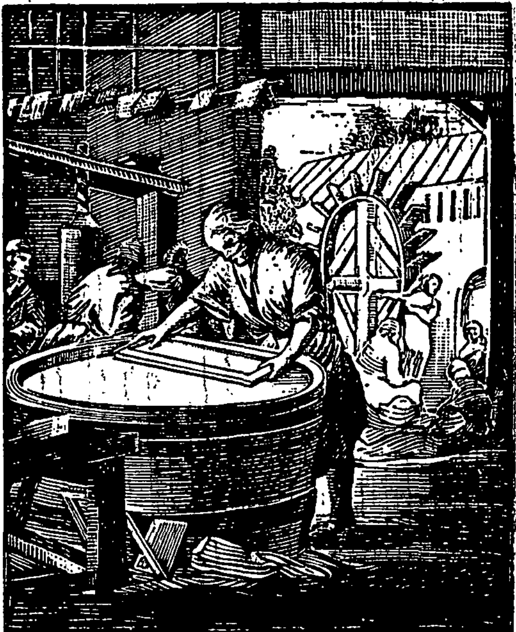

INSTITUTE OF
PAPER CHEMISTRY
Appleton · Wisconsin

STUDIES ON THE FACTORS GOVERNING RETENTION AND EFFECTIVENESS OF STARCH XANTHATES AND XANTHIDES BY WOOD PULP IN PAPERMAKING

Project 2580

Report Eight

A Quarterly Report
to
AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE

September 28, 1967

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SUMMARY

The data presented in Tables IV to VI of Report Seven are interpreted and discussed. Further work is described dealing with the effects of varying xanthate D.S., fiber refining, and storage of dilute starch xanthate before cross-linking and a preliminary interpretation is given.

Xanthide sorption activation energies calculated from the data presented in the earlier report show that retention rates are relatively unaffected by temperature changes but are quite dependent upon the alum concentration over the range of 2×10^{-5} to 2×10^{-3} molar. This suggests that starch xanthide sorption by fines-free bleached softwood kraft fibers is inhibited by a surface potential barrier which is overcome by the addition of alum.

Further activation energy calculations based on dry and wet tensile strength enhancement give conflicting results. The calculations based on dry tensile strength improvement yield slightly higher activation energies than those based on xanthide sorption but are still consistent with a diffusional or a hydrogen bonding mechanism. However, wet tensile strength enhancement is strongly dependent upon sorption temperature at low alum concentration but not at high alum concentration. This may be due to surface charge inhibition of lateral migration of sorbed xanthide to the fiber bonding areas.

The results show the solution may be held as long as 4 hours at 20°C. without drastically affecting the properties of the paper.

INTRODUCTION

Project 2580 is being carried out in cooperation with the Agricultural Research Service of the United States Department of Agriculture. The scope of the project is specified in Contract Number 12-14-100-8308(71) issued under the authority of the Research Marketing Act of 1946 as amended. The purpose of the project is to expand the use of cereal products in papermaking by determining factors governing sorption of starch xanthate and starch xanthide by wood fibers in dilute aqueous suspensions. This is the eighth quarterly report under the terms of the contract.

It has been established in earlier reports that sorption of starch xanthate prior to oxidative coupling to form starch xanthide plays a very minor role in the overall retention of starch xanthide in paper. Consequently, the oxidative coupling step has been isolated from the sorption experiments by treating dilute starch xanthate with sodium hypochlorite under carefully controlled conditions prior to combination with the wood fiber. By doing this, sorption conditions may be varied without introducing factors which might change the xanthide particle size distribution (and hence the sorption rate) of the starch xanthide. Thus, the sorption rate experiments start with the same form of starch xanthide regardless of the sorption conditions being evaluated. Another consideration is that preparing starch xanthide separately from the fiber (ex situ) more closely parallels the concurrent development programs being carried out by the cooperating agency.

The new data generated for this report are given only a preliminary interpretation pending the completion of the analyses for starch xanthide retention. Based on wet tensile strength improvement, sorption of starch xanthide prepared from D.S. 0.08 and D.S. 0.12 starch xanthate is dependent upon both the alum concentration and fiber surface area. However, in the lowest alum concentration (2×10^{-5} $\underline{M}$) the sorption rates for both xanthides pass through maxima as the fiber surface area increases. This suggests that some component of the alum complex system may be sorbed on the fiber to give an optimum density on the fiber surface. Thus, the rate increases with the fiber surface area until the surface area exceeds the supply of the unknown alum component.

A direct comparison of the performance of xanthides from D.S. 0.08 and 0.12 xanthate is not possible at this time. The concentration datum for the D.S. 0.08 xanthate was amended after the experiments were nearly completed. As a consequence, the concentrations used were too low for meaningful comparisons. However, the similarity of the activation energies based on the wet tensile data suggests D.S. 0.08 and D.S. 0.12 xanthide perform equally well.

The logarithm of the wet tensile sorption rate with D.S. 0.12 xanthide is proportional to the fiber surface area at constant xanthide and fiber concentrations in 2×10^{-4} $\underline{M}$ alum. Further, it is proportional to the xanthide concentration at constant fiber consistency and surface area. However, the log of the rate is a complex function of the product of the xanthide concentration and the surface area per unit volume of fiber suspensions suggesting that the fiber consistency and alum to fiber ratio also could be important factors.

A study was run to evaluate the effects of storing dilute starch xanthate (about 0.17 g./100 ml.) before cross-linking to form starch xanthide.

In the preceding report, experiments were described in which starch xanthide sorption rates were studied at three temperatures and three alum concentrations. Since analyses of the xanthide content of the samples was completed just before the report was issued, interpretation of these data was postponed until the present report.

