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SORPTION OF WATER VAPOR BY
PAPERMAKING MATERIALS

II. Effect of Physical and Chemical Processing

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June 37

The average equilibrium moisture content of representative unbleached chemical wood pulps at various relative humidities increased approximately 6 percent as a result of severe beating. Bleaching with calcium hypochlorite decreased the hygroscopicity of the sulfite pulps used.

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The experimental work here reported constitutes a second paper of a series dealing with the sorption of water vapor by papermaking materials.² The major objectives of the series are concerned with hygroscopicity as a fiber property, its relation to other fiber properties, its modification by chemical and physical processing, and its bearing on the phenomenon of "hydration," as the term is used in papermaking.

The previous article in this series (7) dealt with the effect of beating on the water sorption of a spruce sulfite pulp. Determinations of the equilibrium moisture content of the pulp indicated an increase as a result of beating. The difference, however, was small, possibly within the limits of experimental error of the apparatus; in view of the fact that the electrical conductivity of the pulp and stuff were the same, it was concluded that the beating had not effected any change in the equilibrium moisture content of the pulp. With the development of an improved apparatus it was deemed advisable to extend the work on the beating effect. The results of this new work, in conjunction with determinations of the effect of bleaching on hygroscopicity, are presented here.

¹Presented before the Division of Cellulose Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936.

²After this paper was prepared, the paper by Salley (Textile Research, 5, 493-508 (1935)) was brought to the writers' attention.

Apparatus and Procedure

The hygrosopicity determinations were made by means of the same principle as previously described (7). However, the apparatus shown in Figures 1 and 2 represents a considerable improvement.

The original water bath was replaced by an air bath (maintained at 25° C. \pm 0.01°) to avoid difficulties due to leakage. The capacity of the apparatus was increased to accommodate eight samples, and improved quartz spirals of greater sensitivity were provided. The ease of manipulation was also greatly improved, and the humidification load on the saturated salt solutions within the bath was reduced by the use of three sets of prehumidifying towers outside of the bath.

The prehumidifying towers delivered air with a relative humidity from 5 to 10 percent above that desired for the sorption experiments. This prehumidified air was then brought to the desired humidity by passage through one of the several saturated salt solutions within the thermostatic bath.

The several saturated salt solutions used and the respective relative humidities obtained thereby are listed in Table 1. The salts marked with superscript ^a gave the most constant relative humidities and are the only ones now used. All stopcocks within the bath affecting the flow of conditioned air were operated by extensions outside the bath.

Table 1.--Equilibrium relative humidities obtained by 12 saturated salt solutions

Salt solution	:Relative: :humidity: : 25° C. :	Salt solution	: Relative : : humidity : : 25° C. :	Salt solution	: Relative : humidity : 25° C.
	: <u>Percent</u> :		: <u>Percent</u> :		: <u>Percent</u>
LiCl · H ₂ O ^a	: 12.0 :	MnCl ₂ ^a	: 55.0 :	KCl ^a	: 85.0
MgCl ₂ · 6H ₂ O ^a	: 33.0 :	NaHSO ₄ · H ₂ O	: 56.5 :	K ₂ CrO ₄	: 87.0
Zn(NO ₃) ₂ · 6H ₂ O	: 40.0 :	NaNO ₂ ^a	: 63.5 :	KNO ₃ ^a	: 93.0
Na ₂ Cr ₂ O ₇ · 2H ₂ O	: 53.4 :	NaCl ^a	: 74.0 :	K ₂ HPO ₄	: 95.3
	: :		: :		: :

^aGave most constant relative humidities.

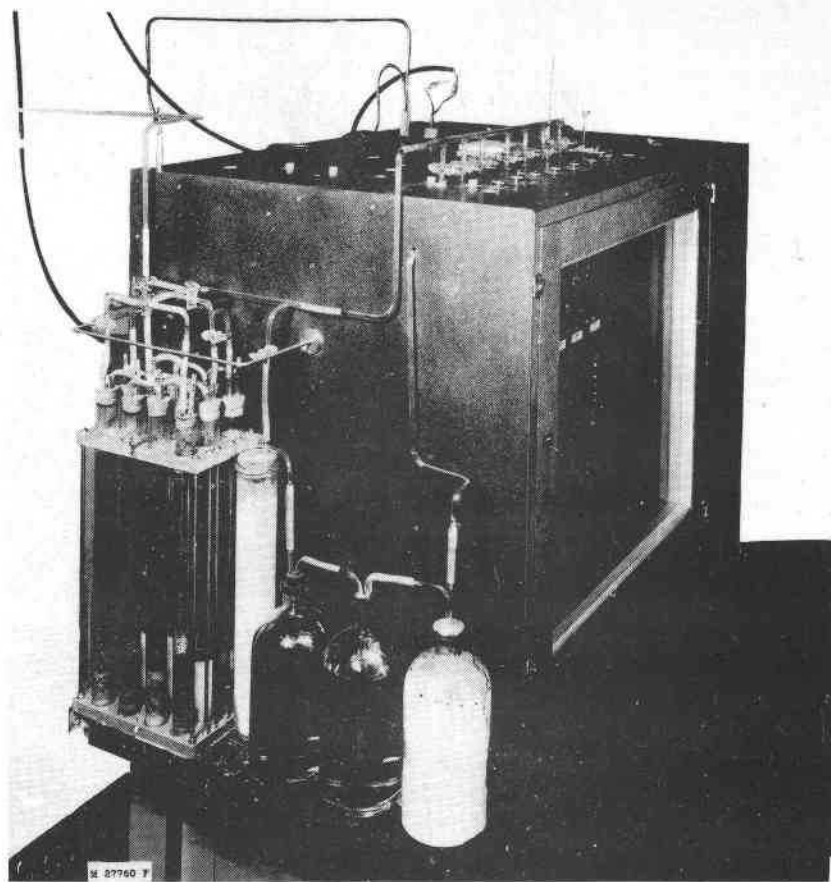


Figure 1.--The sorption apparatus.

