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**SORPTION OF WATER VAPOR BY
PAPER-MAKING MATERIALS**

1 - Effect of Beating

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Synopsis

Measurements were made of the moisture content-relative humidity and moisture content-electrical conductivity relationships of pulps and stuffs.

An apparatus was designed for measuring the relative humidity relationship of materials at atmospheric pressure, using a method in which air, humidified by passing through various saturated salt solutions to give the desired relative humidities, was circulated about the adsorbent material suspended from a sensitive quartz-helix balance. The extensions of this balance were measured with a cathetometer. The hydration (hygroscopicity) of the pulp, which the regularity of the curves showed to be physical rather than chemical, was not affected by beating.

Electrical conductivity-moisture content relations likewise showed no differences between beaten and unbeaten pulp.

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The so-called hydration of the paper industry is not a true hydration. It is probably a phenomenon of fiber-fiber bonding rather than of fiber-water bonding.

Introduction

The objectives in this series of studies are to determine the hygroscopicity of pulps, stuffs, and the various components of wood under normal atmospheric conditions; to determine the relations of the sorption hydration (hygroscopicity) to the so-called hydration of the paper industry, that is, the change in properties of fibers produced by beating which in the past has been assumed to result from a change in their ability to retain water; to determine the extent to which this sorption hydration affects the fiber-bonding properties; and to critically study the desorption-adsorption hysteresis.

The various materials to be studied are sulfite, kraft, soda, and semi-chemical pulps; bleached pulps; beaten pulps; isolated wood components, such as lignin, Cross and Bevan cellulose, and alpha cellulose from both pulp and Cross and Bevan cellulose; and furnishing materials, such as coatings, sizings, and fillers.

This paper deals only with the effect of beating on the sorptive hydration of a sulfite pulp. The word "sorption" is the same as used by McBain (8) to include both adsorption and absorption phenomena.

Previous Sorption Studies

A number of investigators have published papers on subjects pertaining to the hysteresis of the adsorption and desorption of water vapor by various materials, which ranged from silica gel to textiles and paper (1, 2, 6, 7, 11, 12, 13, 15, 16, 17, 18, 19).

All of these investigators, with the exception of Patrick (11) and his co-workers, have obtained definite hysteresis effects. The hysteresis effect in non-elastic gels, such as silica gel, has been attributed by Zsigmondy (19) to a difference under adsorption and desorption conditions in the curvatures of the menisci of the liquid filling the capillary spaces. These differences in curvature are supposedly due to differences in the wetting of the capillary walls, which are less readily wetted after drying. A somewhat different explanation, by Urquhart and Williams (17), is more applicable to elastic gels, such as cellulose, in which the swelling follows adsorption from the start. These investigators attribute the effect to 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. When the cellulose is dried, these hydroxyl groups are freed and, as a result of the shrinking, pairs are drawn together so that the individual groups mutually satisfy each other. Upon adsorption, part of the hydroxyl groups that have mutually satisfied each other are not freed for water adsorption, thus giving a decreased adsorption.

Patrick (11), on the other hand, asserts that the hysteresis effect obtained by all of the other investigators is due to the presence of non-condensable gases, even though a number of them have worked in evacuated systems. Patrick describes the experiments of Davis and Barclay, in which the greatest precautions were taken to remove the last traces of air from their silica gel. Their results not only show the absence of hysteresis effects but the curves -- vapor pressure against moisture content -- are parabolic rather than sigmoid in shape. Holmes and Elder (4) have studied the adsorption of benzene on silica gels prepared by different methods that gave different porosities. With a Patrick silica gel they obtained a parabolic curve; with more porous gels, sigmoid curves; and with the most porous gels, parabolic curves with a reverse curvature.

It thus appears quite probable that the complete reversibility of adsorption, as obtained by Patrick, may hold only for the low-porosity gels that show parabolic sorption curves. Even if Patrick is correct in stating that the hysteresis effect in non-elastic gels is entirely due to the fact that the last traces of non-condensable gases have not been removed, this does not necessarily imply that the hysteresis shown by elastic gels, such as cellulose, is also due to the presence of non-condensable gases. Furthermore, since cellulose cannot be rigorously degassed without decomposition, the hysteresis effect may just as well be accepted as a property of the system as to be attributed to experimental error.

There seems to be little object, therefore, in working in an evacuated system except when diffusion of the vapors is depended upon for the attainment of equilibrium.

