SORPTION OF WATER VAPOR BY

PAPERMAKING MATERIALS

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By C. O. SEBORG
Assistant Chemist

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Abstract

After the original desorption hysteresis in a highly beaten spruce sulphite pulp was found to persist unchanged in magnitude upon repeated sorption cycles over a range of relative humidity from 0 to 95 percent. The ratio of adsorption equilibrium moisture contents to the corresponding desorption values of a wide variety of papermaking pulps and stuffs over a range of relative humidity from 12 to 88 percent, inclusive, is apparently a constant which is slightly higher than the corresponding values for lignins, kapok, and wood. The theory of hysteresis is discussed.

Introduction

The hysteresis observed in the sorption of water vapor by cellulosic materials is now generally accepted as an inherent property of these materials (9). Urquhart and Williams (15, 16, 17) established the actuality of hysteresis, which was later confirmed by Campbell (1), Pidgeon and Maass (6), and Sheppard (10). The most recent review of the subject is found in a publication by Stamm (13).

Practically all the published data on sorption hysteresis have dealt with the hysteresis observed when cellulosic material is subjected to original desorption below fiber saturation to dryness followed by

adsorption. Under such conditions the adsorption isotherm does not join the desorption curve even at high humidities and the second desorption isotherm shows lower moisture content values at corresponding humidities over a considerable range of humidity, joining the original desorption curve only at approximately 30 percent relative humidity. It has been theorized that subsequent sorption cycles would show moisture content values agreeing with those of the second desorption and first adsorption curves, but actual confirmatory data are meager. In view of the importance of the effects of moisture on papermaking materials, the Forest Products Laboratory has made a study of sorption isotherms during the course of several consecutive sorption cycles. This paper presents the results of the study.

Procedure

The method and apparatus used have been described previously (8, 9). Using this procedure, four samples of a commercial spruce sulphite pulp which had been highly beaten in a bronze-tackle beater were subjected to seven consecutive sorption cycles (exclusive of the original desorption) with the same humidities at the extremes of each cycle. The sorption cycle was begun at dryness, passed stepwise through adsorption to equilibrium at 12, 33, 55, 63.5, 74, 85, and 95 percent relative humidity, then similarly through desorption to dryness again. The humidity was not changed until after the quartz spiral balances showed no change in length for 24 hours. At very low and very high humidities an additional period of 48 hours of conditioning was allowed to be certain that moisture equilibrium was established. Similarly, single sorption cycles were run, using unprocessed and processed sulphite and kraft pulps from different species of wood, holocellulose, kapok, cuprammonium lignin, sulphuric acid lignin, and unextracted and extracted wood. The holocellulose was prepared by the method of Ritter and Kurth (7), the cuprammonium lignin by the method of Freudenberg (2), and the sulphuric acid lignin by the method of Sherrard and Harris (12). Loblolly pine kraft and sulphite pulps containing practically all spring-wood or all summerwood were prepared from rings of springwood or summerwood isolated by a band saw.

Hysteresis Under Consecutive Sorption Cycles

The discussion is herein specifically limited to the hysteresis effect observed after the original desorption had been effected, and at 25° C. The sample, dried over phosphorous pentoxide at 25° C. was allowed to adsorb moisture stepwise to equilibrium at 95 percent relative humidity, whereupon it was desorbed stepwise to its original state. The second cycle was then begun, and so on until all the consecutive cycles were completed.

Urquhart and coworkers (14, 15) reported reproducible results with cotton for successive sorption cycles, although the values for the separate cycles were not indicated. Campbell (1) made one and one-half sorption cycles (omitting the original desorption curve, which is not considered in this discussion) on a kraft pulp.

The results obtained in the present study in reference to the consecutive sorption cycles are recorded in Table 1. The average moisture content of four samples of the highly beaten commercial spruce sulphite pulp for each cycle at each of the several humidities is given.

The data show no tendency for the hysteresis effect to vary during the repeated sorption cycles. Small irregular differences in the values were observed for the same relative humidity during the different sorption cycles. Irregularities of this magnitude were often found with the original sorption apparatus (9). They do not, however, affect the trend of the results or the conclusions drawn.

Hysteresis Constant

Another way of showing any tendency of the hysteresis to change is a comparison of the ratios of the adsorption moisture content to the desorption moisture content during the different sorption cycles at corresponding relative humidities. These ratios are also given in Table 1. Any tendency of the hysteresis effect to diminish would at once be evident by the ratio approaching unity. No such tendency was observed. In fact the ratios are sufficiently constant to be called the "hysteresis constant." The constant holds over a range of relative humidities from 12 to 88 percent, but obviously cannot hold over the entire range of humidities covered by the hysteresis loop because the values at the extremes are common to both the adsorption and desorption curves; and, therefore, at these points the ratio must be unity.

Hysteresis constants for a wide range of materials are listed in Table 2. Among these, as indicated in the table, are six values calculated from published sorption data. These calculations were made from smooth curves drawn through the plotted data of Urquhart and Williams (18) on cotton and of Campbell (1) on kraft pulps. It may be noted that there is good agreement between the constants thus calculated and those found in this investigation for the several pulps and stuffs.

