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ABSTRACT

Ten sorption models were tested on the wood-water system using data available in the literature. They were tested solely on the basis of how well they could functionally relate the data for equilibrium moisture content and relative humidity. The two-hydrate form of the Hailwood and Horrobin model is the most accurate of those tested that are written as moisture content equal to a function of relative humidity. The Pierce model is the most accurate of those tested that are written as relative humidity equal to a function of moisture content.

Additional keywords: Relative humidity, vapor pressure, curve fitting.

INTRODUCTION

Understanding the relationship of relative humidity and temperature to equilibrium moisture content (EMC) of wood is important to most phases of wood product processing and to their end use to minimize the problems associated with shrinking and swelling of wood. Numerous sorption theories analytically relate EMC to relative humidity. The objective here was to evaluate some of the analytical expressions of these relationships for how well they can functionally relate available data on EMC, relative humidity, and temperature.

No evaluation of the physical reality of the theories is intended or should be implied from the agreement or lack of agreement between model and actual data since this is essentially a curve-fitting study. Tests more critical than these, like the ability to predict thermodynamic variables or some other quantity that can be independently measured, are necessary before the physical significance of the theory can be evaluated. Therefore, to avoid the impression that the models are necessarily physically valid, the physics of the theories is referred to as little as possible. Most of the theories relate EMC to relative humidity with the help of several material parameters. Most of the parameters have physical significance in the context of the theory, but are not discussed here except when the original equation is modified for the purpose of this study. The reader can refer to the original papers or some of the reviews of sorption theories for the physical meaning of the parameters.

Analytical expressions that relate EMC to relative humidity have potential use as a concise method to store and retrieve EMC-relative humidity data (Simpson 1971) and in mathematical modeling. In moisture diffusion work, interconversions of moisture gradients and diffusion coefficients between moisture content and vapor pressure are sometimes made (Skaar 1954; Kubler 1957; Choong 1963); thus an analytical expression to relate the two would be helpful. Mathematical modeling is also used in describing the mechanical properties of wood, particularly the rheological properties. Moisture content changes have a pronounced effect on rheological behavior (Hearmon and Paton 1964), and when rheological modeling advances to the stage where it can deal with changing moisture content, expressions of this nature may be of value.

The widespread use of computers makes both the determination of the model pa-

[1] Maintained in cooperation with the University of Wisconsin.

rameters and the use of the analytical expressions much easier than was previously possible. Many of the expressions are complex, and their use, particularly the determination of the model parameters, requires many calculations. Now that computers make the calculations, new uses for the expressions can be considered.

SORPTION THEORIES FOR HYGROSCOPIC MATERIALS

Moisture sorption theories can be divided into two general groups. In one group water molecules are considered attached to specific sorption sites on internal surfaces. In the other, the water-polymer system is considered a solution. King (1960) states that both approaches are partly correct: the "sorption sites" at low moisture contents, the "solution" at high moisture contents. Both approaches lead to equations, many of which either relate moisture content to relative humidity or can be rewritten in a form to give this relationship. Reviews of sorption theories have been prepared by McLaren and Rowen (1951), King (1960), Morton and Hearle (1962), Barrie (1968), and Venkateswaran (1970). Skaar (1972) has discussed a number of sorption theories with particular reference to the wood-water system. The sorption theories and their mathematical forms analyzed in this study are as follows:

(1) Hailwood and Horrobin (1946)

$$M = \frac{1800}{M_p}\left[\frac{Kh}{1-Kh} + \frac{\sum_{i=1}^{n} i(Kh)^i K_1K_2\cdots K_i}{1+\sum_{i=1}^{n}(Kh)^i K_1K_2\cdots K_i}\right] \quad (1)$$

where

M = per cent moisture content
h = relative vapor pressure
n = number of hydrates formed
M_p, K, K_1, K_2 . . . K_i = material parameters.

This model was evaluated for the one (n = 1) and two (n = 2) hydrate models, where the appropriate equations are:

for n = 1,

$$M = \frac{1800}{M_p}\left[\frac{Kh}{1-Kh} + \frac{K_1Kh}{1+K_1Kh}\right] \quad (2)$$

and for n = 2,

$$M = \frac{1800}{M_p}\left[\frac{Kh}{1-Kh} + \frac{K_1Kh + 2K_1K_2K^2h^2}{1+K_1Kh+K_1K_2K^2h^2}\right] \quad (3)$$

(2) Brunauer, Emmett, and Teller (BET) (1938)

$$m = \left[\frac{W_mCh}{1-h}\right]\left[\frac{1-(n+1)h^n + nh^{n+1}}{1+(C-1)h - Ch^{n+1}}\right] \quad (4)$$

where

m = fractional moisture content
h = relative vapor pressure
W_m, C, and n = material parameters.