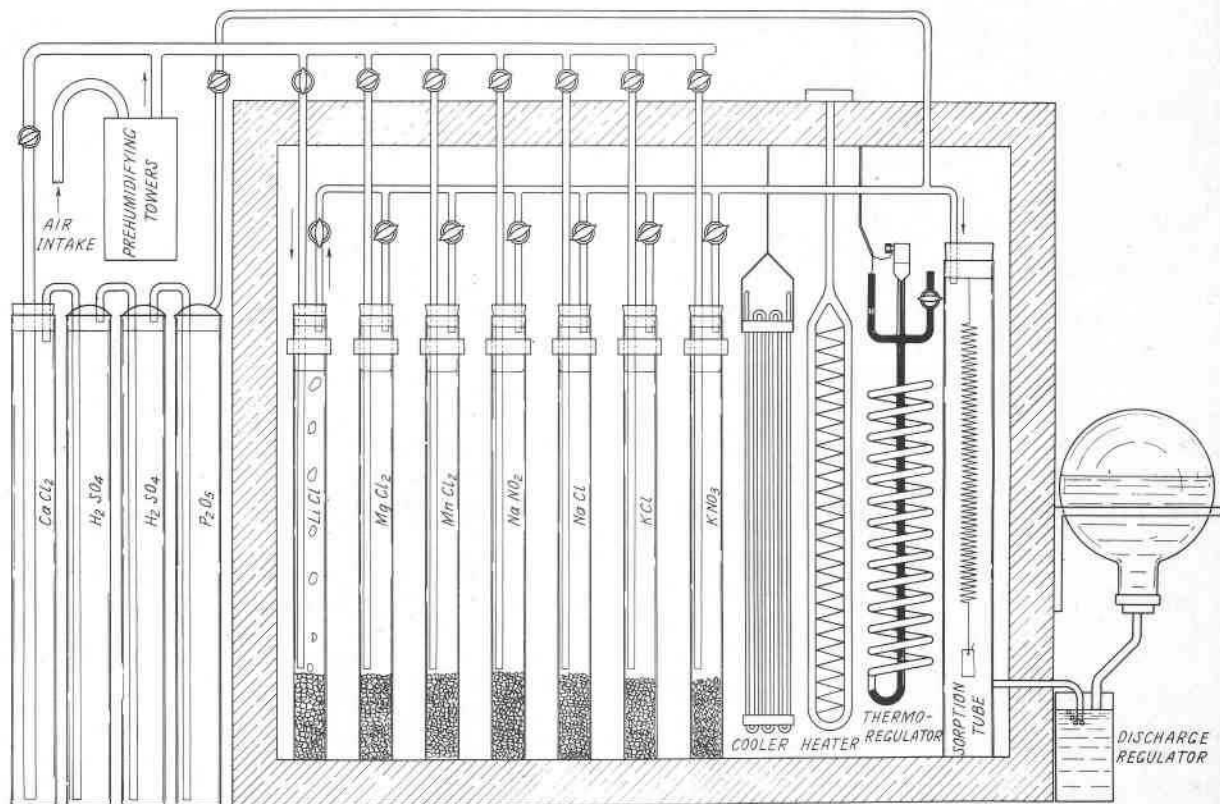


Figure 2.--Diagrammatic drawing of the sorption apparatus.

Dry air was obtained by passing air from the atmosphere through a series of towers containing, in the order named, anhydrous calcium chloride, concentrated sulfuric acid, and phosphorus pentoxide suspended on glass wool.

The air flow was distributed evenly throughout the eight sorption tubes by controlling the pressure through side-arm outlets projecting from the base of the tubes through the bath wall and into a trough of water at constant level. The depth of immersion of each side-arm tube was adjusted to obtain a rate of flow of three bubbles per second.

The quartz spirals, to which the pulp and stuff samples were attached in sheet form, gave, on an average, a deflection of about 30 cm. with a 100-mg. load.

The sorption samples ranged in weight from 30 to 75 mg., the lighter samples being used with the more sensitive spirals. All samples came to equilibrium in from 7 to 12 hours except in relative humidities near 90 percent in which instances the time required was frequently 24 hours. When drying the samples, a 24-hour period was used to ensure equilibrium, although the sample weight at the end of 12 hours usually was the same as that after 24 hours of drying.

The papermaking materials used in this study varied considerably in form and composition. They comprised sulfite pulps and stuffs from spruce, silver fir, and western hemlock; kraft pulps and stuffs from silver fir, loblolly pine, and slash pine; also spruce wood, cuprammonium lignin from spruce wood, and siliceous mineral matter from the pebbles and porcelain lining of a pebble mill. The materials are described later.

Effect of Extreme Beating on Hygroscopicity

Adsorption and desorption equilibrium moisture contents of unbeaten and highly beaten spruce, western hemlock, and silver fir sulfite pulps, and of silver fir and loblolly pine kraft pulps are given in Tables 2, 3, and 4. The curves presented in Figure 3 illustrate a part of these data.

That these pulps were beaten beyond even the degree normally used in preparing stuffs in the production of glassine (transparent) papers is indicated by the freeness values reported in the tables. This extreme degree of beating was considered essential to exaggerate any possible effect on pulp hygroscopicity which, in view of previous results obtained at this and other laboratories (2, 3, 5, 7, 8), was anticipated as being small if it existed at all.