INTERPRETATION OF SORPTION DATA PRESENTED IN REPORT SEVEN

INTRODUCTION

The endeavor to control and reproduce the oxidative cross-linking of starch xanthate to form starch xanthide in the laboratory resulted in the data shown in Tables IV to VI of Report Seven. For easy reference, these tables are reproduced in the Appendix of this report (p. 42 to 45). The major goal of the work described in earlier reports has been to obtain data showing the temperature dependence of the starch xanthide sorption rate. With this information, the activation energy of the process may be calculated. The value of the apparent activation energy makes certain judgments possible concerning the mechanism of the rate controlling step of the sorption process.

The activation energy is related to the rate constant as shown in the Arrhenius equation:

$$k = A \exp (- E_a/RT) \qquad (1)$$

where

$\underline{k}$ = reaction rate constant

$\underline{A}$ = constant

$\underline{E_a}$ = energy of activation

$\underline{R}$ = gas constant

$\underline{T}$ = absolute temperature

Thus, the rate constant is the critical value to be determined from the sorption data. However, neither the concentration dependence nor the order of the process is known. Consequently, the absolute rate constant is not available from the data on hand. This is not an unusual situation for studies dealing with polymer sorption.

The process rate may be substituted in the Arrhenius equation (1, 2) since it is proportional to the rate constant. However, by doing this the effect of component concentrations is also introduced (1). Therefore, the rate value inserted must be determined at a point in the process where the initial concentrations are relatively unchanged so that sorption conditions may be specified as precisely as possible. If this is done, the effect upon the Arrhenius equation is to change the value of the proportionality constant A. The exponential function containing the activation energy is unaffected.

If we substitute the rate, r, for the rate constant and set Equation (1) in logarithmic form we obtain:

$$\ln r = \ln A_r - \frac{E_a}{RT} = 2.303 \log r \qquad (2)$$

where A_r denotes the changed value of the proportionality constant due to the substitution. In this form, the logarithm (base 10) of the sorption rate should be a linear function of $1/T$ with its slope equal to $E_a/2.303\ R$. The intercept ($\ln A_r$) is not utilized in this evaluation. Further reference to Equation (2) will occur as this discussion proceeds.

DETERMINATION OF SORPTION RATES

The technique of fitting the sorption data to a mathematical model in order to calculate an apparent sorption rate at a small but finite sorption time (2) was selected for this study. This procedure makes maximum use of the data available and does not place undue emphasis upon the less precise data obtained early in each sorption run.

It has been shown in Report Six that both the xanthide content of the handsheets and the logarithms of the xanthide content increase linearly with the logarithm of the contact time. The log-log relationship is the preferred representation for the problem being faced at this point:

$$\log \frac{\text{mg. xanthide}}{\text{g. fiber}} = \log a + b \log t \qquad (3)$$

where *a* and *b* are constants and *t* is sorption time in seconds. An equivalent representation of Equation (3)(2,3):

$$\frac{\text{mg. xanthide}}{\text{g. fiber}} = at^{b} \qquad (4)$$

takes the form of the Freundlich equation where time replaces concentration or pressure (4).

$$\frac{x}{m} = kc^{1/n} \qquad (5)$$

Here *x* and *m* are the masses of substance absorbed and of adsorbent, respectively; *c* is the concentration of the solution at equilibrium and *n* is an empirical constant greater than unity.

In dealing with a system before equilibrium is attained and where desorption is negligible it is not unreasonable that the sorption rate be a function of the total number of effective particle collisions. That is, collision frequency (a function of particle size, number per unit volume, and temperature) multiplied by the time.

ACTIVATION ENERGY FROM XANTHIDE RETENTION

The xanthide sorption data were fitted to Equation (3) by means of the least squares procedure. The intercept, log a at log t = 0, is equal to the logarithm of the apparent rate at 1 second. These rate values are used to calculate the apparent activation energy by the least squares analysis of Equation (2). The results are shown in Table I and Fig. 1.

The activation energies for starch xanthide sorption in 2×10^{-5}, 2×10^{-4} and 2×10^{-3} molar alum are low: -1.5, +1.1, and -3.8 kcal./mole, respectively. Thus, the effective rate-controlling process is relatively unaffected by temperature. However, the slight curvature of the lines shown in Fig. 1 suggest that the process is complex and the rate-controlling step may be changing with the temperature.

A negative activation energy may or may not have meaning. However, in dealing with polymer sorption, negative values are found occasionally. For example, Pearl (5) shows that amylose sorption by paper fibers increases with decreasing temperature.

It was known from earlier work (see Report Six) that xanthide sorption is very low in the absence of alum. Figure 1 illustrates the strong dependency of the log sorption rate upon the log of the alum concentration. This suggests that mutual repulsion of like surface charges may inhibit or prevent xanthide sorption in the absence of alum.

ACTIVATION ENERGY FROM DRY AND WET TENSILE STRENGTH ENHANCEMENT

If it is assumed that wet and dry tensile strength enhancement are linear functions of the starch xanthide content of the handsheets, two additional

TABLE I

CALCULATION OF ACTIVATION ENERGIES BASED ON XANTHIDE SORPTION DATA: LEAST SQUARES ANALYSIS

Alum Concentration, molar	Sorption Temp., °C.	10^4 x 1/T, °K^{-1}	Slope[a]	Log Apparent Rate at 1 Sec.[b]	No. Points Used	Arrhenius Gradient, °K	E_a kcal/mole
2×10^{-3}	15	34.78	0.196	1.017	6	+820	-3.8
	25	33.52	0.276	0.682	6		
	35	32.45	0.166	0.839	6		
2×10^{-4}	15		0.232	0.694	6	-232	+1.1
	25		0.214	0.705	6		
	35		0.162	0.749	6		
2×10^{-5}	15		0.328	-0.0427	6	+516	-1.5
	25		0.309	0.0030	5		
	35		0.181	-0.0665	2		

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[a] Slope = 1/m in $S = at^{1/m}$.