(3) Brunauer, Emmett, and Teller plus a term to approximate the effect of capillary condensation. The Kelvin equation relates the radius of a capillary (assuming a cylindrical capillary) to the relative vapor pressure at which capillary condensation will occur.

$$r = \frac{2\sigma M'}{\rho RT\ln(1/h)} \quad (5)$$

where
r = radius of capillary
σ = surface tension of the liquid
M^1 = molecular weight of the liquid
p = density of the liquid
R = gas constant (1.987 cal-mole^{-1} - K^{-1})
T = temperature (K)
h = relative vapor pressure.

If V is the volume of capillary and ℓ is the total length of capillary, then

$$r = \sqrt{V/\pi\ell} = \frac{2\sigma M'}{\rho R T \ell n (1/h)} \quad (6)$$

Since the density of water is 1, the moisture content due to capillary condensed water, m_c, is

$$m_c = \frac{\pi\ell}{W_d}\left[\frac{2\sigma M'}{R T \ell n (1/h)}\right]^2 \quad (7)$$

where W_d is the dry weight. This term was added to the BET equation, and the combination tested.

(4) Malmquist (1958)

$$m = \frac{m_s}{1 + n\ [1/h - 1]^{i/3}} \quad (8)$$

where
m = fractional moisture content
h =relative vapor pressure
m_s, n, and i = material parameters.

(5) Freundlich (1922)

$$M = kh^{1/n} \quad (9)$$

where
M = per cent moisture content
h = relative vapor pressure
k and n = material parameters.

(6) Bradley (1936)

$$h = \exp\left[-(K_2 K_1^M + K_3)\right] \quad (10)$$

where
M = per cent moisture content
h = relative vapor pressure
K_1, K_2, K_3 = material parameters.

(7) King (1960)

$$A = \frac{BK_1 h}{1 + K_1 h} + \frac{DK_2 h}{1 - K_2 h} \quad (11)$$

where
A = moles of water
B, D, K_1, and K_2 = material parameters
h = vapor pressure.

To convert this model into moisture content terms, moisture content can be written as

$$M = \frac{1800A}{M_p} \quad (12)$$

where M_p is the molecular weight of polymer and 1800 is the molecular weight of water times 100. The sorption model then becomes:

$$M = \frac{1800}{M_p}\left[\frac{BK_1 h_o (h/h_o)}{1 + K_1 h_o (h/h_o)} + \frac{DK_2 h_o (h/h_o)}{1 - K_2 h_o (h/h_o)}\right] \quad (13)$$

where h_0 is the saturation vapor pressure

(8) Anderson and McCarthy (1963)

$$h = \exp\left[\left(\frac{-18BE}{RT}\right)\exp(Bm)\right] \quad (14)$$

where
h = relative vapor pressure
m = fractional moisture content
R = gas constant
T = temperature (K)
B and E = material parameters.

(9) Pierce (1929)

$$h = 1 - \left[1 - K\left(1 - \exp(-3Gm)\right)\right] \exp\left[-B\left(\exp(-3Gm) - 1 + 3Gm\right)\right] \quad (15)$$

where
h = relative vapor pressure

m = fractional moisture content
K, B, and G = material parameters.

An alternative to the preceding expressions is a polynomial of the form

$$m = a_0 + a_1 h + a_2 h^2 + a_3 h^3 + a_4 h^4 + a_5 h^5 + \ldots + a_n h^n \quad (16)$$

If enough terms are used, a polynomial could certainly offer a better fit than any of the models tested here. A check on the data at some of the temperatures indicated that at least a 5th degree polynomial (six parameters) would be necessary to match the fit offered by the best of the models from sorption theory. Since the greatest number of adjustable parameters in the sorption theory models is only five, it was decided not to include a polynomial in the analysis.

ANALYSIS

The sorption models outlined here were evaluated with the sorption data listed in Table 38 of the Wood Handbook by the U.S. Forest Products Laboratory (1955) and a nonlinear regression technique described by Scarborough (1962), which was extended to an iterative technique to improve the fit. The method involves making initial estimates of the model parameters and using a least-squares technique to make corrections to the parameters. The corrected parameters become new estimates, and the iterations continue until the values of the parameters and the sum of the squared deviations approach a constant value.