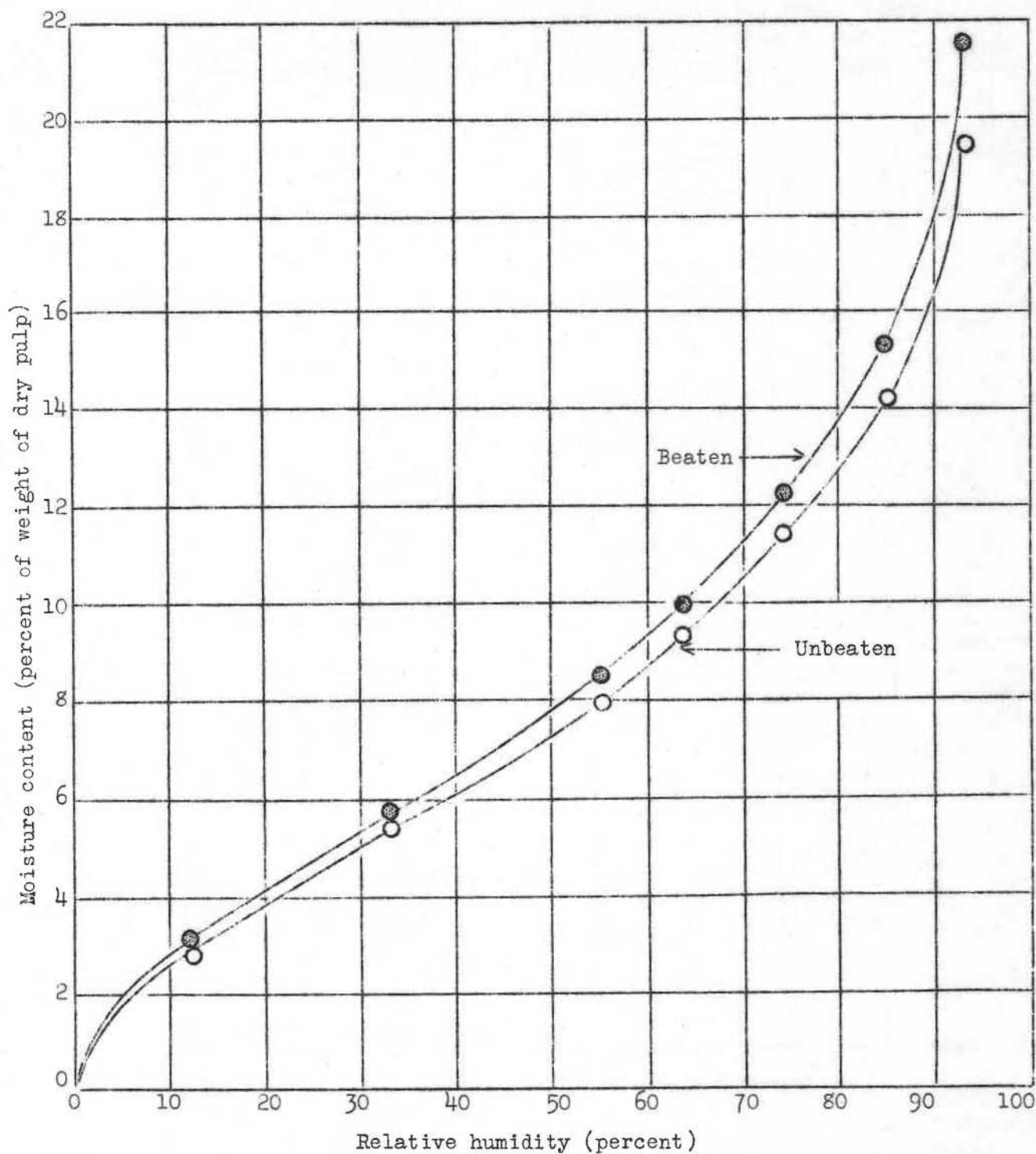


Figure 3a.--Effect of beating on adsorption equilibrium moisture content of silver fir sulfite pulp 3660-I.

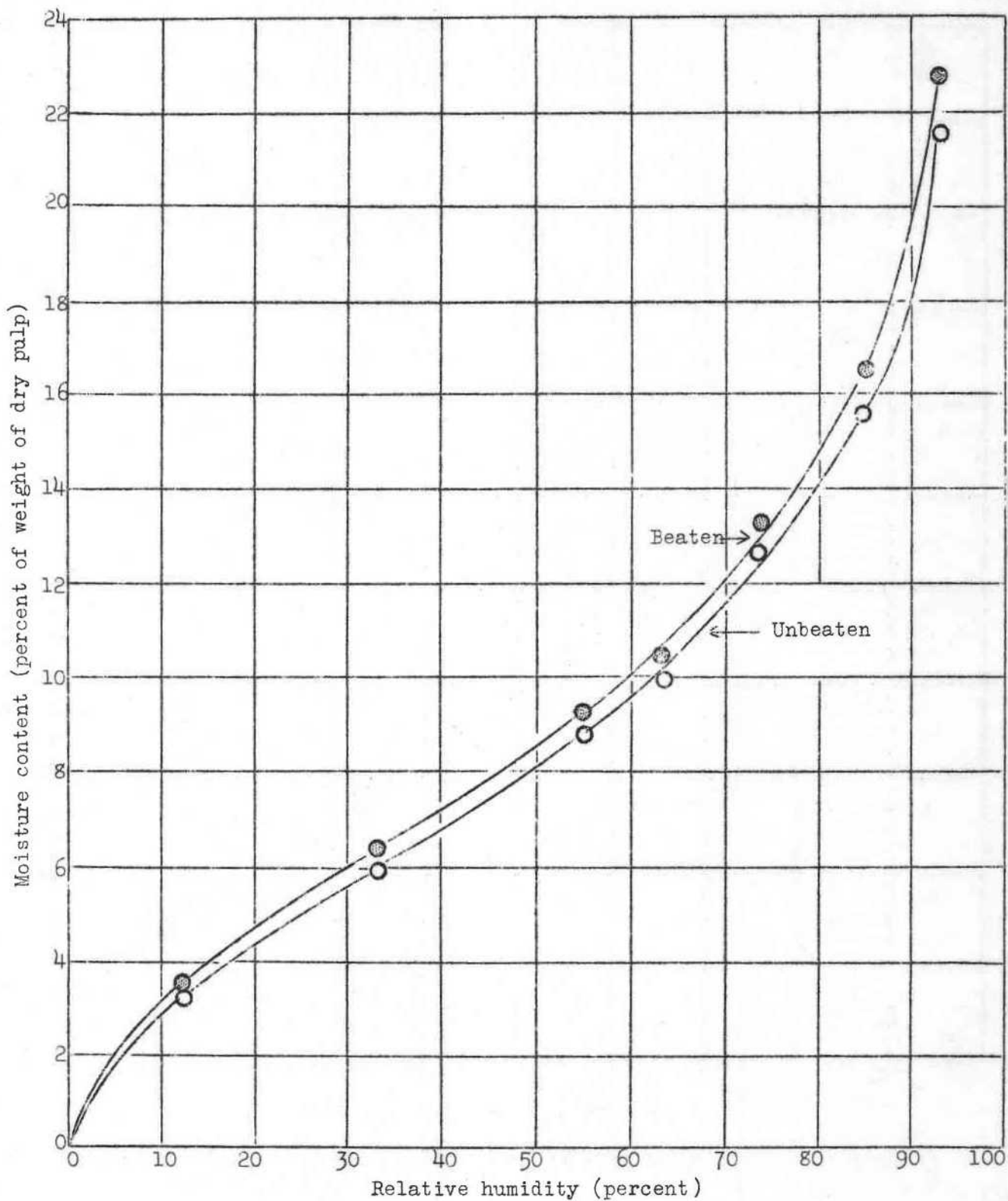


Figure 3b. -Effect of beating on adsorption equilibrium moisture content of loblolly pine kraft pulp 2450.

Table 2.--Effect of beating on equilibrium moisture content of spruce and western hemlock sulfite pulps

		Moisture content (percent on dry basis)											
		Spruce sulfite 3403-I				Spruce sulfite 3443-I				Western hemlock sulfite 3536-I			
Percent relative humidity, 25° C.	Un-beaten	:Beaten		:Percent	:Un-beaten		:Percent	:Un-beaten		:Percent	:Un-beaten		:Percent
		:minus	:un-beaten		:minus	:un-beaten		:minus	:un-beaten		:minus	:un-beaten	
95.0	27.4	30.9	3.5	12.8	32.50	33.25	0.75	2.3	27.7	29.1	1.4	5.1	
87.0	--	--	--	--	20.90	21.80	0.90	4.3	--	--	--	--	
80.0	17.1	18.4	1.3	7.6	--	--	--	--	--	--	--	--	
74.0	14.9	15.6	0.7	4.7	14.43	15.25	0.82	5.7	13.4	14.2	0.8	6.0	
56.5	9.9	10.3	0.4	4.0	9.43	10.05	0.62	6.6	--	--	--	--	
53.0	--	--	--	--	--	--	--	--	7.7	8.2	0.5	6.5	
40.0	6.8	7.0	0.2	3.0	6.63	6.75	0.12	1.8	--	--	--	--	
12.0	3.0	3.2	0.2	6.7	2.77	2.85	0.08	2.9	--	--	--	--	
Desorption													
Adsorption													
12.0	2.4	--	--	--	2.40	2.50	0.10	4.2	--	--	--	--	
40.0	5.9	6.1	0.2	3.4	5.57	5.85	0.28	5.0	--	--	--	--	
53.0	--	--	--	--	--	--	--	--	--	--	--	--	
56.5	8.4	8.6	0.2	2.4	7.23	7.80	0.57	7.9	--	--	--	--	
74.0	11.6	12.1	0.5	4.3	10.50	11.20	0.70	6.7	--	--	--	--	
80.0	13.3	14.5	1.2	9.0	--	--	--	--	--	--	--	--	
87.0	--	--	--	--	14.60	15.50	0.90	6.2	--	--	--	--	
95.0	24.4	26.5	2.1	8.6	22.27	23.35	1.08	4.9	--	--	--	--	
Average percent increase												4.9	5.8

^aGreen freeness, 0 cc.