[b] Log mg./g. fiber/sec.

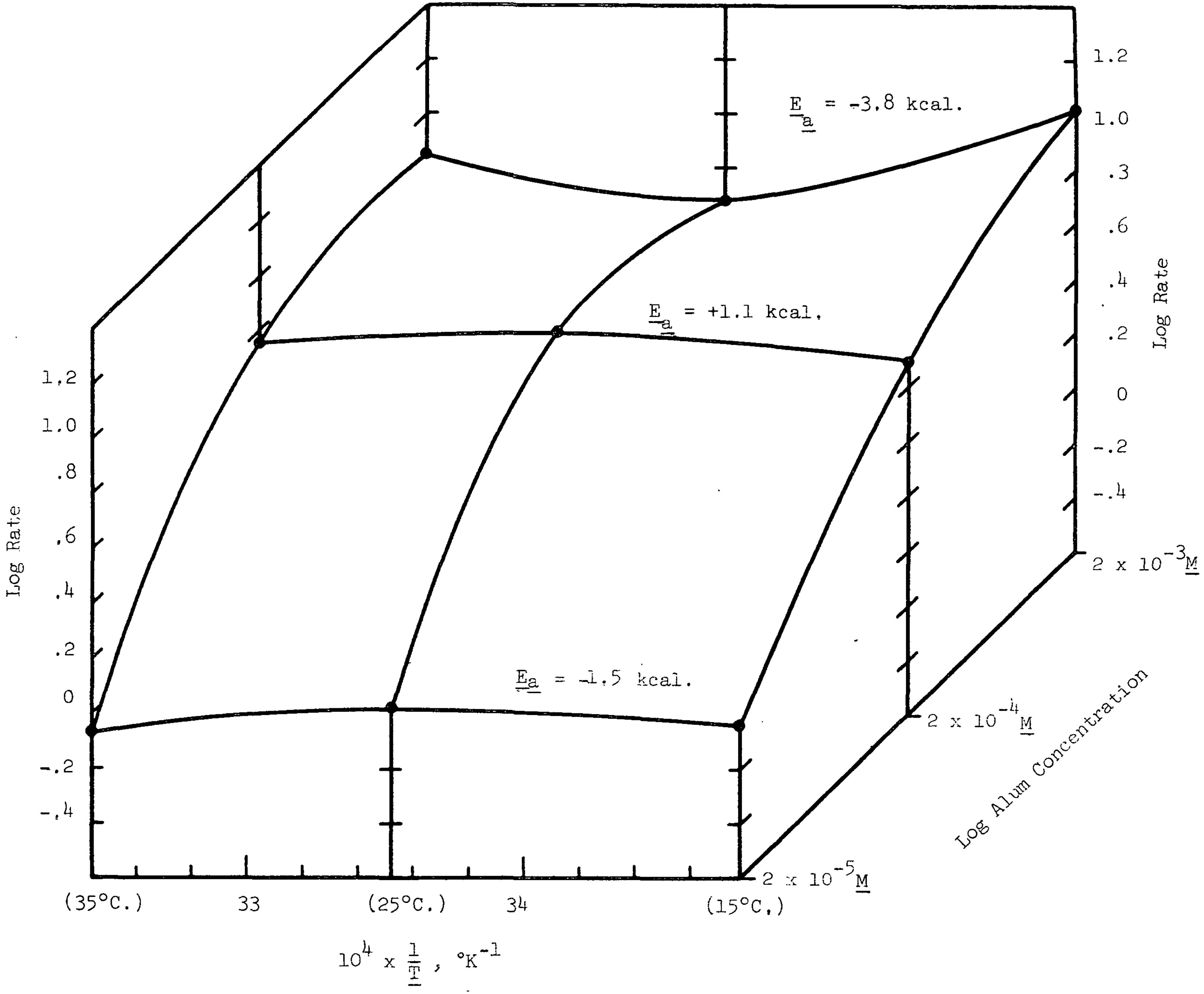

Figure 1. Sorption Rate as a Function of Temperature and Alum Concentration: Xanthide Data

estimates of sorption activation energy are available. It is admitted that the estimation of thermodynamic characteristics from physical properties imparted to paper is not based on firm ground. However, it is such properties as these that are a fundamental concern for the whole effort dealing with starch xanthide. Moreover, the analytical method for starch xanthide content itself is indirect. The estimate is based upon the difference in reducing power of hydrolyzed alkaline extracts and not on the starch xanthide as such.

The differences between the tensile strength of the handsheets treated with starch xanthide and the blank are introduced into Equation (3) to obtain the apparent rate logarithms at 1 second and then into the logarithmic form of the Arrhenius equation [Equation (2)]. Least squares procedures were used in both instances after determining that the data fit the log-log representation expressed in Equation (3). The results of these computations are shown in Tables II and III.

It will be noted by examining Tables IV-VI of Report Seven, (shown in the Appendix) that the values of the dry tensile strength blanks are affected by the alum concentration. This was taken into account in calculating the dry tensile increments.

The activation energies derived from the dry tensile data are somewhat higher than those obtained by analysis of the starch xanthide content. However, the departure is not large and the values show the same trends according to the alum concentration. The process is relatively unaffected by the sorption temperature and the activation energy values are consistent with diffusional and hydrogen bonding rate-controlling processes.