Nonlinear regression was necessary because of the form of the sorption models. The variables of moisture content and relative humidity are functionally related by expressions that include several parameters (such as M_p, K, K_1, and K_2 in the Hailwood and Horrobin model). The manner in which these parameters appear in the mathematical model is the basis for classifying two general types of regression analysis: linear regression and nonlinear regression. In linear mathematical models, the parameters are raised to only the first power and are connected only by addition or subtraction. Polynomials are examples of mathematical models that are linear in this sense. The calculations of linear regression are relatively simple and require no prior estimates of the values of the parameters.

In nonlinear mathematical models, the parameters are raised to other than the first power, are functionally connected other than by addition or subtraction, or each appears as an exponent. All of the sorption models listed are nonlinear in this sense. The calculations required in nonlinear regression are much more extensive than they are in linear regression, require an initial estimate of the parameters, and even then a long iterative process may be required before the technique converges on a minimum sum of squares and parameter values that are constant. Also, some models will not converge if the data are erratic or do not fit the model well.

Some nonlinear models can be transformed so that linear regression techniques can be used. However, the sum of squares that is minimized is no longer based on the dependent variable but rather some transformation of the dependent variable; this can distort the results. For example, the one-hydrate form of the Hailwood and Horrobin model can be transformed so that linear regression can be used (Hailwood and Horrobin 1946). This transformation, however, can result in the regression equation's predicting too low moisture contents in the high relative humidity range. Nonlinear regression applied to the untransformed equation considerably improves the fit in the high relative humidity range. In their original paper, Hailwood and Horrobin used this transformation and considered the poor agreement at high relative humidities in their evaluation of their theory. They attributed it to inadequacies in the model, whereas it was at least partially due to the method of analysis. The application of this nonlinear technique to the data presented in their paper does improve the fit at high relative humidities.

As mentioned, the BET equation was evaluated by two different methods. If n becomes infinite in the BET equation, it can be written as:

$$\frac{1}{W_m}\frac{h}{h_o - h} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\frac{h}{h_o} \qquad (17)$$

where

h = vapor pressure
h_o = saturation vapor pressure.

The first, or usual, method of evaluation (Brunauer, Emmett, and Teller 1938) of the BET equation is to plot $(l/W_m)(h/(h_o - h))$ versus h/h_o from about $h/h_o = 0.1$ to 0.4. This plot is usually linear in this range of vapor pressure, and linear regression is used to determine the slope of the curve $((C - 1)/(W_m C))$ and the intercept $(1/(W_m C))$; thus W, and C. The particular value of n that gives the best fit for the entire range of vapor pressure is then chosen. The second method of evaluating the BET equation is adding the capillary water term and using nonlinear regression to estimate all of the model parameters.

RESULTS

The results of analyzing the effectiveness of the sorption models are shown in Table 1. It should be understood that the results of the curve fitting are restricted to the data of the Wood Handbook, and caution should be used. The data for equilibrium moisture content-relative humidity-temperature, hence the relationships presented here, do not distinguish between adsorption and desorption. The original data were taken on Sitka spruce in a manner to establish an equilibrium moisture content for each relative humidity that is intermediate between the two extremes of the hysteresis loop. The details of the experimental procedures can be found in Stamm and Loughborough (1935). The values of each model parameter as well as any temperature-dependent constants in the models are listed for each temperature in Table 1. The total sum of the squared deviations (residual sum of squares) of the calculated moisture contents or relative humidities from the values given in the Wood Handbook of the U.S. Forest Products Laboratory is listed for each model, as well as the average of the absolute values of the deviations and the absolute value of the worst deviation between the calculated and Wood Handbook values. These three comparative statistics are based, according to the model, on either per cent moisture content or per cent relative humidity.

Of the models written in the form of moisture content as a function of relative vapor pressure, the King model and the two-hydrate form of the Hailwood and Horrobin model best fit the sorption data. The King model has a total sum of squares of 6.8, an average deviation of 0.1% moisture content, and the greatest deviation was 0.8% moisture content. The respective values for the two-hydrate form of the Hailwood and Horrobin model were 7.9, and 0.1% and 0.5% moisture content.