The values of the ratios for the cotton over the range of 20 to 90 percent relative humidity showed more of a tendency to approach unity at the extremes of the hysteresis loop than in the case of the pulps and stuffs. This pinching in at the ends of the hysteresis loop may have been caused by the establishment of equilibrium under slightly oscillating conditions of adsorption and desorption. Such conditions could occur in the closed system used by Urquhart and Williams (18) in which temperature fluctuations of 0.5° C. were observed.

Table 1.--Average equilibrium moisture contents and hysteresis constants during repeated sorption cycles of four samples of an unbleached, highly beaten, commercial spruce sulphite[1]

Relative humidity at 25° C.	Moisture content (percent on dry basis) for sorption cycles number --							
	1	2	3	4	5	6	7	Average
Percent								
Adsorption								
12	3.1	3.2	3.2	3.3	3.2	3.1	3.2	3.1
33	5.2	5.3	5.4	5.4	5.2	5.1	5.3	5.3
55	8.3	8.4	8.4	8.2	8.4	8.4	8.4	8.3
74	11.5	11.5	11.6	11.6	11.6	11.5	11.6	11.6
88	17.1	17.4	17.3	17.1	17.1	17.2	17.2	17.2
95	26.5	26.5	26.5	26.2	26.0	26.1	26.1	26.3
Desorption								
88	21.0	20.7	20.7	20.7	20.9	20.7	20.5	20.7
74	13.7	13.7	13.7	13.6	13.7	13.8	13.7	13.7
55	9.6	9.6	9.7	9.6	9.6	9.7	9.7	9.6
33	6.1	5.9	6.0	6.2	6.1	6.0	6.0	6.1
12	3.7	3.7	3.6	3.8	3.7	3.7	3.7	3.7
Hysteresis Constants[2]								
12	0.84	0.86	0.89	0.87	0.86	0.84	0.86	0.84
33	.85	.90	.90	.87	.85	.85	.88	.87
55	.86	.88	.87	.85	.88	.87	.87	.86
74	.84	.84	.85	.85	.85	.83	.85	.85
88	.82	.84	.84	.83	.82	.83	.84	.83

Final average hysteresis constant............ 0.85

[1] Schopper-Riegler freeness 100.

[2] Ratio of adsorption equilibrium moisture content to desorption equilibrium moisture content.

Table 2.--<u>Hysteresis constants of pulps, two lignins, and other cellulosic materials</u>

Materials	Average hysteresis constant[1]
Sulphuric acid lignin..	0.78
Cuprammonium lignin...	.79
Kapok, raw, unwashed..	.81
Western hemlock wood, unextracted...............................	.84
Western hemlock wood, extracted with ether.....................	.84
Western hemlock wood, extracted with alcohol benzol............	.84
Western hemlock wood, extracted with hot water.................	.82
Loblolly pine kraft, unbeaten..................................	.85
Loblolly pine kraft, highly beaten............................	.86
Loblolly pine kraft, unbeaten 90 percent springwood...........	.87
Loblolly pine kraft, unbeaten 90 percent summerwood...........	.87
Loblolly pine sulphite, unbeaten, 100 percent springwood......	.86
Loblolly pine sulphite, unbeaten, 100 percent summerwood......	.88
Silver fir kraft, unbeaten.....................................	.88
Silver fir kraft, highly beaten...............................	.85
Silver fir sulphite, unbeaten.................................	.87
Silver fir sulphite, highly beaten............................	.85
Silver fir sulphite, 8 percent bleach.........................	.87
Silver fir sulphite, 15 percent bleach........................	.86
Silver fir sulphite, 25 percent bleach........................	.87
Spruce sulphite, commercial, highly beaten....................	.85
Western hemlock, sulphite, unbeaten...........................	.87
Holocellulose...	.87
Unbeaten kraft, by Campbell....................................	.87
Beaten kraft, by Campbell.....................................	.88
Raw sea island cotton by Urquhart and Williams................	.87
Raw Texas cotton by Urquhart and Williams.....................	.84
Water boiled sea island cotton by Urquhart and Williams.......	.89
Water boiled Texas cotton by Urquhart and Williams............	.86

[1] Obtained by averaging the constants for each relative humidity over the whole range of humidities studied, 12 to 93 percent.

The ratios calculated from Campbell's (1) data on unbeaten and beaten kraft pulp up to 70 percent relative humidity agree well with the ratios obtained in this investigation. Ratios in the case of Campbell's data were not calculated above 70 percent relative humidity because he reported no moisture content values between 70 and 94 percent relative humidity.

A comparison of the hysteresis constants of the two lignins, kapok, and wood with those of the pulps, stuffs, and cotton suggests a possible influence of the nature of the material on this ratio. For the papermaking materials as a class, however, the small variations observed cannot, at the present, be considered significant. In fact, the agreement in this class of materials is remarkably good in view of their heterogeneous nature.

