . Also shown is the constant  $M_0$ .

TABLE 4. Tabulation of Hailwood-Horrobin and Dent coefficients calculated using data from various sources.

		A	B	C	$K_1$	$K_1'$	$K_2$	$M_0(\%)$
This study								
10 woods	(ads.)	1.64	14.3	12.1	12.21	10.26	0.777	5.94
	(des.)	2.23	8.3	7.0	6.23	5.15	0.712	8.70
10 barks	(ads.)	1.48	14.6	12.4	13.55	11.48	0.789	5.91
	(des.)	1.18	12.5	10.1	14.25	11.50	0.754	6.94
From Spalt (1958)								
softwds.	(ads.)	2.37	12.8	11.0	8.30	7.05	0.758	6.12
	(des.)	2.00	9.5	7.8	7.83	6.30	0.714	8.13
hardwds.	(ads.)	2.44	13.5	11.8	8.41	7.19	0.765	5.83
	(des.)	2.32	8.7	7.0	6.98	5.61	0.703	8.38
From Martin (1967)								
barks	(ads.)	2.91	12.7	10.9	6.92	5.84	0.737	5.89
	(des.)	0.92	13.9	10.9	21.40	16.61	0.742	6.53
From Choong and Manwiller (1976)								
22 woods	(des.)	1.98	14.9	13.6	10.16	9.20	0.824	5.50
From Wood Handbook*								
wood	(ads.-des.)	2.84	9.8	8.87	5.62	4.93	0.745	7.13

\* Wood Handbook data were analyzed by Simpson (1973). It is not stated whether they are adsorption or desorption data.

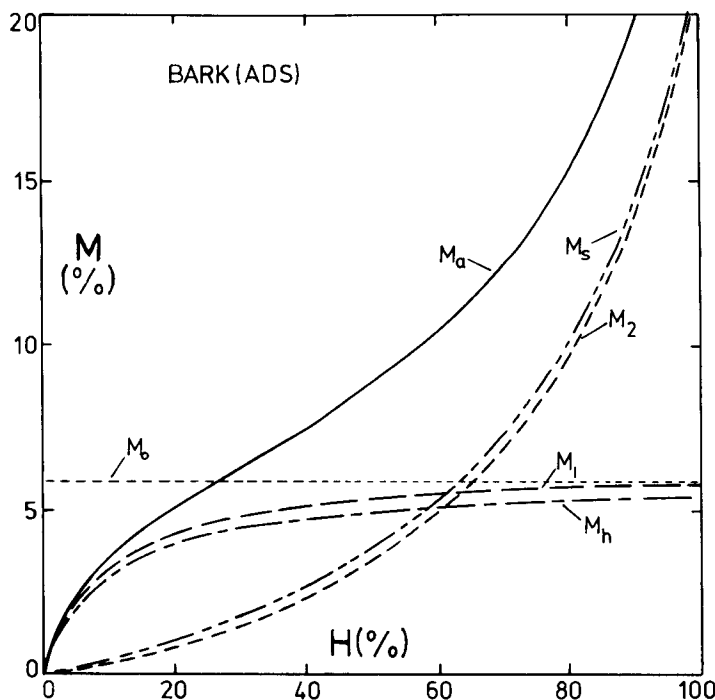


FIG. 6. Mean adsorption isotherms for the barks of the ten selected species and of the curves of  $M_b$ ,  $M_s$ ,  $M_1$ , and  $M_2$ , as functions of  $H$ . Also shown is the constant  $M_b$ .

using Eq. 1. From these the equilibrium values  $M_a$  and  $M_d$  were calculated at 70% humidity, corresponding approximately to the air-dry condition.

The results of a simple t-test, summarized in Table 5, indicate that there were no significant differences in the adsorption equilibrium moisture contents  $M_a$  between wood and bark at 70% humidity. However, the wood was consistently more hygroscopic than the bark during desorption.

The curves shown in Fig. 3 indicate that the standard wood isotherm at 25 C, taken from data given in the Wood Handbook (1974), is nearly equal to the adsorption isotherms but considerably lower than the desorption isotherms for wood or bark obtained in this study.

It is clear from Fig. 4 that the hysteresis ratio,  $M_a/M_d$ , is greater for barks than for the woods. The reason for this is not known but may reside in differences in the cell wall structure and in the chemical constituents of wood and bark. The curves calculated from Martin's (1967) data indicate ratios similar to those for wood over the range from about 30 to 70% humidity.