The . Freundlich model (not listed in Table 1) offered the worst fit, with a total sum of squares of 555, and an average and a largest deviation of 0.7% and 3.9% moisture content, respectively.

The BET analysis in which linear regression was used to determine C and W_m also gave a very poor fit. The calculated values of moisture content fall below the values of the Wood Handbook at the high relative vapor pressures. The sum of squares is 404; the average and the greatest deviations are 0.5% and 3.2% moisture content, respectively. The fit was considerably improved at high vapor pressures by adding the capillary water term and by using nonlinear regression. The total sum of squares was reduced to 38.0; the average and the greatest deviations are 0.2% and 0.9% moisture content, respectively.

The Malmquist model gave a fairly good fit, with a total sum of squares of 14.8 and an average and a greatest deviation of 0.1% and 0.6% moisture content, respectively.

Table 1.--Parametervalues of sorptionmodels

Temperature		Hailwood and Horrobin--one hydrate (n = 1)			Hailwood and Horrobin--two hydrates (n = 2)				King						Malmquist		
K	F	K	K_1	M_p	K	K_1	K_2	M_p	B	K_1 x 10^5	D	K_2 x 10^5	M_p	h_o x 10^{-5}	m_s	n	i
272	30	0.677	4.15	205	0.794	5.39	2.19	343	2.13	23.6	0.291	16.3	204	0.0562	0.262	1.72	2.26
274	35	.706	5.03	224	.810	6.31	2.34	362	1.72	28.7	.437	12.6	224	.0687	.282	1.94	2.13
280	45	.719	4.81	230	.830	5.03	3.56	392	2.20	17.6	.347	10.8	232	.0838	.304	2.25	2.07
282	50	.753	6.13	252	.834	7.18	2.39	385	1.62	20.6	.541	7.01	252	.123	.364	2.90	1.87
284	55	.735	5.74	243	.799	7.13	.97	317	1.14	23.9	.863	5.15	242	.148	.334	2.56	1.92
289	60	.733	5.49	241	.815	6.26	2.55	375	1.52	13.8	.606	4.68	241	.175	.318	2.41	1.99
291	65	.730	5.13	239	.815	5.14	3.16	381	1.67	9.34	.543	3.94	233	.210	.313	2.38	2.01
294	70	.746	5.80	252	.824	6.22	2.73	388	1.67	9.06	.554	3.39	251	.249	.342	2.75	1.89
297	75	.745	5.28	250	.820	5.82	2.49	383	1.56	7.47	.591	2.80	243	.296	.327	2.61	1.98
300	80	.757	5.76	261	.827	6.35	2.40	392	1.58	6.91	.612	2.39	260	.350	.347	2.87	1.90
302	85	.745	5.24	255	.821	5.23	2.86	394	1.78	4.64	.559	2.04	255	.410	.319	2.58	1.98
305	90	.754	5.87	266	.827	5.69	2.95	407	1.91	3.93	.502	1.79	264	.481	.335	2.80	1.90
308	95	.755	5.22	264	.827	5.30	2.68	403	2.08	2.86	.482	1.54	265	.562	.328	2.77	1.96
311	100	.762	6.09	278	.824	6.25	2.33	406	1.67	3.46	.607	1.28	278	.655	.339	2.95	1.87
314	105	.754	5.22	271	.818	5.55	2.17	398	1.94	2.27	.546	1.11	273	.761	.318	2.75	1.96
316	110	.772	5.81	289	.831	5.97	2.20	418	1.91	2.14	.551	.981	289	.876	.342	3.12	1.89
319	115	.773	5.68	293	.844	4.54	3.62	451	2.96	1.10	.357	.902	294	1.01	.348	3.28	1.86
322	120	.771	5.82	297	.826	5.67	2.19	425	1.92	1.54	.569	.727	296	1.17	.325	3.03	1.90
325	125	.779	6.11	309	.836	5.30	2.62	447	2.09	1.25	.542	.645	309	1.34	.336	3.26	1.86
328	130	.782	5.91	315	.838	5.28	2.53	456	2.15	1.04	.526	.568	313	1.53	.332	3.30	1.87
333	140	.782	5.74	327	.831	5.12	2.17	459	1.96	.843	.597	.427	322	1.99	.305	3.11	1.93
339	150	.790	5.49	345	.842	3.84	2.97	494	2.31	.517	.575	.335	345	2.57	.301	3.27	1.95
344	160	.799	5.89	370	.850	3.33	3.64	531	3.07	.299	.493	.271	371	3.26	.303	3.52	1.91
350	170	.806	5.93	393	.864	1.06	12.68	596	6.62	.100	.340	.224	393	4.13	.305	3.78	1.89
355	180	.807	5.61	411	.847	3.22	2.89	563	2.52	.218	.618	.166	409	5.19	.266	3.41	2.01
361	190	.814	5.58	438	.852	3.03	2.85	593	2.77	.116	.426	.137	340	6.43	.264	3.61	2.01
366	200	.818	4.72	451	.844	3.86	1.24	561	2.26	.143	.721	.108	451	7.95	.252	3.66	2.10
372	210	.821	3.82	462	.843	3.19	1.07	562	2.26	.102	.761	.088	462	9.72	.241	3.74	2.19
Residual sum of squares		19.2			7.9				6.8						14.8		
Average deviation		.1[a]			.1[a]				.1[a]						.1[a]		
Greatest deviation		.8[a]			.5[a]				.8[a]						.6[a]		