It thus seemed not only justifiable but also advantageous to use for the present experimental work an atmospheric-pressure system in which air, humidified by passing through different saturated salt solutions to give the desired relative humidities (3), is circulated about the adsorbent material suspended from a sensitive quartz helix balance (8) the extension of which is measured with a cathetometer. With such a system the measurements are normally made under conditions corresponding to those for which the data will be used. The method has a further advantage in that each equilibrium point is obtained under constant vapor-pressure conditions. In all of the researches cited, in which a vacuum system was used (the recent work of Pidgeon and Maas (12) is excepted), a definite

volume of water vapor was admitted, and, as adsorption progressed, the vapor pressure diminished. Under such a system the most readily accessible part of the material may initially adsorb more water vapor than the final equilibrium amount, thus permitting a subsequent combination of both adsorption and desorption to take place at the same time. Such a condition might readily affect the normal hysteresis. For the same reason a number of simultaneous determinations cannot be made in a single apparatus under changing vapor pressures, whereas they can be made when the humidity and temperature are held constant.

The more recent measurements of Pidgeon and Maas (12) have been made at a constant vapor pressure in an evacuated system by holding the temperature of the vapor-supply bulb (which is left open to the rest of the system after evacuation) below that of the rest of the sorption apparatus by an amount that gives the desired relative humidity in the sorption system. Under these conditions the accuracy with which the relative humidity is maintained depends directly upon the accuracy with which the two temperatures are held. At high relative humidities, 95 per cent for example, a deviation of 0.2° C. from the required temperature difference between the vapor-supply bulb and the sorption system at 25° C. causes a deviation in relative humidity of 1.2 per cent. When saturated salt solutions are used to maintain the relative humidity, the effect of temperature deviation is much less. For example, a saturated potassium sulfate solution that gives approximately the relative humidity just mentioned (95 per cent) would require a temperature deviation of 30° C. to cause the same deviation (1.2 per cent) in relative humidity (5).

Apparatus and Experimental Methods

Sorptive Method

The apparatus used in this part of the research is shown in Figure 1. Four simultaneous measurements were made in the sorption tubes f, g, h, and i. These tubes, connected in parallel at the distributing head d, were in series with d, the spray trap c, and the humidifying train b. The humidified air, after circulating about the test samples suspended from quartz helices, was discharged through the glass tubing of the hooks j, k, l, and m, that were sealed into the top of the sorption tubes. The conditioning tubes were immersed in a thermostatic water bath having glass windows on two opposite faces. The temperature of the bath was maintained at $25^{\circ} \pm 0.02^{\circ}$ C. and that of the room at $23^{\circ} \pm 1.0^{\circ}$ C. In making measurements at high relative humidities, the slight drop in temperature of the exhaust air was sufficient to cause condensation in the upper part of the exit tubes, which were substantially at room temperature; so in order to prevent this condensation heat was applied

Figure 1.--Diagram of sorption apparatus

a; inlet
b; humidifying chambers
c; spray trap
d; manifold
e; stop cocks
f, g, h, and i; sorption chambers
j, k, l, and m; hooks of glass tubing
n, o, p, and q; local heating elements