TABLE II

CALCULATION OF ACTIVATION ENERGIES BASED ON INCREASE[a] IN DRY TENSILE STRENGTH; LEAST SQUARES ANALYSIS

Alum Concentration, molar	Sorption Temp., °C.	$10^4 \times 1/T$, $°K^{-1}$	Slope[b]	Log Apparent Rate at 1 Sec.[c]	No. Points Used	Arrhenius Gradient, °K	E_a, kcal/mole
2×10^{-3}	15	34.78	0.0960	1.872	6	+386	-1.8
	25	33.52	0.121	1.769	6		
	35	32.45	0.0974	1.785	6		
2×10^{-4}	15		0.273	1.189	6	-1482	+6.8
	25		0.277	1.111	6		
	35		0.160	1.549	6		
2×10^{-5}	15		0.266	0.811	6	-1007	+4.6
	25		0.186	1.015	6		
	35		0.164	1.042	6		

---

[a] Calculated from blank obtained at constant alum concentration.

[b] Slope = $1/m$ in $S = at^{1/m}$.

[c] Log (10 x Δ lb./in./2.4 g. handsheet/sec.).

TABLE III

CALCULATION OF ACTIVATION ENERGIES BASED ON INCREASE IN WET TENSILE STRENGTH: LEAST SQUARES ANALYSIS

Alum Concentration, molar	Sorption Temp., °C.	Temperature $10^4 \times 1/\underline{T}$, °K^{-1}	Slope[a]	Log Apparent Rate at 1 Sec.[b]	No. Points Used	Arrhenius Gradient, °K	$\underline{E}_a$, kcal/mole
2×10^{-3}	15	34.78	0.245	1.666	6	-603	2.8
	25	33.52	0.249	1.621	6		
	35	32.45	0.120	1.813	6		
2×10^{-4}	15		0.320	1.235	6	-2324	10.6
	25		0.278	1.406	6		
	35		0.148	1.872	6		
2×10^{-5}	15		0.448	0.0682	5	-4467	20.5
	25		0.277	0.829	6		
	35		0.111	1.095	6		

---

[a] Slope = $1/\underline{m}$ in $\underline{S} = \underline{at}^{1/\underline{m}}$.

[b] Log ($10^2 \times \Delta$ lb./in./2.4 g. handsheet/sec.).

Figure 2 illustrates a similar dependency upon the alum concentration as shown in Fig. 1. Both xanthide content and dry tensile strength improvement are affected more by the alum concentration than by the sorption temperature.

The results from the wet tensile data are surprisingly different (Table III). In this case, the activation energy changes greatly with the alum concentration and the adsorption process is definitely temperature dependent in 2×10^{-5} and 2×10^{-4} molar alum (Fig. 3). It is difficult to rationalize these significantly higher apparent activation energies. One possibility may be that lateral diffusion of sorbed xanthide over the fiber surface is inhibited by fairly high repulsive electrostatic surface charges. Higher temperature and alum concentrations would tend to favor migration over the fiber surface to fiber cross-over points to enhance fiber-to-fiber bonding. The surface free energy of the xanthide layer would be reduced by concentrating xanthide in the fiber-to-fiber bonding area. However, the same mechanism should enhance dry tensile strength unless xanthide particle penetration into the hydrated fiber surface is low. That is, xanthide strengthens the fiber-to-fiber bond but not the bonding within the cell wall. This in turn may mean the xanthide and cell wall bonds are of similar strength when dry but the xanthide bond is stronger when wet.

A further implication is that the bond strength enhancement continues after the sheet is formed, up to some point in the drying process.

TEMPERATURE DEPENDENCE OF WET TENSILE STRENGTH

There is further information indicating a temperature dependence for the wet tensile strength imparted by a given amount of starch xanthide sorption. This is illustrated in Fig. 4. A regression curve was fitted visually to the plot of xanthide sorption _vs._ wet tensile increase with arbitrary limits drawn