Table 1.--Parameter values of sorption models--continued

Temperature		BET C and W_m from linear regression			BET plus capillary water (all parameters from nonlinear regression)					Pierce			Anderson and McCarthy		Bradley		
K	F	C	W_m	n	C	W_m	n	$\ell/W_d \times 10^{-10}$	σ dynes/centimeter	K	B	G	-B	-E	K_1	K_2	$K_3 \times 10^1$
272	30	4.92	0.0645	5.2	4.33	0.0683	3.80	3.78	75.7	0.455	4.38	1.78	16.7	6.22	0.842	3.50	0.190
274	35	6.42	.0597	5.9	5.49	.0631	4.28	3.05	75.3	.491	5.96	1.53	17.2	6.36	.835	3.70	.328
280	45	4.79	.0647	5.3	5.17	.0623	4.55	2.35	74.6	.657	7.22	1.34	17.1	6.31	.838	3.54	.190
282	50	6.64	.0591	6.1	7.10	.0573	5.17	2.20	74.2	.176	2.06	3.05	17.4	6.48	.829	3.79	.451
284	55	7.91	.0561	6.7	8.27	.0548	6.01	1.22	73.8	.160	1.95	3.18	17.3	6.51	.833	3.70	.309
289	60	6.68	.0585	6.3	7.11	.0564	5.73	1.23	73.4	.332	3.77	2.07	17.5	6.56	.834	3.68	.235
291	65	5.25	.0623	5.8	7.11	.0553	6.03	.990	73.0	.450	4.72	1.78	17.3	6.51	.838	3.55	.133
294	70	6.31	.0587	6.3	7.67	.0546	5.93	1.23	72.6	.238	2.62	2.64	17.6	6.57	.833	3.65	.240
297	75	5.23	.0610	6.0	7.36	.0536	6.31	.945	72.2	.324	3.01	2.38	17.5	6.50	.833	3.56	.245
300	80	5.94	.0582	6.3	7.94	.0525	6.35	1.07	71.8	.212	2.12	3.06	17.8	6.53	.828	3.63	.318
302	85	5.23	.0593	6.1	7.60	.0522	6.46	.831	71.3	.361	3.31	2.27	17.7	6.47	.833	3.50	.181
305	90	6.89	.0547	6.8	7.97	.0517	6.29	.975	70.9	.269	2.75	2.63	18.1	6.51	.828	3.59	.207
308	95	5.23	.0574	6.3	7.21	.0515	6.37	1.01	70.5	.371	3.02	2.42	18.0	6.41	.829	3.48	.250
311	100	6.48	.0538	6.8	9.73	.0482	7.05	.698	70.0	.183	1.91	3.44	18.5	6.43	.825	3.56	.232
314	105	5.96	.0536	6.8	7.76	.0493	6.73	.785	69.6	.324	2.58	2.75	18.3	6.32	.828	3.41	.184
316	110	6.42	.0514	7.1	8.64	.0472	6.98	.854	69.2	.195	1.63	3.86	18.7	6.26	.820	3.48	.307
319	115	6.13	.0510	7.1	7.76	.0475	6.69	.990	68.7	.291	2.16	3.17	18.7	6.16	.822	3.37	.222
322	120	6.65	.0492	7.3	9.93	.0447	7.46	.612	68.2	.200	1.64	3.95	19.1	6.13	.820	3.39	.217
325	125	6.33	.0491	7.2	11.0	.0432	7.67	.645	67.8	.153	1.32	4.67	19.3	6.04	.816	3.38	.253
328	130	5.96	.0484	7.3	9.79	.0428	7.60	.691	67.3	.174	1.33	4.69	19.6	5.94	.813	3.35	.283
333	140	6.39	.0453	7.6	12.0	.0397	8.33	.435	66.3	.179	1.26	5.03	20.1	5.73	.810	3.24	.228
339	150	5.59	.0440	7.7	13.4	.0372	8.78	.450	65.3	.231	1.28	5.03	20.3	5.45	.807	3.08	.225
344	160	6.09	.0411	8.1	14.5	.0353	8.83	.521	64.3	.189	1.05	6.09	21.0	5.24	.801	3.02	.228
350	170	4.54	.0418	7.5	13.4	.0338	8.80	.605	63.3	.314	1.38	5.02	21.5	4.99	.798	2.88	.188
355	180	6.23	.0362	8.8	31.9	.0303	10.2	.307	62.2	.193	.888	7.42	22.3	4.76	.790	2.83	.211
361	190	5.73	.0351	8.7	37.5	.0285	10.5	.342	61.1	.128	.629	10.2	22.9	4.52	.783	2.74	.241
366	200	5.22	.0339	8.9	49.4	.0269	11.2	.328	60.0	.051	.380	16.2	23.0	4.27	.779	2.60	.287
372	210	5.09	.0314	9.7	38.4	.0256	11.7	.321	58.9	.108	.391	15.8	23.0	4.03	.779	2.40	.280
Residual sum of squares			404				38.0				230		379		233		
Average deviation			.5[a]				.2[a]				.4[b]		.6[b]		.4[b]		
Greatest deviation			3.2[a]				.9[a]				1.6[b]		2.8[b]		2.4[b]		