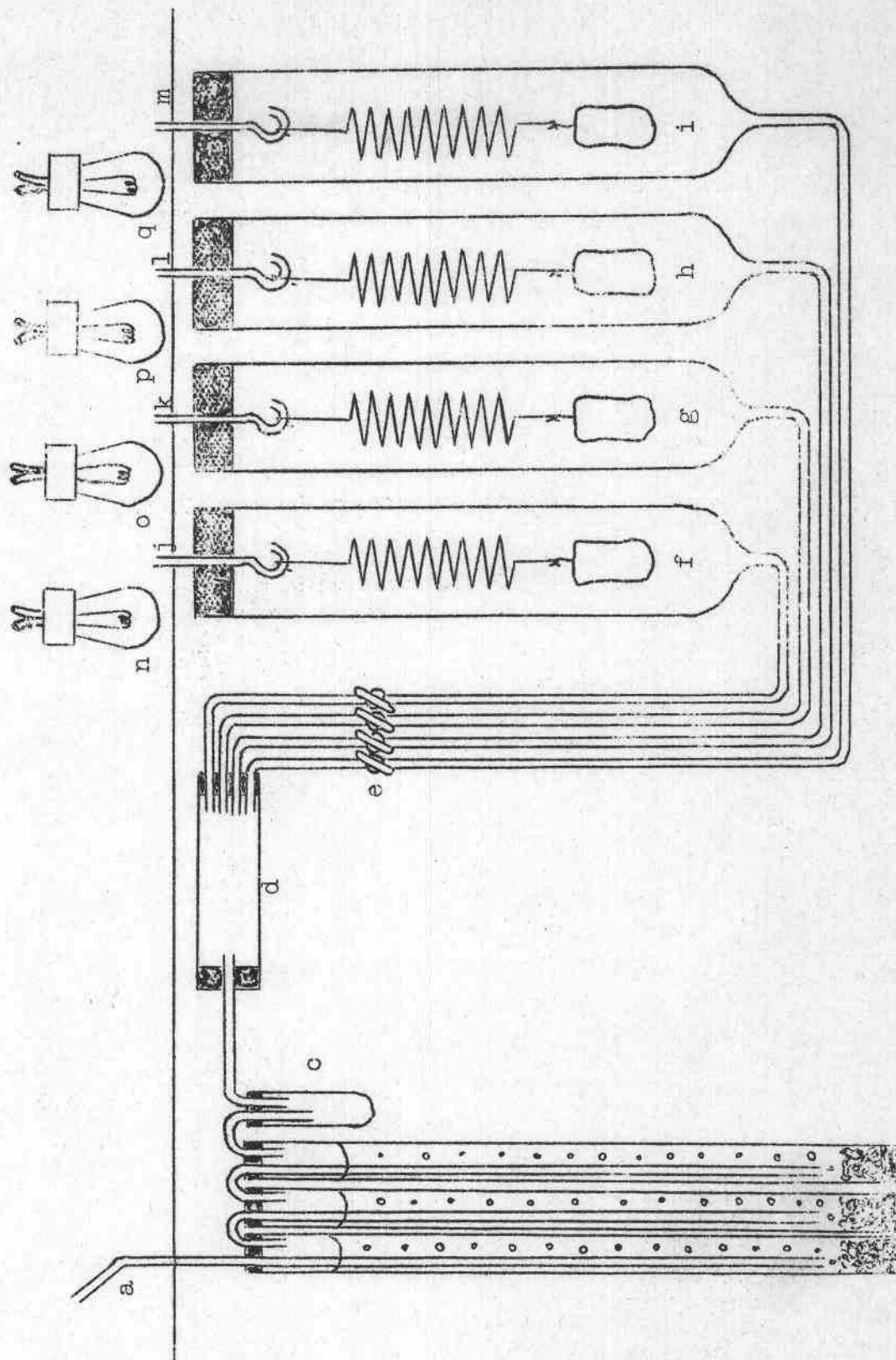


Figure 1

near the ends of the tubes by means of small electric light bulbs, n, o, p, and q. The discharge tubes were bent over with the ends barely dipping into a beaker of water to permit observation of the velocity of discharge. The pressures in the tubes were made equal by adjustment of the stopcocks to give equal velocity.

The helices, which were made of quartz fibers, were of such size that a helix with a diameter of about 1.0 cm. and 30 to 35 turns in a length of 2 to 3 cm. was able to carry a load of 300 to 1000 mg. and to weigh to an accuracy of 0.1 per cent. Cathetometer measurements were made at the fixed ends of the helices as well as at the deflecting ends to avoid any possible errors that might otherwise have been caused by creeping of the sealed-in rubber stoppers; all cathetometer readings were made to 0.005 cm.

The humidifying train b consisted of three glass tubes, 35 cm. in length and 2.5 cm. internal diameter, connected in series. The tubes contained short lengths of glass tubing to increase the solid-liquid contact surface of the ascending air bubbles. An excess of the salt was placed in the bottom of the tubes before sealing to insure the maintenance of saturation. A pre-humidifying train with large-bore tubes was set up outside of the thermostat. This arrangement served to bring the air to approximately the desired humidity before it entered the humidifying train b, thus preventing it from taking out appreciable quantities of water from the salt solutions in b, which would have resulted in crystallization and consequent clogging of the system.