The constants  $K_2$  and  $M_0$ , which are common to both the Hailwood-Horrobin and Dent sorption theories, yielded similar values to those previously reported for wood at room temperature. As is shown in Table 4, the constant  $M_0$  is lower for adsorption than for desorption. This is as anticipated, as Spalt (1958) points out, because hydroxyl groups tend to form hydrogen bonds between each other when the wood has been dried. They are then not available for sorption of water

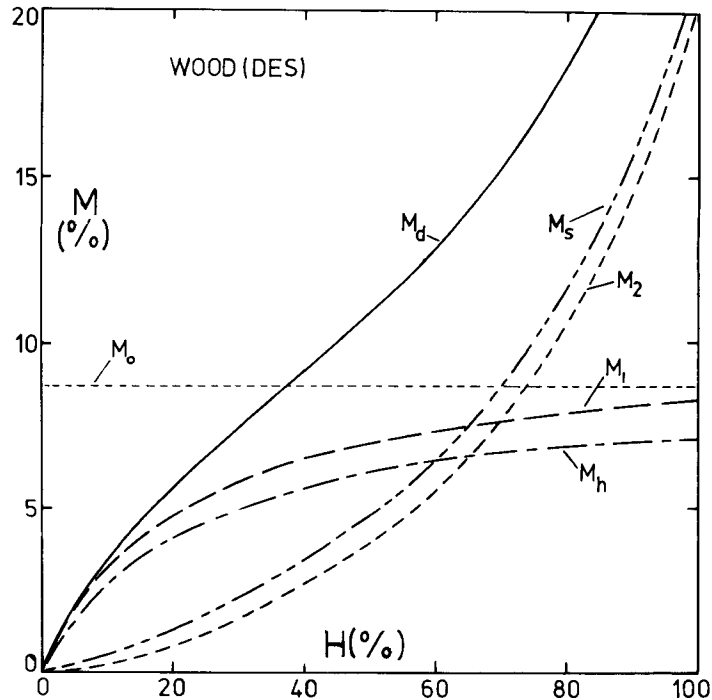


FIG. 7. Mean desorption isotherms for the woods of the ten selected species, and of the curves of  $M_h$ ,  $M_s$ ,  $M_1$ , and  $M_2$ , as functions of  $H$ . Also shown is the constant  $M_0$ .

until they are broken at high moisture contents due to swelling pressures in the cell wall. During desorption a greater number of them are hydrated or attached to water molecules. Therefore, there is less probability that they will form hydrogen bonds with other hydroxyl groups and thus reduce the number of sorption sites. Consequently, fewer sorption sites are available for primary water sorption, or for hydration, during adsorption than for desorption. The first constant in the classical BET sorption model is equivalent to  $M_0'$  in the Dent model.

The constant  $K_2'$  in the Dent model can be defined as the ratio of the attachment rate to the escape rate of the secondary water molecules in the cell wall per unit relative vapor pressure  $h$ . In the original BET equation, this is taken to be unity that would be the case if the secondary water behaved as ordinary liquid water. However, its value, as shown in Table 4, varies between 0.7 to 0.8, approximately. Dent (1977) gives values ranging from 0.70 to 0.85 for water sorption on various textile fibers.

TABLE 5. Calculated mean EMC (%) at 70%  $H$  for wood and bark of ten species at 25 C.

	Wood	Bark	T-test results
Adsorption	12.26 ± 0.38	12.49 ± 0.84	0.85 (not signif.)
Desorption	15.27 ± 0.47	13.97 ± 0.62	5.42 (highly signif.)