[a] By percent moisture content.

[b] By percent relative humidity.

The model did well for most of the moisture content range except below about 4%, where it predicted moisture contents that were too high.

The Pierce isotherm gives the best fit of the expressions written in the form of relative vapor pressure as a function of moisture content. The total sum of squares is 230; the average and the greatest deviations are 0.4% and 1.6% relative humidity, respectively. The Bradley isotherm also gives a fairly good fit; analysis is simpler than it is for the Pierce isotherm. The total sum of squares is 233, whereas the average and the greatest deviations are 0.4% and 2.4% relative humidity, respectively.

Since the parameters of the models are temperature-dependent, it is useful analytically to relate the parameters to temperature so that the moisture content-relative humidity relationship can be completely independent of any tables and so that values intermediate between tabulated temperature values can be calculated. This has been done for the one-hydrate form of the Hailwood and Horrobin model (Simpson 1971), and is done here for the best model of each of the functional forms, i.e., moisture content as a function of relative humidity and vice versa. The two-hydrate form of the Hailwood and Horrobin theory was judged the most accurate of the group written in the form of moisture content as a function of relative humidity. Even though the Hailwood-Horrobin model results in a slightly higher total sum of squares than does the King model, it has the same average deviation and its greatest deviation is lower. Furthermore, with one less adjustable parameter than the King model, it is easier to use. The temperature dependence of the parameters can be represented as follows:

$$M_p = 330 + 0.452T + 0.00415T^2 \quad (18)$$

$$K = 0.791 + 0.000463T - 0.000000844T^2 \quad (19)$$

$$K_1 = 6.17 + 0.00313T - 0.0000926T^2 \quad (20)$$

$$K_2 = 1.65 + 0.0202T - 0.0000934T^2 \quad (21)$$

where T is in F.

When the isotherms are calculated with these values of the four parameters, the average deviation is still 0.1% moisture content and the greatest deviation is 0.8% moisture content compared to the 0.5% when the actual parameters are used.

The Pierce model gave the best fit of the models written in the form of relative humidity as a function of moisture content. However, the temperature-dependence of the parameters is somewhat erratic, and some of the smoothed values that result from the regression are far enough from the actual values to cause large deviations when used in the sorption model. The Bradley model was almost as good as the Pierce model, and the smoothed values of the parameters worked well in the model. Their temperature dependence can be represented as follows:

$$K_1 = 0.839 + 0.0000202T - 0.00000156T^2 \quad (22)$$

$$K_2 = 3.56 + 0.00392T - 0.0000445T^2 \quad (23)$$

$$K_3 = 0.0219 + 0.0000164T \quad (24)$$

where T is in F.