The relative humidity in equilibrium with each of the saturated salt solutions was determined by a dynamic method as nearly comparable with the conditions under which the humidifying tubes were used as possible. Air was passed at a constant speed through one of the humidifying systems just described and then through an absorption train, consisting of a U-tube filled with calcium chloride, followed by another filled with phosphorus pentoxide suspended on glass wool. The dry air discharged from the phosphorus pentoxide tube was then passed through another humidifying system which was similar to b except that it was filled with distilled water. The saturated air coming from the distilled-water humidifier was passed through another absorption train. Both sets of humidifying tubes and absorption trains were kept in the thermostatic bath. The ratio of the amount of moisture absorbed in the first absorption train to the amount of moisture in the second, after making volume corrections for the difference in the total air pressure obtained after passing through each of the sets of humidifying tubes, gave the relative humidity of the air in equilibrium with the particular saturated salt solution under consideration. In preliminary tests air was passed through the system in increasing speeds to determine the speed at which the humidity of the air was no longer in equilibrium with the humidifiers. One-third of the maximum permissible speed of 45 liters per hour was used in this investigation so as to insure the attainment of equilibrium.

Table 1.--Equilibrium relative humidities of various saturated salt solutions

Salt	Relative humidity			
	100° C.	25° C.	20° C.	0° C.
	Calculated:	Experimental:	Obermiller (10)	Calculated
	Per cent	Per cent	Per cent	Per cent
Potassium acid phosphate, K_2HPO_4	87.8	95.3	92.0	
Potassium chromate, K_2CrO_4	84.7	87.0	88.0	
Sodium chloride, NaCl	73.8	74.2	^a 74.9	75.8
Sodium dichromate, $Na_2Cr_2O_7 \cdot 2 H_2O$		53.4	52.0	
Zinc nitrate, $Zn(NO_3)_2 \cdot 6 H_2O$		40.0	42.0	
Lithium chloride, $LiCl \cdot H_2O$	10.9	11.1	15.0	11.5

^a24° C.

In Table 1 are listed the relative humidities obtained at $25^\circ \pm 0.02^\circ$ C. in equilibrium with each of the saturated salt solutions used in this research. The experimental values represent the averages of at least six determinations. Variations among individual measurements rarely exceed 0.5 per cent. The results obtained by Obermiller (10), using a static method, as well as values calculated from vapor pressure and solubility data at 0° and 100° C. obtained from the literature, are given for comparison. Unfortunately, data are not available to complete the table. In general, the relative humidity decreases slightly with an increase in temperature. Obermiller's value for lithium chloride is apparently high, whereas the results of this investigation for potassium acid phosphate and sodium dichromate seem a little high in comparison with the other values. Since good checks were obtained for both of these

measurements, the deviations were probably due to differences in the purity of the salts.

In these studies the experimental zero humidity was obtained by passing the air through the towers filled with phosphorus pentoxide suspended on glass wool.

Measurements were made upon an unbleached spruce sulfite pulp and the same pulp after it had been physically processed for 8 hours in a beater. The beaten and unbeaten pulps were thoroughly washed for 24 hours with running distilled water and were then made up into thin test sheets. The wet sheets (containing about 60 per cent water) were cut to a size that would weigh approximately 0.5 gram when air dry, were rolled into the shape of a cylinder, and prior to the final measurements were suspended for about two weeks in an atmosphere of about 96 per cent relative humidity. This was done to remove the large excess of free moisture, thus making it possible to use more sensitive helices as well as to cut down the time required for the actual measurements.

The desorption measurements were started at the moisture content induced by 95.3 per cent relative humidity and were continued stepwise at decreasing relative humidities to zero humidity. The adsorption was then followed by using the same sets of humidifying tubes in the reverse order. Equilibrium was obtained in the desorption measurements at high relative humidities in approximately 2 days and at lower relative humidities in one day. In the adsorption measurements equilibrium was obtained somewhat more rapidly, requiring approximately 1 day at high relative humidities and considerably less than 1 day at lower relative humidities. In each case an additional day was allowed as a factor of safety.

Electrical-Conductivity Method

The results of the sorptive method were confirmed by electrical conductivity-moisture content measurements, using an apparatus previously developed for determining the fiber-saturation point of wood (14). This apparatus consisted essentially of a brass screw clamp with circular contact faces, 1.0 sq. cm. in cross section, for making contact with the pulp disk. The two contact faces were insulated from each other by 4 cm. of the hard-rubber base. The reading apparatus consisted of a portable suspension galvanometer, an Ayrton shunt, a key switch, and a single 1.5-volt dry cell. The shunt, which allowed 1.0, 0.1, 0.01, or 0.001 of the current to pass through the galvanometer, was connected in parallel with the galvanometer and in series with the dry cell, contact clamp, and key switch. Readings of specific electrical conductance could be made from 10^{-9} to 10^{-3} mho with this simple apparatus.