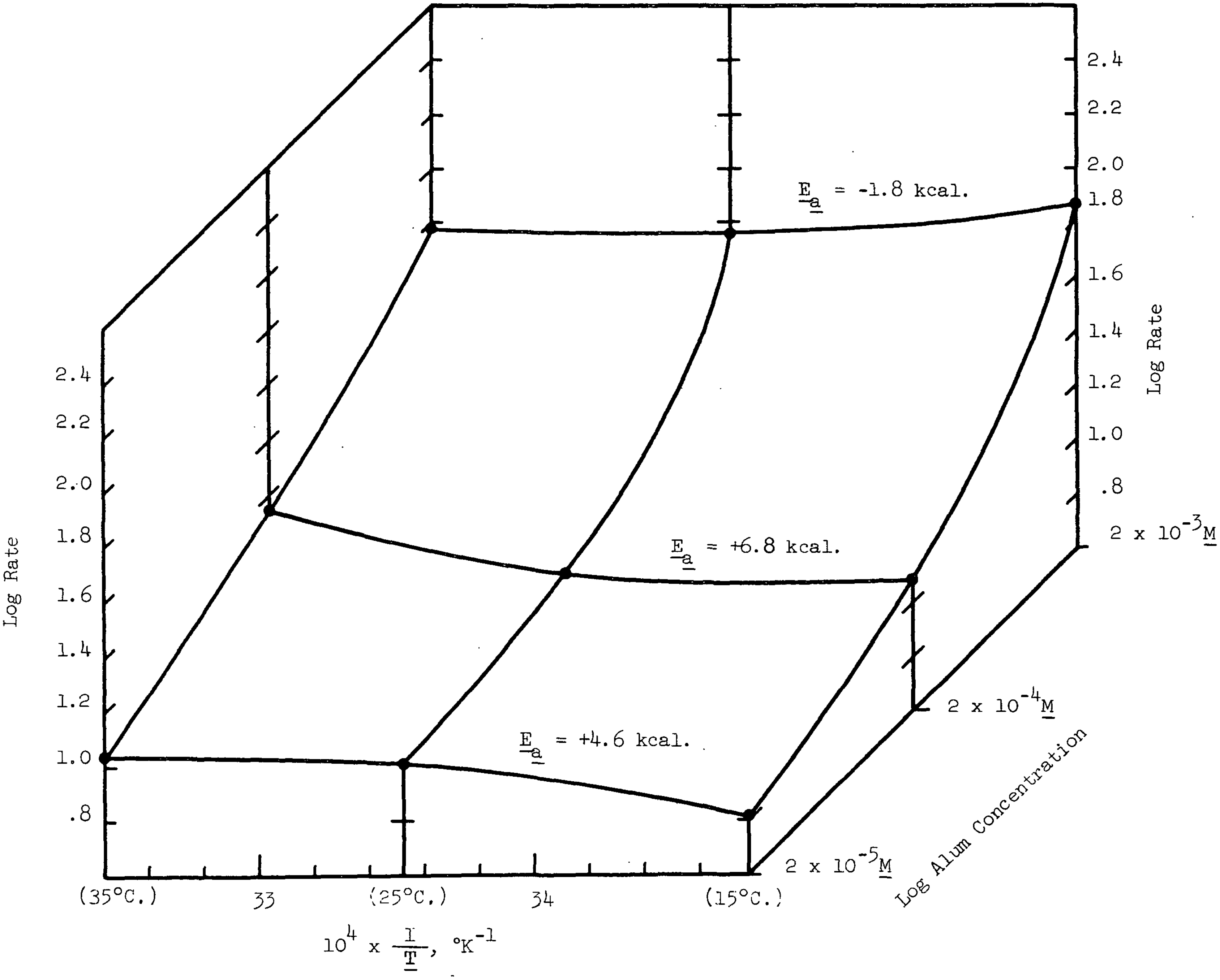

Figure 2. Sorption Rates as Functions of Temperature and Alum Concentration: Dry Tensile Data

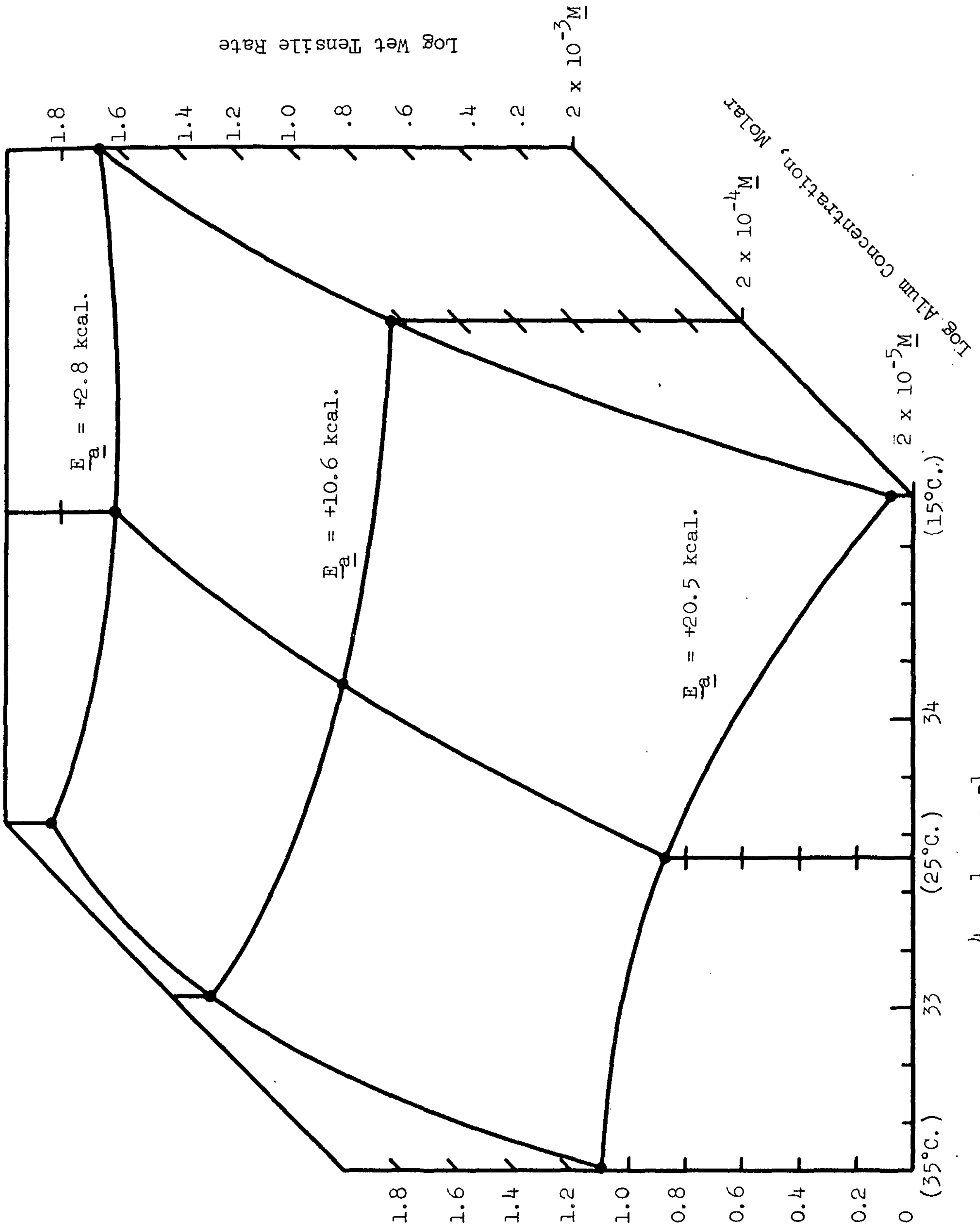

Figure 3. Sorption Rates as Functions of Temperature and Alum Concentration: Wet Tensile Data