When the isotherms are calculated from these values the average deviation is 0.8% relative humidity and the greatest deviation is 2.7% (compared with 0.4% and 2.4% with the actual parameters).

SUMMARY

A number of sorption theories have been tested as analytical expressions that relate equilibrium moisture content to relative humidity. Testing included fitting (by non-

linear regression) the sorption data of the U.S. Forest Products Laboratory (1955) to the various expressions. The expressions were judged solely on how well they could predict the data for the relationship of moisture content to relative humidity. The two-hydrate form of the Hailwood and Horrobin theory (1946) and the King theory (1960) are the most accurate of the group that are written as moisture content equal to a function of relative humidity. The Brunauer, Emmett, and Teller (BET) (1938) theory is not satisfactory for prediction purposes. An attempt was made to improve the BET theory for prediction purposes by adding a term that would account for capillary condensed water. This greatly improved the fit, but the model still was not as effective as the Hailwood and Horrobin model or the King model.

Of the models written as relative humidity equal to a function of moisture content, the Pierce (1929) model and the Bradley (1936) model predict relative humidity the most accurately.

REFERENCES

ANDERSON, N. T., AND J. L. MCCARTHY. 1963. Two-parameter isotherm equation for fiber-water systems. Ind. Eng. Chem. Process Des. Develop. 2:103–105.

BARRIE, J. A. 1968. Water in polymers. *In* J. Crank and G. S. Park, eds., Diffusion in polymers. Academic Press, New York.

BRADLEY, R. S. 1936. Polymolecular adsorbed films. Part II. The general theory of the condensation of vapors on finely divided solids. J. Chem. Soc. 1799–1804.

BRUNAUER, S., P. H. EMMETT, AND E. TELLER. 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60:309–319.

CHOONG, E. T. 1963. Movement of moisture through a softwood in the hygroscopic range. For. Prod. J. 13(11):489–498.

FREUNDLICH, H. 1922. Colloid and capillary chemistry. E. P. Dutton and Co., New York.

HAILWOOD, A. J., AND S. HORROBIN. 1946. Absorption of water by polymers: Analysis in terms of a simple model. Trans. Faraday Soc. 42B:84–102.

HEARMON, R. F. S., AND J. M. PATON. 1964. Moisture content changes and creep of wood. For. Prod. J. 14(8):357–359.

KING, G. 1960. Theories of multi-layer adsorption. *In* J. W. S. Hearle and R. H. Peters, eds., *Moisture in textiles*. Textile Book Publ. Inst., Inc., New York.

KÜBLER, H. 1957. Studies on the movement of moisture through wood. Holz Roh- Werkst. 15(11):453–468.

MALMQUIST, L. 1958. Sorption as deformation of space. Svenska Traforsknings Institut. Träteknik Medd. 983, Stockholm.

MCLAREN, A. D., AND J. W. ROWEN. 1951. Sorption of water vapor by proteins and polymers: A review. J. Polymer Sci. 7:289–324.

MORTON, W. E., AND J. W. S. HEARLE. 1962. Physical properties of textile fibres. Text. Inst., Butterworths, London.

PIERCE, F. T. 1929. A two-phase theory of the absorption of water vapor by cotton cellulose. J. Text. Inst. 20:T133–T150.

SCARBOROUGH, J. F. 1962. Numerical mathematical analysis. 5th ed. Johns Hopkins Press, Baltimore.

SIMPSON, W. T. 1971. Equilibrium moisture content prediction for wood. For. Prod. J. 21(5):48, 49.

SKARR, C. 1954. Analysis of methods for determining the coefficients of moisture diffusion in wood. For. Prod. J. 4(6):403–410.

SKARR, C. 1972. Water in wood. Syracuse Wood Science Series, Syracuse Univ. Press, Syracuse, N.Y.

STAMM, A. J., AND W. K. LOUGHBOROUGH. 1935. Thermodynamics of the swelling of wood. J. Phys. Chem. 39(1):121–132.

U.S. FOREST PRODUCTS LABORATORY. 1955. Wood handbook. U.S. Dep. Agr. Handb. No. 72. For. Prod. Lab., For. Serv., Sup. Doc., Washington, D.C.

VENKATESWARAN, A. 1970. Sorption of aqueous and nonaqueous media by wood and cellulose. Chem. Rev. 70(6):619–637.

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