The measurements were made upon circular disks approximately 3.0 mm. thick and 1.0 sq. cm. in cross section when in water-soaked and swollen condition. The disks were dried in air for a few minutes, and then held in small weighing bottles for about an hour in order to approximate uniform moisture distribution before weighing and making measurement of the electrical conductivity and of the dimensions. The disks were then dried for a few minutes, after which the procedure was repeated.

Experimental Results

The sorption measurements of four samples of pulp and corresponding stuff, conditioned simultaneously, are recorded in Table 2 and plotted in Figure 2. The results show that beating has a negligible effect upon the moisture content-relative humidity relationship of pulp. This same result was obtained by Campbell and Pidgeon (2) in an evacuated system. The hysteresis loop is not closed at high relative humidities nor does the hysteresis effect disappear at low finite relative humidities. The fiber-saturation point obtained from extrapolation of the adsorption curve to 100 per cent relative humidity is approximately 29 per cent. This too is practically the same as the value obtained from the extrapolation of Campbell and Pidgeon's curve (2).

The electrical measurements plotted in Figure 3 show that beating has no effect upon the electrical conductivity-moisture content relationship of pulp. Drying and re-soaking the pulp also shows no effect upon the relationship. This is in harmony with Murphy and Walker's findings (9) that there is no difference between the electrical conductivity-moisture content relationship of cotton fibers under adsorption and desorption conditions, thus showing that the electrical conductivity is a function of the absolute moisture content and is independent of the means of attaining that moisture content. A linear relationship exists between the logarithm of the conductivity and the moisture content from the dry condition up to fiber saturation. Above this moisture content, the conductivity changes but slightly. Over the whole range the results for the beaten and the unbeaten pulp are identical within experimental error. The fiber-saturation point -- the point at which deviation from the linear relationship starts (28 per cent) -- corresponds quite well with the value obtained by extrapolating the relative humidity-moisture content curves to 100 per cent relative humidity.

Figure 2.--Moisture content-relative humidity
relationship of beaten and unbeaten
pulps