^bGreen freeness, 680 cc.

Table 3.--Effect of beating on equilibrium moisture content of silver fir sulfite and kraft pulps

Moisture content (percent on dry basis)										
Percent relative humidity: 25° C.	Silver fir sulfite 3660-I					Silver fir kraft 2442-I				
	Un-beaten ^a	Beaten ^b	Beaten minus unbeaten	Percent increase	Un-beaten ^c	Beaten ^b	Beaten minus unbeaten	Percent increase	Un-beaten ^c	Beaten ^b
Adsorption										
12.0	2.85	3.06	0.21	7.4	--	--	--	--	--	--
33.0	5.34	5.66	0.32	6.0	--	--	--	--	--	--
55.0	7.92	8.55	0.63	8.0	--	--	--	--	--	--
63.5	9.39	9.95	0.56	6.0	--	--	--	--	--	--
74.0	11.48	12.30	0.82	7.1	--	--	--	--	--	--
85.0	14.28	15.35	1.07	7.5	--	--	--	--	--	--
93.0	19.47	21.50	2.03	10.4	--	--	--	--	--	--
Desorption										
85.0	16.03	17.50	1.47	9.2	16.90	17.95	1.05	6.2		
74.0	13.25	14.44	1.19	9.0	14.00	14.47	0.47	3.4		
63.5	10.83	11.72	0.89	8.2	11.43	11.80	0.37	3.2		
55.0	9.39	10.05	0.66	7.0	9.75	10.22	0.47	4.8		
33.0	6.14	6.70	0.56	9.1	6.50	6.64	0.14	2.2		
12.0	3.29	3.64	0.35	10.6	3.48	3.58	0.10	2.9		
Average percent increase				8.1						3.8

^aSchopper-Riegler freeness 865 cc.

^bSchopper-Riegler freeness 125 cc.

^cSchopper-Riegler freeness 850 cc.

Table 4.--Effect of beating on equilibrium moisture content of loblolly pine kraft pulp 2450

Moisture content (percent on dry basis)														
Percent relative humidity, 25° C.	Unbeaten ^a			Beaten			Average: Percent							
	1	2	Av.	1	2	3	Av.	1	2	3	Av.			
	Wet lap from wet machine ^b			Air drier prior to beating ^c			minus : average: due							
	12.0	3.25	3.17	3.21	3.44	3.47	3.48	3.46	3.49	3.37	3.49	3.45	0.25	7.8
	33.0	5.95	5.93	5.94	6.27	6.36	6.33	6.32	6.26	6.39	6.30	6.32	0.38	6.4
	55.0	8.82	8.78	8.80	9.30	9.25	9.29	9.28	9.23	9.37	9.26	9.29	0.49	5.7
	63.5	9.98	9.95	9.97	10.44	10.45	10.49	10.46	10.52	10.52	10.46	10.50	0.51	5.1
	74.0	12.63	12.62	12.63	13.24	13.20	13.34	13.26	13.32	13.20	13.33	13.28	0.64	5.0
	85.0	15.54	15.75	15.65	16.42	16.43	16.60	16.48	16.68	16.59	16.73	16.66	0.92	5.9
	93.0	21.60	21.60	21.60	22.21	22.44	22.81	22.49	22.85	23.10	23.36	23.10	1.19	5.5
Adsorption														
	85.0	17.72	17.80	17.76	18.31	18.44	18.61	18.45	18.68	18.57	18.79	18.68	0.81	4.6
	74.0	14.56	14.58	14.57	15.09	15.23	15.29	15.20	15.36	15.25	15.34	15.31	0.69	4.7
	63.5	11.97	11.99	11.98	12.39	12.58	12.67	12.55	12.48	12.55	12.53	12.52	0.56	4.7
	55.0	10.44	10.55	10.50	11.09	11.04	11.14	11.09	11.14	11.00	11.08	11.07	0.58	5.5
	33.0	---	6.88	6.88	7.32	7.37	7.38	7.36	7.25	7.28	7.29	7.27	0.44	6.4
	12.0	3.93	3.71	3.82	4.06	4.21	4.13	4.13	4.09	4.13	4.09	4.10	0.30	8.1
Desorption														
Average percent increase.....													5.8	

^aSchopper-Riegler freeness 880 cc.; ash content 1.4 percent.

^bSchopper-Riegler freeness 35 cc.; ash content 1.6 percent.

^cSchopper-Riegler freeness 40 cc.; ash content 1.6 percent.

The results show that the highly beaten portions of the foregoing six pulps have a consistently higher equilibrium moisture content, expressed as a percentage of the dry sample, than the corresponding unbeaten pulps. The actual arithmetical difference between these percentages showed the beaten pulps to be from 0.2 to 3.5 higher in moisture content from the low to high humidities, respectively. When these differences were expressed as a percentage of the moisture content of the unbeaten pulps and averaged, the result was 6 percent, which is probably near the maximum increase in hygroscopicity that can be obtained by extreme beating. Other investigators have obtained similar results although they have been reluctant to ascribe the effect to anything other than experimental error. Campbell (2) reported an increase of roughly 4 percent on the same basis for sulfate and sulfite stuffs that apparently had not been beaten quite so much as those discussed here. Mark (5) found that treating a wood pulp in a colloid mill resulted in an increased hygroscopicity, the amount of which was not reported. He used such sorption data to measure the relative increase of fiber surface caused by mechanical processing. Results reported by Sheppard and Newsome (8) for an "unbeaten and 'hydrated' pulp dried from water" showed an increased equilibrium moisture content of approximately 2 percent over a range of 50 to 100 percent relative humidity, but this difference was not considered significant.

In Table 4, dealing with loblolly pine kraft pulp 2450, the data for all check determinations are recorded. Of the 39 sets of check determinations only four have a variation larger than the smallest difference in moisture content between the unbeaten and beaten pulp. Of the remaining 35 sets the average maximum spread of the check determinations is 0.09. And for the entire 39 sets the average spread is 0.14.

These results show that the observed differences between the equilibrium moisture contents of the representative unbeaten and highly beaten pulps were not due to experimental or chance errors. Therefore, it is concluded that the beaten pulps were more hygroscopic.

The difference between the equilibrium moisture contents of the unbeaten and beaten pulps increased with increasing relative humidity up to 95 percent relative humidity. Whether this difference increases further at still higher humidities is not known.

The mechanism of water vapor sorption by cellulose and wood pulp was ably discussed on the basis of both theoretical and experimental considerations by several investigators (2, 5, 8, 10) who advanced closely related hypotheses which appear entirely satisfactory. Sheppard and Newsome (8) hold that the sorption involves two phases: The first, occurring at low vapor pressure, comprises the adsorption of water molecules to free hydroxyl groups, and the second (a volume sorption) is a capillary condensation.