Urquhart (14) attributes hysteresis to the effect of the free secondary-valence bonds of the hydroxyl groups of the cellulose molecules. In the original water-soaked condition, the free hydroxyl groups are practically all satisfied by water. Upon drying, water is removed from the hydroxyl groups, shrinkage occurs, and the secondary valencies of proximate hydroxyl groups become mutually satisfied. Upon adsorption, part of the hydroxyl groups that have mutually satisfied one another are not freed for water adsorption, thus giving a decreased amount of adsorption.

According to Sheppard (10, 11), probably no more than 5 percent water is held by primary sorption to the hydroxyl groups and there is a residual sorption independent of the presence of free hydroxyls. He concluded from his work on the esterification and etheration of cellulose that the additional sorption can be attributed to the condensation of water vapor in the inner capillaries in the fine structure of the cellulose. This, he says, probably accounts for the bulk of the moisture absorbed above 50 percent relative humidity.

Whatever the sorption mechanism responsible for hysteresis may be it is shown to function with precision, not only in maintaining a constant ratio between adsorption and desorption but also in its ability to reproduce the same moisture contents during repeated sorption cycles.

When the arithmetical differences between the desorption and adsorption moisture contents of the spruce sulphite pulp (Table 1) at corresponding humidities were calculated as a percentage of the desorption moisture content an approximately constant value of 14 was obtained. The same percentage difference was observed for the pulps and cotton listed in Table 2. This difference is independent of the equilibrium moisture content between 12 and 88 percent relative humidity. According to Urquhart's theory of sorption this difference may be related to the ratio of the hydroxyls involved in adsorption and desorption. It is difficult, however, to believe that the chance coupling and uncoupling of the hydroxyl groups as a result of shrinking and swelling takes place with such uniformity and

with such reproducibility, especially at the higher relative humidities where capillary condensation becomes increasingly important.

It may be argued that the number of hydroxyl groups available for desorption and adsorption are the same but that these groups are less active during adsorption. It is not easy, however, to conceive of any mechanism causing such a change in the degree of activity of such groups.

Evidence that hysteresis cannot be attributed to the hydroxyl groups alone is shown by Sheppard (10) who found that cellulose acetate (about 40 percent acetyl), which has approximately 90 percent of the hydroxyls acetylated, had a "considerable hysteresis in the adsorption-desorption cycle."

According to Urquhart's theory the magnitude of sorption hysteresis in the case of cellulose and lignin is likely to be very different considering the difference in number and reactivity of the hydroxyl groups of the two materials. Haworth (5) shows that cellulose has three hydroxyl groups, assuming 162 as the molecular weight of a unit of glucose anhydride in the chain of cellulose units, whereas Harris and coworkers (3, 4) show that softwood lignin has five hydroxyl groups, assuming 900 as the molecular weight of lignin. The three hydroxyl groups of cellulose have approximately the same degree of reactivity whereas the hydroxyl groups of lignin vary among themselves in this respect. The hydroxyl groups of cellulose and lignin not only differ as to number but also differ as to reactivity. Lignin contains, in addition to the five hydroxyl groups, five methoxyl groups which are also polar and therefore likely influence the adsorption of moisture.

Furthermore, it is not likely that either the degree or the mechanics of the swelling or shrinking, which is important in Urquhart's theory, is the same for lignin as for cellulose. It therefore seems unlikely that the ratio of the number of hydroxyl groups available during adsorption to those during desorption would be the same for the two materials.

The fact that the hysteresis ratio of lignin is shown to be not greatly different from that of cellulose, in spite of the difference in number and reactivity of the hydroxyl groups of the two materials as well as the probable difference in the degree and mechanics of swelling and shrinking, indicates that Urquhart's theory of the mechanism of sorption hysteresis is inadequate.

Although the author has no satisfactory hypothesis to advance, it seems apparent that any full explanation of hysteresis should include a consideration of some additional factor of a physical nature. Regardless of its nature, its effect on the sorption of moisture by pulps, as evidenced by the hysteresis constant, persists unaltered even after bleaching (chemical processing) and extreme beating (physical processing), though both of these treatments are known (8) to modify the equilibrium moisture content.

Conclusions

After the original desorption, hysteresis was found to persist unchanged in magnitude upon repeated sorption cycles on a highly beaten spruce sulphite pulp over a range of relative humidity of 0 to 95 percent.

The ratio of adsorption equilibrium moisture contents to those of desorption of a wide variety of papermaking pulps and stuffs over a range of 12 to 88 percent relative humidity is apparently a constant. This constant is slightly higher for pulps and stuffs than for kapok, wood, cuprammonium lignin, and sulphuric acid lignin.

The hysteresis constant is believed to be associated with some physical force or molecular characteristic of the cellulose molecule associated with the mechanism of sorption. The theory that sorption hysteresis can be attributed to the difference in number of hydroxyl groups available for attachment of water molecules during adsorption and desorption appears inadequate. An adequate explanation of the hysteresis phenomenon should include the consideration of some additional factor of a physical nature.

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