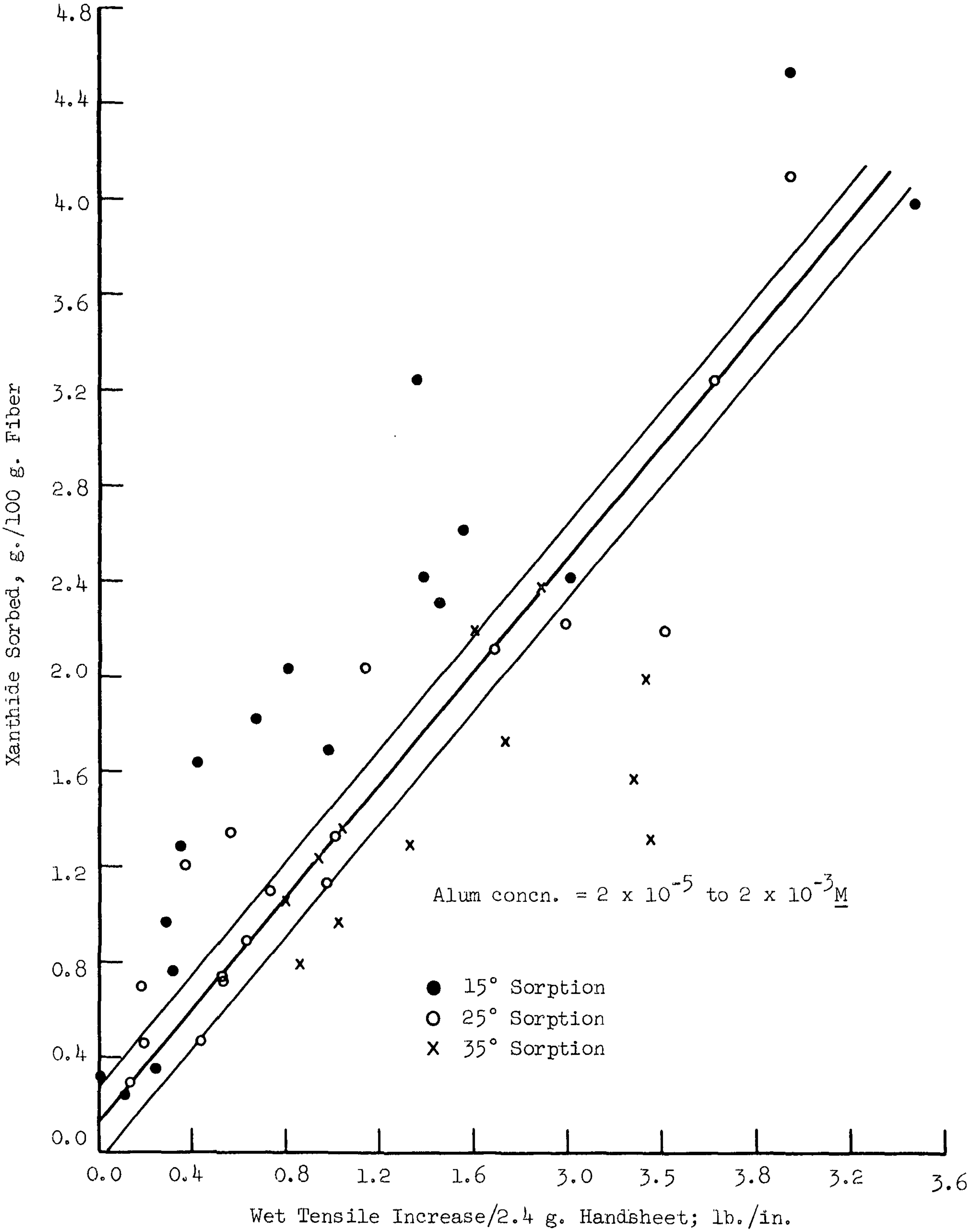

Figure 4. Effect of Temperature on Correlation of Xanthide Content and Wet Tensile Strength Increase Produced by Xanthide Addition

in. The area outside the regression band was assigned + and - values indicating the desirability of obtaining the maximum wet strength from a given amount of xanthide sorbed. Table IV is a tabulation of points outside the regression band according to the sorption temperature. The 15°C. data fall largely in the negative zone while over half the 35° data are in the positive zone with none in the negative portion. Thus, sorbed xanthide wet tensile efficiency increases with the sorption temperature. However, by inspecting the original data (see Appendix) it is seen that the lowest temperature produces the greatest total sorption and hence the highest wet tensile strengths.