It seems reasonable to ascribe the increased equilibrium moisture content that resulted from the severe beating to an increase of free hydroxyl

groups available to the adsorption of water vapor in conjunction with an increase in the volume of fine structure capillaries in which condensation occurs. The first may be considered an increase of inner surface available to the adsorption of water vapor. Argue and Maass (1) found the heat of wetting of pulp to increase from 2 to 10 percent as a result of beating and they attribute it to an increase in the internal area of the crystallites.

As may be observed from the data in Table 4, the beating experiments with loblolly pine kraft pulp involved both wet-lap and air-dried pulp. Apparently the air drying prior to beating had no effect on the equilibrium moisture content of the beaten pulp.

Effect of Pebble-Milling

When studying the effect of physical processing on hygroscopicity, it is essential that such effects be due to the physical processing only and not be influenced by other factors. The effect produced by other factors might well be of such magnitude as to minimize greatly, if not even reverse, the effect observed when these influences are not present. This is illustrated in the case of a slash pine kraft pulp that was processed in a pebble mill for 6 hours to an almost gelatinous condition.

A comparison of the hygroscopicity of this pulp before and after milling as well as of the mineral matter from the pebbles and porcelain linings of the pebble mill is afforded by the data in Table 5 and Figure 4. The hygroscopicity of the pebble-milled pulp containing such mineral matter was found to be lower over the whole range of humidities in both the adsorption and desorption curves, the amount of reduction increasing from low to high humidities. This result is just the reverse of that obtained by beating in a beater. The action of the two types of processing equipment is different, but the reduction in hygroscopicity produced by the pebble mill is due, in the main, to the mineral matter imparted to the pulp during milling. Pebble-milling increased the ash content of the pulp from 1 to 6 percent in contrast to a negligible increase of ash in the case of the beaten pulps previously discussed. The purpose of these determinations is to characterize the pebble-milled pulp and not the individual fibers. Since the impartation of mineral matter to the pulp is an unavoidable result of the process, it must be considered with the pulp. For example, when the pebble-mill method is used for testing the strength development of pulps, the test sheets made from the stuff contain mineral matter which consequently affects the hygroscopicity of the sheets. The hygroscopicity of the fibers only, as processed by this method, is undeterminable, since the imparted mineral matter cannot be removed.

The effect of the mineral matter acting merely as a diluent in reducing the weight of the cellulosic material in the sample may be seen from its abnormally low hygroscopicity as compared with cellulosic materials. For purposes of calculation the following assumptions are made: (1) the

Table 5.--Effect of pebble-milling on equilibrium moisture content of slash pine kraft pulp 2348

Percent relative humidity, 25° C.	Moisture content (percent on dry basis)			
	Unprocessed	Pebble-milled 6 hours ^a	Unprocessed minus pebble-milled	Mineral matter from pebble mill
Desorption				
95	26.20	24.85	1.35	--
87	16.90	16.00	0.90	3.15
74	12.50	11.75	0.75	1.01
53	7.95	7.40	0.55	0.73
40	5.85	5.40	0.45	0.63
12	2.40	2.45	-0.05	0.14
Adsorption				
12	2.00	1.90	0.10	--
40	4.95	4.70	0.25	--
53	6.65	6.15	0.50	--
74	10.05	9.25	0.80	--
87	13.30	12.40	0.90	--
Ash, percent:	1.0	6.0		

^aNot corrected for mineral content.

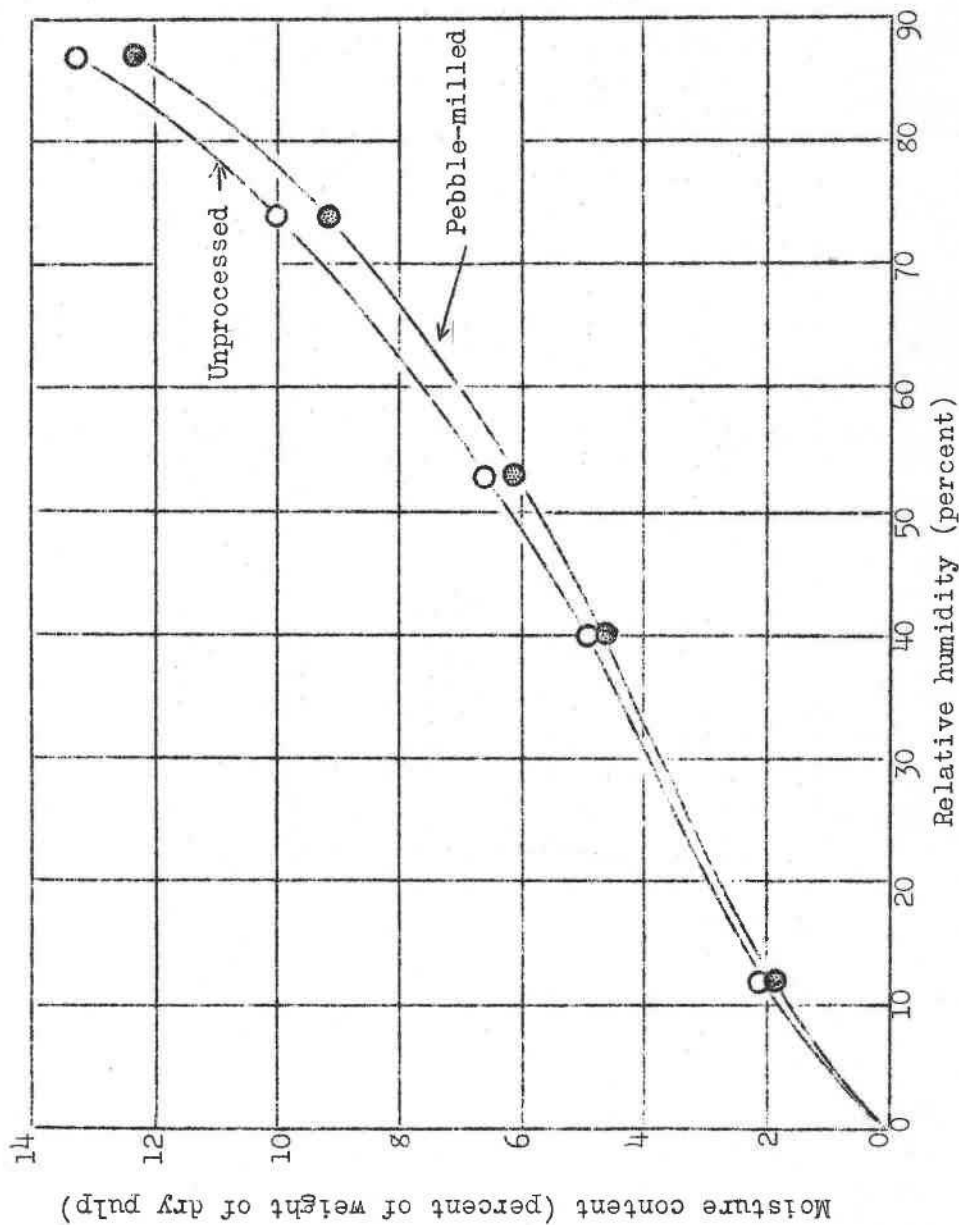


Figure 4.--Effect of pebble-milling on equilibrium moisture content of slash pine kraft pulp 2348.