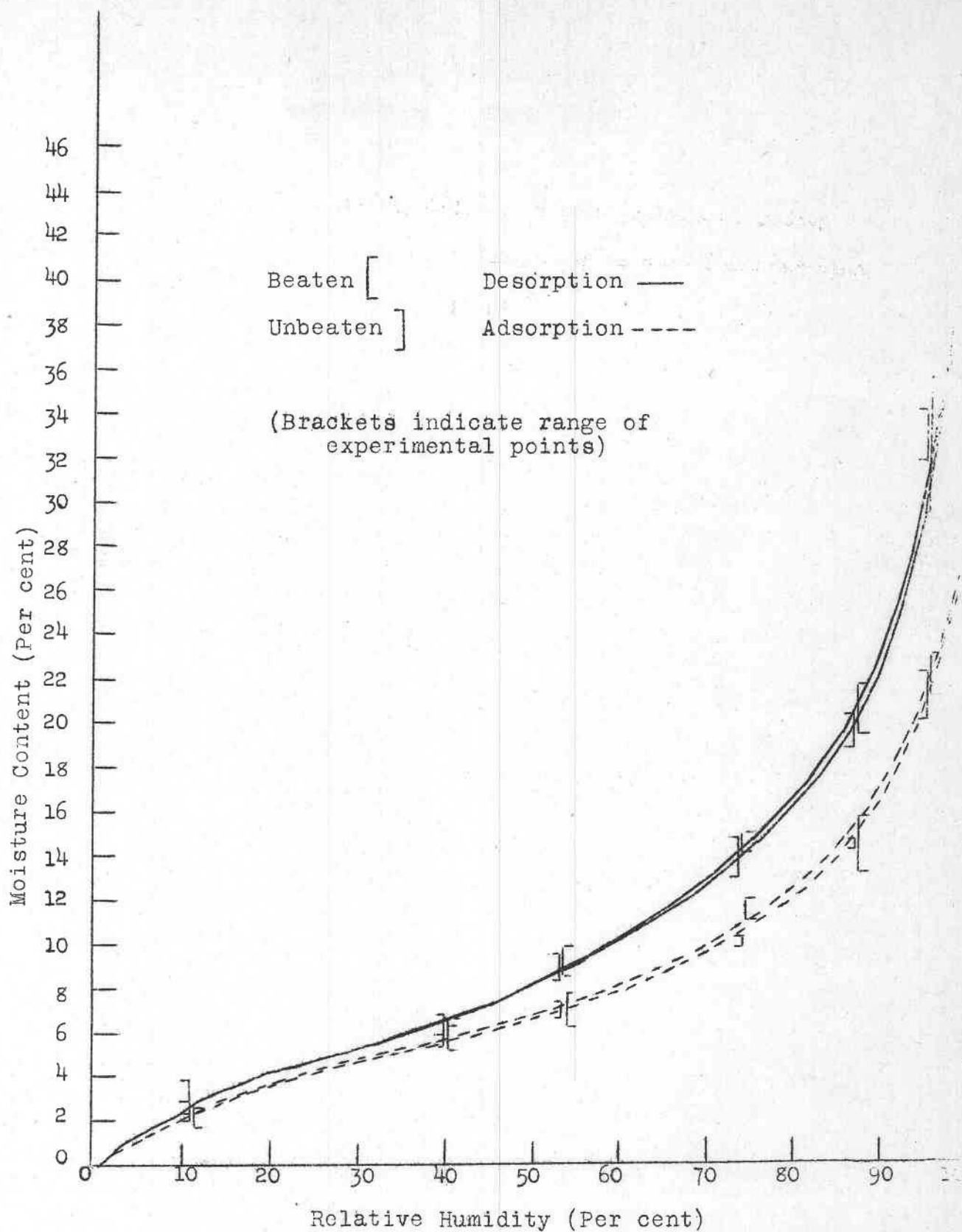


Figure 2

Figure 3.--Electrical conductivity-moisture content
relationship of beaten and unbeaten
pulps