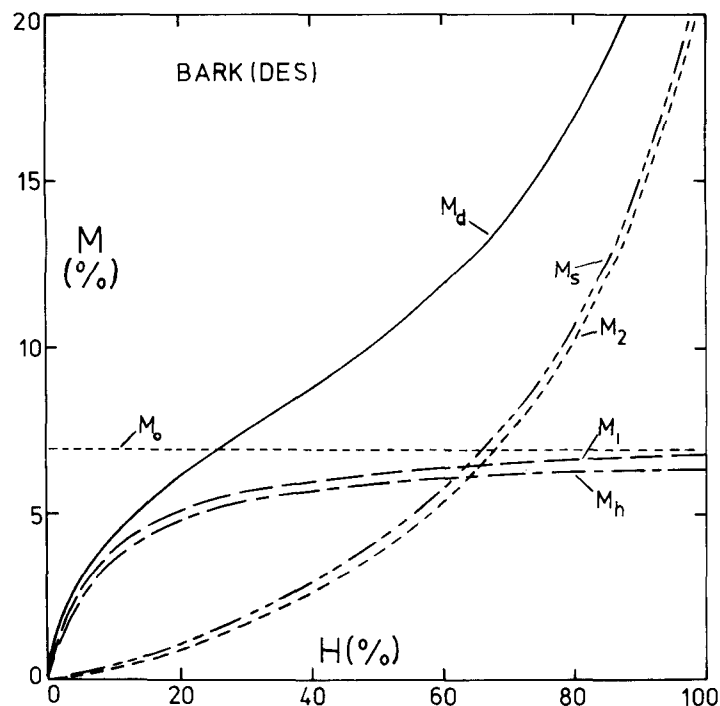


FIG. 8. Mean desorption isotherms for the barks of the ten selected species, and of the curves of  $M_h$ ,  $M_s$ ,  $M_1$ , and  $M_2$ , as functions of  $H$ . Also shown is the constant  $M_0$ .

In the Hailwood-Horrobin (1946) model,  $K_2$  is defined as the activity of dissolved water (analogous to the secondary water of the Dent model) per unit relative vapor pressure  $h$ . If it is assumed that the activity of this water is equal to the ratio of the condensation to evaporation rate at a given relative vapor pressure, it should be equivalent to the corresponding Dent constant. Its value should be unity if it has the same activity as liquid water.

The constant  $K_1'$  of the Dent model ranged from 5 to 12 in this study, consistently lower than the corresponding Hailwood-Horrobin constant  $K_1$ , which varied from 6 to 14 (Table 3). The Dent constant  $K_1'$  is essentially equivalent to the second classical BET constant, designated here as  $C_1$ .

The corresponding free energy changes,  $\Delta G_1'$ ,  $\Delta G_1$ , and  $\Delta G_2$ , calculated from  $K_1'$ ,  $K_1$ , and  $K_2$  by use of Eq. 9 and 10, ranged from  $-0.93$  to  $-1.47$ ,  $-1.06$  to  $-1.56$ , and  $+0.13$  to  $+0.21$  K-calories per mole of water, respectively, at 25 C ( $T = 298.1$  Kelvin). These are similar in range to those calculated by Dent (1977) for a variety of textile materials. These varied from  $-0.51$  to  $-1.50$ , and from  $+0.10$  to  $+0.23$  K-calories per mole of water for  $\Delta G_1'$  and  $\Delta G_2$ , respectively. In the present study data were not obtained on the variation of  $K_1'$ ,  $K_1$  and  $K_2$  with temperature. Therefore, it was not possible to calculate the total enthalpy and entropy changes associated with the sorption process (Skaar 1972).

It is evident from Figs. 5 to 8 that the shapes of the Hailwood-Horrobin hydrated water ( $M_h$ ) curves of both woods and barks were similar to those of the corresponding Dent primary water ( $M_1$ ) curves. However,  $M_h$  was always slightly

less than  $M_1$  at any given humidity. Figures 5 to 8 also show that curves of  $M_s$ , the water of solution of the Hailwood-Horrobin model, were similar to those of the secondary water ( $M_2$ ) of the Dent model, although  $M_s$  was always slightly greater than  $M_2$ . The sum of  $M_h$  and  $M_s$ , that is, the total moisture content at any given humidity, was equal to the sum of  $M_1$  and  $M_2$ , as Eq. 7 indicates. It should be noted that both  $M_h$  and  $M_1$  approach  $M_0$  as humidity increases but that the latter does so more rapidly.

It should be emphasized that the above relationships assume that water sorption is perfectly reversible. This is not strictly true however, since hysteresis is present. Nevertheless, the departure from reversibility is believed to be small for small changes in sorption and the general interpretations are believed to be valid.

Based on the results of this study, it is concluded that:

1. The adsorption isotherms for the inner barks of the species tested were essentially identical with those for the corresponding woods. However, the desorption isotherms for the barks were consistently lower than those for the woods.
2. The sorption data gave a parabolic relationship between  $H/M$ , the ratio of the relative humidity  $H$  to equilibrium moisture content  $M$ , and relative humidity over the hygroscopic range of moisture contents. This is as predicted by both the Hailwood-Horrobin (1946) model and the more recent Dent (1977) model.
3. Although the Hailwood-Horrobin and Dent models are derived from different assumptions, two of the three fundamental constants arising from each model are identical with the analogous constants of the other model, and the third constant in each model is nearly identical with that of the other model. Both models assume two kinds of water in the cell wall, one strongly and the other, weakly bound. Furthermore, although the proportions of these vary with wood moisture content, they vary in approximately the same proportion for the two models.

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