pebble-mill processing, representing attrition in the presence of free mineral matter, had no specific effect in itself on the pulp, (2) the ash content of the 300-mg. sorption sample was exactly 6 percent, and (3) the ash content can be considered exactly equivalent to the original mineral content. When, on this basis, the desorption equilibrium moisture contents listed in column 3, Table 5, are "corrected" for the mineral content of the sample, the reduction in hygroscopicity observed is still greater than can be accounted for on the basis of increased mineral content acting only as a diluent. It is possible that some of the extremely finely divided siliceous material was precipitated or adsorbed on the external surfaces of the milled pulps, thus actually preventing adsorption of water by the pulp wherever the mineral was adsorbed. Strachan (9) has shown that relatively large amounts of inorganic materials can be strongly precipitated on finely divided pulps and that it is difficult to remove such material even with extensive washing. A decrease in the hygroscopicity of the pulp because adsorbed mineral matter inhibited the adsorption of water would be relatively small, owing to the availability of internal pulp and cellulose surfaces to water.

Effect of Bleaching

The decreased hygroscopicity of the spruce and silver fir sulfite pulps resulting from bleaching by a single-stage calcium hypochlorite method (6) is shown by the data in Tables 6 and 7. Included in Table 6 are the moisture relations for a sample of spruce sapwood from which the sulfite pulps were prepared, and also the cuprammonium lignin isolated from this wood according to the method of Freudenberg (4). The lignin contents and bleach requirements of pulps 3443-I and 3403-I were, respectively, 3.5 and 25, 2 and 18 percent. The wood in storage for 18 months contained 29 percent lignin.

On adsorption the trend of the lignin was toward a slightly lower hygroscopicity than the wood from which it was isolated; likewise the pulp, but to an even greater extent (Figure 5). At 95 percent relative humidity, however, the equilibrium moisture contents of these materials were about the same. Overbleaching the pulp caused a further reduction in the hygroscopicity, averaging about 10 percent. On desorption no definite trend in hygroscopicity was noted. The fact that the wood, lignin, and unbleached pulp have so nearly the same equilibrium moisture contents indicates that the reduction in hygroscopicity cannot be entirely explained on the basis of the removal of the lignin.

Bleaching the silver fir sulfite pulp 3660-I resulted in decreased hygroscopicity, the reduction increasing with increasing severity of bleaching. Moisture relations are shown in Table 7 and Figures 6 and 7, and chemical analyses are given in Table 8. From 8 to 25 percent bleach ratio a practically linear reduction in hygroscopicity resulted (Figure 7).

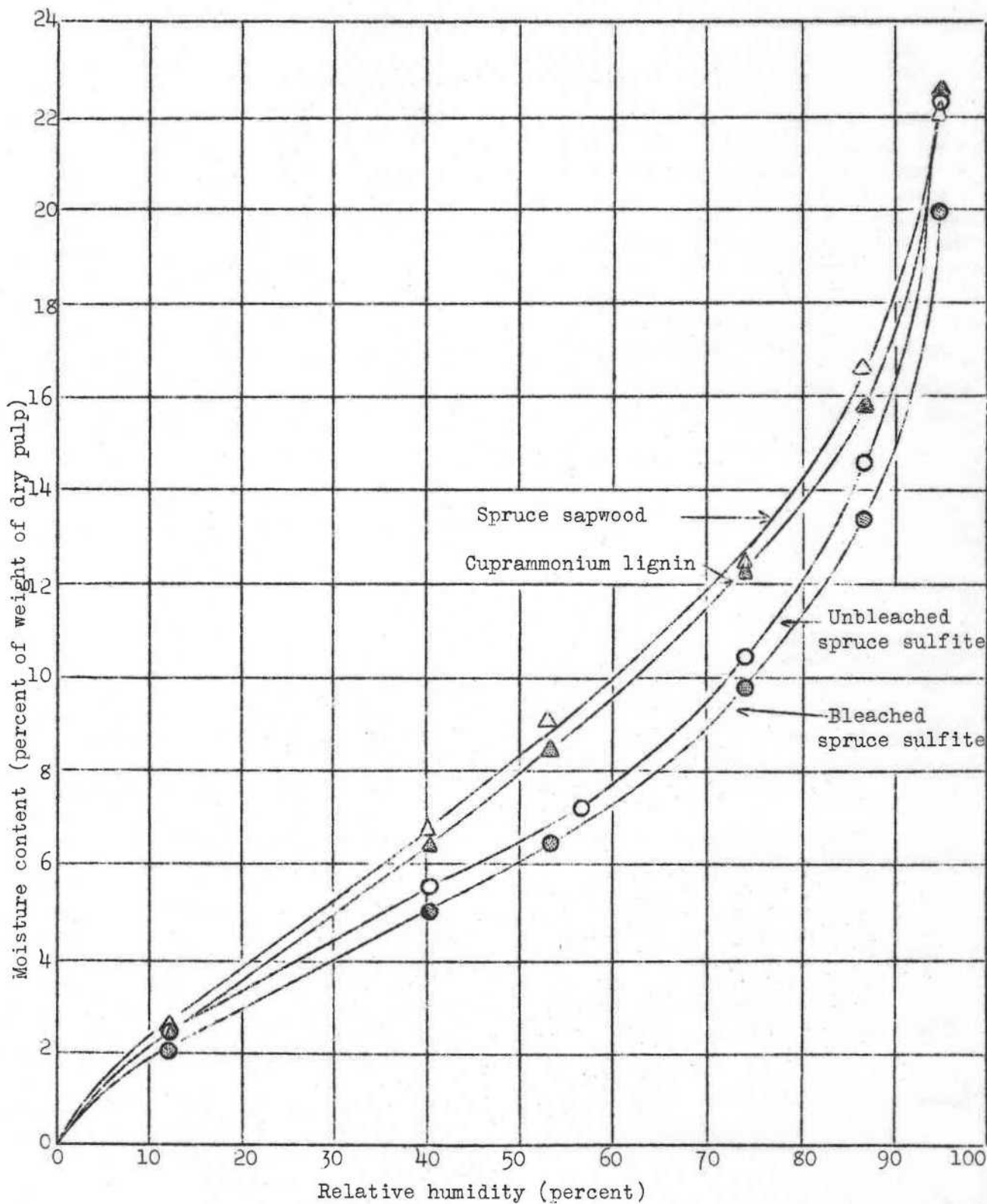


Figure 5.--Relation of adsorption equilibrium moisture content of cuprammonium lignin, spruce sapwood, and a spruce sulfite pulp, 3443-I, bleached and unbleached.