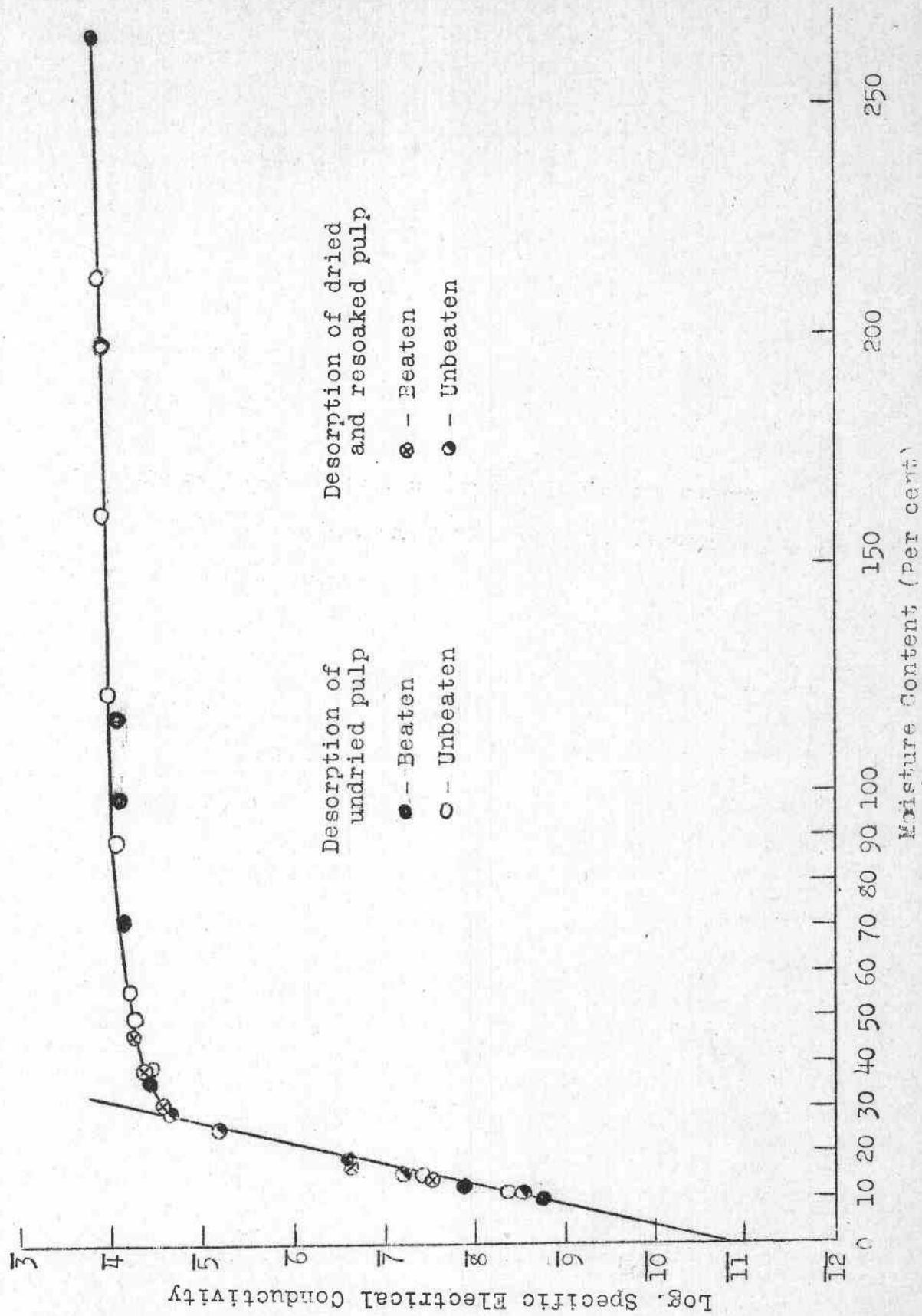


Table 2.--Effect of physical processing on equilibrium moisture content of sulfite pulp

		Moisture content (O. D. basis)					
:Relative:		:humidity:-----					
Sample:	at	Unbeaten pulp			Stuff (highly beaten pulp)		
:	25°	:			:		
:	C.	Desorption:	Adsorption:	:	Desorption	:	Adsorption
-----		-----	-----	-----	-----	-----	-----
	Per cent:	Per cent	Per cent		Per cent		Per cent
1	95.3	32.7	20.4		43.0		21.7
	87.0	19.2	14.7		22.1		14.6
	74.2	13.2	10.4		14.9		11.2
	53.4	8.8	6.6		9.2		7.4
	40.0	5.6	5.9		6.3		5.3
	11.1	2.0	4.1		2.7		1.8
	0	0	0		0		0
2	95.3	34.7	22.1		36.3		23.4
	87.0	20.7	14.7		21.9		15.3
	74.2	15.1	10.0		15.3		11.9
	53.4	9.5	6.7		9.9		7.9
	40.0	6.8	5.5		6.6		5.6
	11.1	2.7	2.4		2.9		2.3
	0	0	0		0		0
3	95.3	32.5	22.1		32.7		22.2
	87.0	20.5	14.4		21.7		15.7
	74.2	14.8	10.0		15.2		12.2
	53.4	9.4	6.9		10.2		8.2
	40.0	6.5	5.6		6.5		6.2
	11.1	2.9	2.7		2.6		2.8
	0	0	0		0		0
4	95.3	32.7	22.6		29.7		22.3
	87.0	20.3	14.7		19.9		13.3
	74.2	14.5	10.0		14.5		11.6
	53.4	9.4	7.3		9.5		7.7
	40.0	6.6	5.6		6.3		5.5
	11.1	2.7	2.3		2.6		2.5
	0	0	0		0		0

Conclusions

The continuous unbroken form of the moisture content-relative humidity relationship indicates that the hydration of pulp is a physical sorptive hydration rather than a chemical hydration in which the bonding is in definite molecular proportions.

The desorption-adsorption hysteresis is similar to that obtained by other investigators who used an evacuated system. The presence of air thus seems to have no effect upon the extent of hysteresis.

The results show that beating has no effect upon the true sorptive hydration of the pulp examined. The total internal adsorptive surface remains unchanged, though the outer surface of the fibers and fibrils may be increased considerably. It is presumably the increase in the available bonding surfaces of the fibers and fibrils for each other that affects the physical properties of the resultant sheet of paper (18). The so-called hydration of the paper industry is not a phenomenon of fiber-water bonding as the name implies, but appears rather to be a phenomenon of fiber-fiber bonding.

The fact that beating has no effect upon the electrical conductivity-moisture content relationship indicates that the conduction is a function of the amount of sorbed water and is not dependent upon the fiber-fiber bonding. Such a relationship is to be expected when it is realized that the dry fiber is a very poor conductor (specific conductance: 10^{-12} to 10^{-13} mho).

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