TABLE IV

ANALYSIS OF TEMPERATURE DEPENDENCE OF WET STRENGTH PER UNIT STARCH XANTHIDE SORBED

Temp., °C.	No. Points, total	No. Points, (-)	No. Points, (+)	Points, % (-)	Points, % (+)
15	18	12	1	67	5
25	18	5	2	28	11
35	12	0	7	0	58

EFFECT OF pH of 2×10^{-3} $\underline{M}$ ALUM

The role alum plays in improving sorption appears to be complex. Figure 5 shows that the extent of xanthide sorption is reduced by neutralizing part of the acidity imparted by 2×10^{-3} molar alum. Neutralization with sodium hydroxide reduces the amount of aluminum hexahydrate ($Al(H_2O)_6^{+3}$), and increases the amount of more complex aluminum ions. Using less alum also decreases the amount of $Al(H_2O)_6^{+3}$ ion in the system and is accompanied by lower apparent sorption rates. If xanthide sorption is controlled by the electrical double layer, $Al(H_2O)_6{}^{+3}$ should be more effective than the higher D.P. aluminum ions in reducing the effects of double layer repulsions.

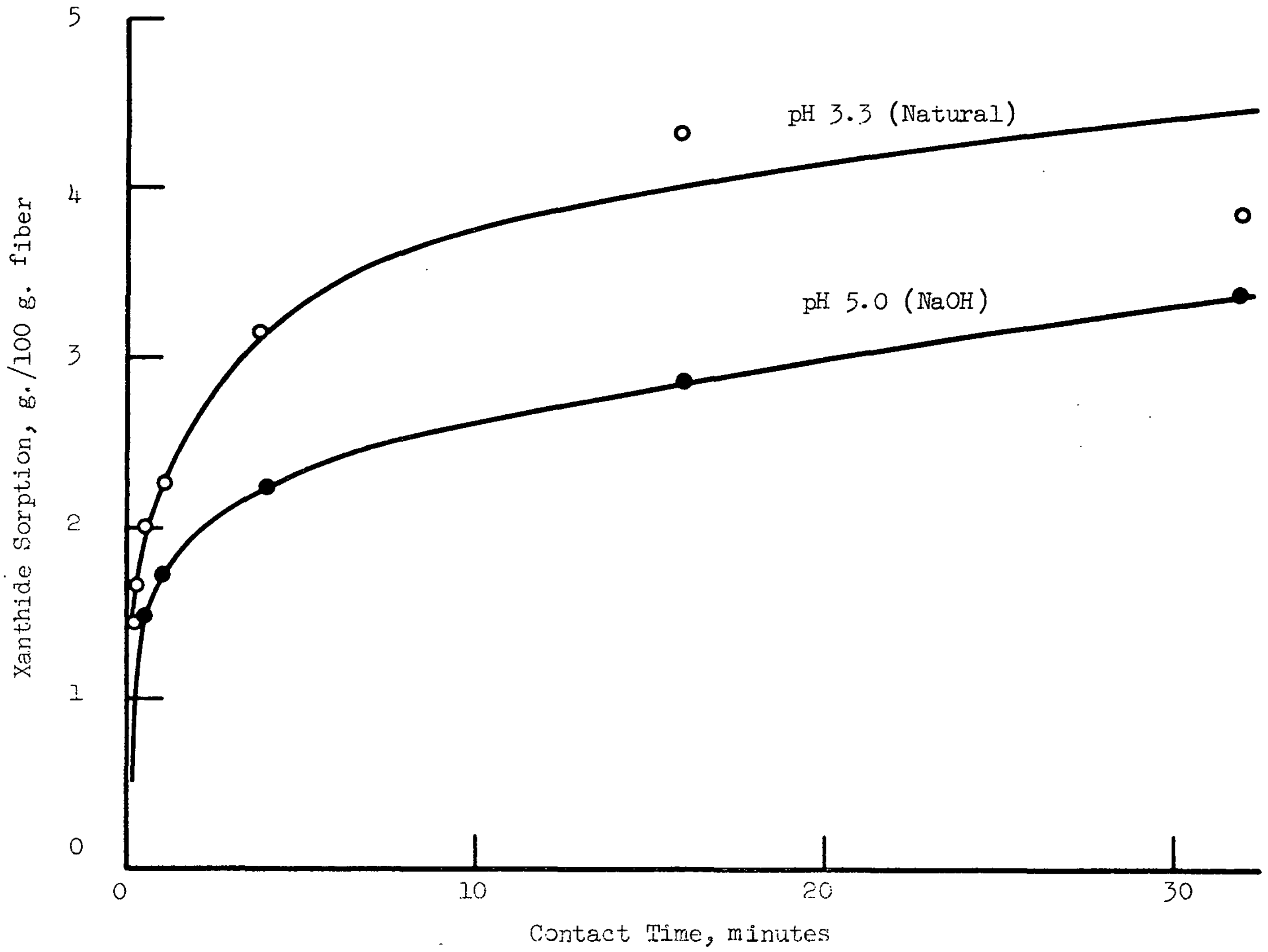

Figure 5. Effect of Changing Composition of $2 \times 10^{-3}\underline{M}$ Alum System by Neutralizing to pH 5 at 15°C.

The hydrogen ion concentration, of course, changes upon neutralizing the alum or changing the alum concentration. However, it is not yet possible to study pH effects upon xanthide sorption independently of the alum system. The composition of the hydrated aluminum in equilibrium in aqueous solution varies with the pH in a complex way depending on such things as the age of the solution before and after adjusting the pH and the way the adjustment is brought about. In view of the complications involved in maintaining a specified pH as the alum concentration changes it was deemed advisable to accept the pH imparted by the alum.

EXPERIMENTAL

D.S. OF XANTHATE VS. FIBER REFINING LEVEL AND ALUM CONCENTRATION

The sorption rate procedures described in Report Seven were used to evaluate the effects of increasing the fiber surface area upon sorption rates and to study the sorption rates of xanthide prepared from starch xanthate of differing degrees of substitution (D.S. = 0.08 vs. 0.12). One procedural modification was made. Where the short-term sorption samples had been blended by manual shaking, mechanical stirring was used. By doing this blending, conditions were nearly identical for all six samples in a given run. However, the reproducibility was not greatly affected. Sorption runs duplicating conditions used several months earlier, reproduced the previous responses within the normal variations.