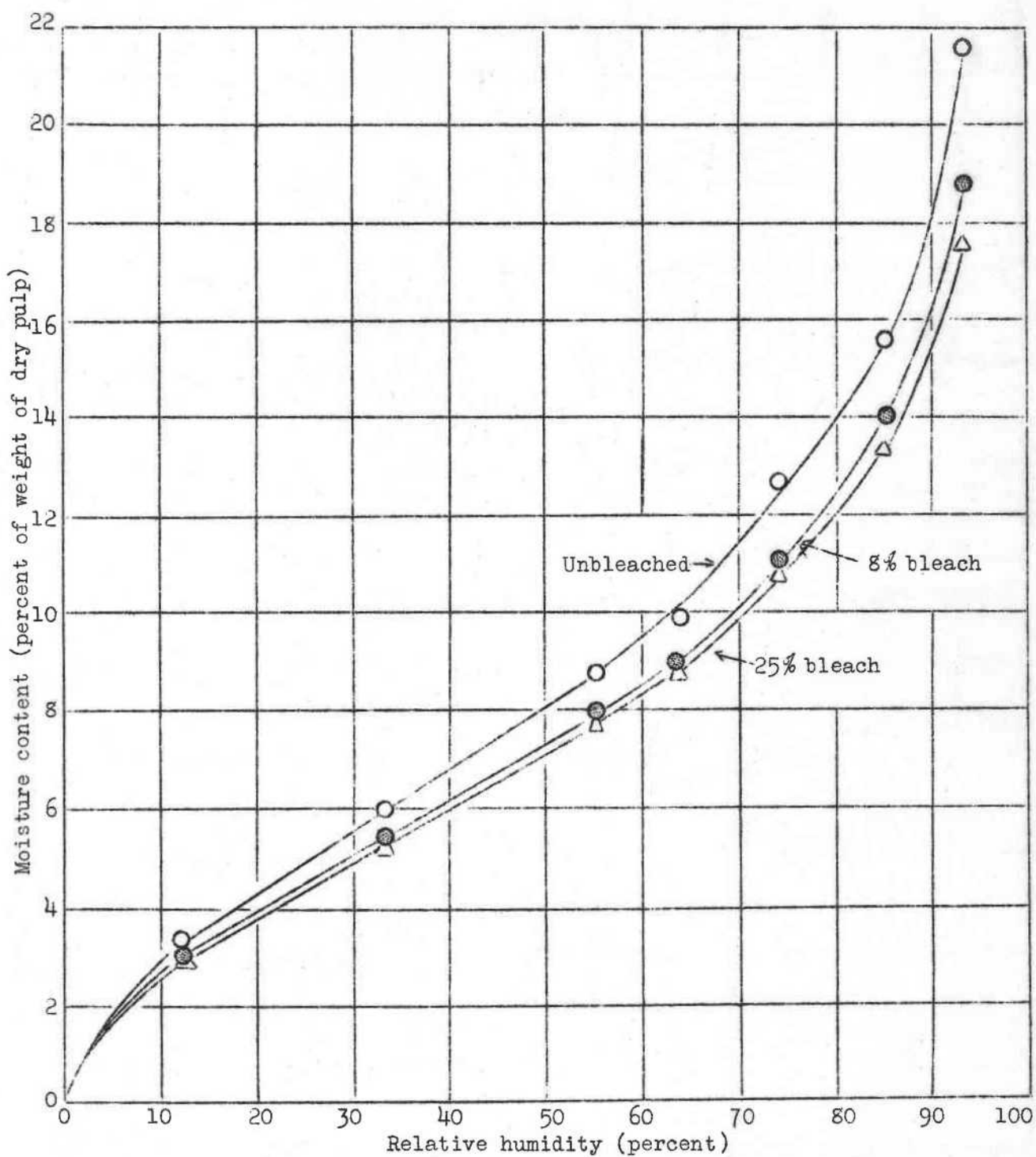


Figure 6.--Effect of various degrees of bleaching on adsorption equilibrium moisture content of a silver fir sulfite pulp 3660-I.

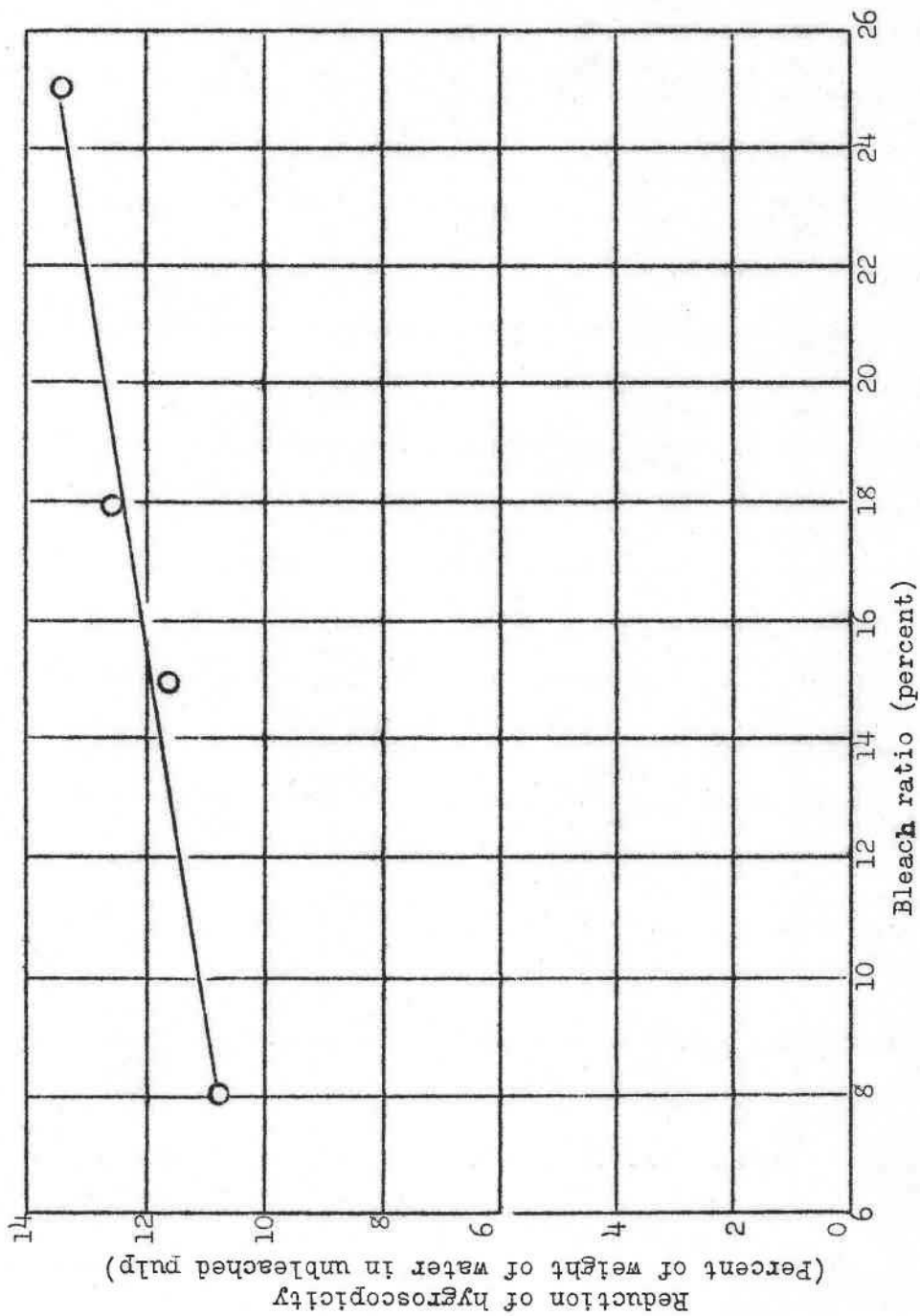


Figure 7.--Relation of hygroscopicity and bleach ratio for silver fir sulfite pulp 3660-I.

Table 6.--Moisture relations of spruce sapwood, cuprammonium lignin, and unbleached and bleached spruce, sulfite pulps

Moisture content (percent on dry basis)									
Percent relative humidity, 25° C.	Spruce sapwood shipment 1291	Cuprammonium lignin	Spruce sulfite unbleached	Spruce sulfite 3443-I Bleached ^a	Percent decrease	Spruce sulfite 3403-I unbleached	Spruce sulfite 3403-I Bleached ^a	Percent decrease	
Desorption									
95	26.25	37.87	32.50	30.07	7.5	27.4	25.6	6.6	
87	21.35	23.83	20.90	19.03	9.0	--	--	--	
80	--	--	--	--	--	17.1	15.9	7.0	
74	16.85	18.43	14.43	13.27	8.0	14.9	14.0	6.0	
56.5	--	--	9.43	--	--	9.9	9.4	5.0	
53	11.60	11.43	--	8.13	--	--	--	--	
40	9.00	8.57	6.63	5.93	10.5	6.8	6.6	3.0	
12	3.70	3.40	2.77	2.30	17.0	3.0	2.8	6.7	
Adsorption									
12	2.65	2.43	2.40	2.07	13.7	2.4	2.2	8.3	
40	6.75	6.47	5.57	5.07	9.0	5.9	5.5	6.8	
53	9.10	8.53	--	6.50	--	--	--	--	
56.5	--	--	7.23	--	--	8.4	7.8	7.2	
74	12.50	12.43	10.50	9.87	6.0	11.6	10.8	6.9	
80	--	--	--	--	--	13.3	12.6	5.3	
87	16.65	15.80	14.60	13.47	7.7	--	--	--	
95	22.15	22.53	22.27	20.00	10.0	24.4	21.7	11.0	
Average decrease by bleaching (percent)					9.8			6.6	

^aOverbleached using 35 percent bleach powder on basis of dry pulp.

Table 7.--Effect of degree of bleaching on equilibrium moisture content of silver fir sulfite pulp 3660-I

Percent relative humidity, 25° C.	Moisture content (percent on dry basis) for bleach ratios ^a of:					Percent decrease in hygroscopicity ^b for bleach ratios ^a of:				
	0	8	15	18	25	8	15	18	25	

Adsorption

12	3.21	2.95	2.99	2.90	2.90	8.1	6.9	9.7	9.7
33	5.94	5.38	5.29	5.33	5.29	9.4	10.9	10.3	10.9
55	8.80	7.93	7.82	7.74	7.72	9.8	11.1	12.0	12.3
63.5	9.97	8.98	8.86	8.92	8.89	9.9	11.1	10.5	10.8
74	12.63	11.06	10.75	10.87	10.81	12.4	14.9	13.9	14.4
85	15.65	14.06	13.77	13.58	13.37	10.2	12.0	13.2	14.6
93	21.60	18.85	18.24	18.00	17.53	12.7	15.6	16.7	18.8

Desorption

85	17.76	15.82	15.52	15.35	15.11	10.9	12.6	13.6	14.9
74	14.57	13.17	13.06	12.94	12.32	9.6	10.4	11.2	15.4
63.5	11.98	10.78	10.67	10.53	10.42	10.0	10.9	12.1	13.0
55	10.50	9.33	9.16	9.02	8.96	11.1	12.8	14.1	14.7
33	6.88	6.14	6.23	6.09	6.06	10.7	9.5	11.5	11.9
12	3.82	3.26	3.35	3.32	3.32	14.7	12.3	13.1	13.1

Color (Hess-Ives)									
Red	68	87	90	90	91	--	--	--	--
Green	62	84	88	91	91	--	--	--	--
Blue	60	78	86	91	91	--	--	--	--
Average percent decrease						10.7	11.6	12.5	13.4

^aWeight (basis dry pulp) of bleaching powder containing 35 percent available chlorine.

^b $\frac{\text{Unbleached} - \text{bleached}}{\text{Unbleached}} \times 100.$

Table 8.--Chemical analysis of an unbleached and bleached silver fir sulfite pulp

Bleach ratio	Lignin	Total pentosans	1% NaOH solubility	Hess-Ives color		
				Red	Green	Blue
Percent	Percent	Percent	Percent			
0	1.0	4.8	7.4	68	62	60
8	0.7	4.7	7.1	87	84	78
15	0.04	4.5	9.5	90	88	86
18	--	--	--	90	91	91
25	0.03	4.7	15.7	91	91	91

How far below 8 percent this linear relation obtains cannot be predicted, but it probably varies from pulp to pulp, depending upon such factors as species and bleach requirement of the pulp. Bleach ratios of 8, 15, 18, and 25 percent produced an average decrease in hygroscopicity of 10.7, 11.6, 12.5, and 13.4 percent, respectively, the calculations being based on the moisture content of the unbleached pulp. In each case the percentage decrease remained roughly the same over the whole range of humidities for the adsorption and desorption curves.

An interesting observation was the distinct difference in hygroscopicity at the high humidities between bleached samples which showed no discernible difference in color with a Hess-Ives tint photometer. Small differences in hygroscopicity resulting from other effects were also magnified at the high humidities. Sorption studies at high humidities may be a means of detecting small differences in properties of pulp that might not be discernible by other methods.

Conclusions

Highly beaten kraft and sulfite stuffs have higher equilibrium moisture contents than the unbeaten pulps. The arithmetical difference between the percentage moisture contents showed the beaten pulps to be from 0.2 to 3.5 higher from the low to high humidities, respectively. When these differences were expressed as percent moisture content of the

unbeaten pulps and averaged, the result was 6 percent, which is probably near the maximum increase in hygroscopicity that can be obtained by extreme beating.

A stuff resulting from pebble-mill processing was less hygroscopic than the corresponding unprocessed pulp. The pebble mill imparts mineral matter of low hygroscopicity to a pulp; this mineral matter lowers the hygroscopicity of the pulp by a diluent effect and possibly an inhibitive effect.

Bleaching produced a marked decrease in the hygroscopicity of the spruce and silver fir sulfite pulps. A series of bleaches in the case of the silver fir pulp indicated that the relation between degree of bleaching and decrease in hygroscopicity is apparently linear.

There was little difference in hygroscopicity between wood, cuprammonium lignin, and pulp, except that on adsorption there was a tendency for the cuprammonium lignin and the pulp to be lower than the wood.

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