During the preparation of samples using xanthate Run No. 541 (D.S. 0.80) the concentration data were amended. For this reason the xanthide concentration as prepared is but 0.836 that used with the higher D.S. That is, 0.1045 rather than 0.125 g./100 ml. solution. Thus, 0.209 g. of xanthide was blended with 2.4 g. fiber to give a xanthide-to-fiber ratio of 8.71 g. per 100 g. fiber as compared with 10.42 g. per 100 g. fiber for the xanthide prepared from D.S. 0.12 xanthate.

Rayonier bleached softwood kraft fibers were beaten to 700, 500, and 300-ml. Schopper-Riegler freeness, classified to remove fines and characterized as to Specific Surface Area, and Specific Volume by the hydrodynamic procedure. This information is shown in Table V.

TABLE V

CHARACTERISTICS OF BLEACHED KRAFT FIBERS BEATEN TO THREE FREENESS LEVELS

Beaten Freeness, ml.S.-R.	Classified Freeness, ml. S.-R.	Specific Surface, $cm.^2/g.$	Specific Volume, $cm.^3/g.$
700	850	11,840	2.62
500	850	14,150	2.69
300	830	17,950	2.80

For the evaluation of the 0.08 D.S. xanthide a partial factorial design was used based on that used in Report Seven. The alum concentration was varied at 15°C. from 2×10^{-5} to 2×10^{-4} to 2×10^{-3} <u>M</u> and the sorption temperature was varied from 15° to 25° to 35°C. at 2×10^{-4} <u>M</u> alum, (Tables VI to VIII).

The effect of fiber surface area upon D.S. 0.12 xanthide was studied only at 25°C., using 2×10^{-5}, 2×10^{-4}, and 2×10^{-3} molar alum, (Tables IX to XI).

Further studies with D.S. 0.12 xanthide varied the concentration of both the fiber and xanthide while maintaining the specified alum concentrations and sorption temperatures, (Table XII). A summary of concentration effects is presented in Table XIII.

TABLE VI

D.S. 0.08 XANTHIDE SORPTION BY 300 ML. S.-R. FREENESS FIBERS

Sample File No.	Temp., °C.	Alum 2 x 10^{-N} M, N	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate[a], log 100 Δw/sec.
205488	15	3	Blank	15.6	0.60	
89			1/4	19.4	1.13	1.44
90			1/2	22.1	1.31	
91			1	22.0	1.39	
92			4	24.6	1.94	
93			16	25.6	2.21	
94			32	26.1	2.12	
205495	15	4	Blank	15.8	0.59	0.80
96			1/4	17.8	0.80	
97			1/2	20.6	1.00	
98			1	19.0	0.96	
99			4	23.4	1.46	
500			16	24.4	1.74	
501			32	25.2	1.68	
205502	15	5	Blank	17.8	0.62	0.10
03			1/4	16.1	0.62	
04			1/2	17.6	0.63	
05			1	18.4	0.69	
06			4	18.8	0.68	
07			16	18.5	0.74	
08			32	20.2	0.84	
205509	25	4	Blank	18.3	0.64	1.06
10			1/4	18.8	0.88	
11			1/2	19.2	0.94	
12			1	21.1	1.13	
13			4	23.1	1.42	
14			16	24.2	1.68	
15			32	25.6	1.84	
205516	35	4	Blank	13.9	0.53	1.39
17			1/4	20.8	0.96	
18			1/2	20.1	1.21	
19			1	21.2	1.32	
20			4	20.5	1.64	
21			16	23.4	1.83	
22			32	24.2	1.72	

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[a] Apparent rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE VII

D.S. 0.08 XANTHIDE SORPTION BY 500 ML. S.-R. FREENESS FIBERS

Sample File No.	Temp., °C.	Alum $2 \times 10^{-N}M$, N	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate,[a] log 100 Δw/sec.
205453	15	3	Blank	15.3	0.56	1.48
54			1/4	19.0	1.09	
55			1/2	21.3	1.28	
56			1	21.1	1.36	
57			4	23.2	1.88	
58			16	25.4	2.14	
59			32	22.8	2.08	
205460	15	4	Blank	13.8	0.51	1.16
61			1/4	15.8	0.73	
62			1/2	19.2	0.90	
63			1	18.4	1.01	
64			4	19.4	1.29	
65			16	22.1	1.46	
66			32	21.7	1.42	
205467	15	5	Blank	13.8	0.50	0.51
68			1/4	14.4	0.58	
69			1/2	15.2	0.58	
70			1	16.2	0.60	
71			4	17.5	0.64	
72			16	16.4	0.64	
73			32	17.0	0.74	
205474	25	4	Blank	15.6	0.52	1.30
75			1/4	16.7	0.83	
76			1/2	15.7	0.90	
77			1	19.3	1.06	
78			4	21.3	1.42	
79			16	24.0	1.70	
80			32	22.0	1.58	
205481	35	4	Blank	16.6	0.48	1.38
82			1/4	13.9	0.80	
83			1/2	17.8	1.00	
84			1	18.7	1.08	
85			4	19.3	1.50	
86			16	21.9	1.60	
87			32	21.0	1.68	

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[a] Apparent rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE VIII

D.S. 0.08 XANTHIDE SORPTION BY 700 ML. S.-R. FREENESS FIBERS

Sample File No.	Temp., °C.	Alum 2 x 10^{-N} M, N	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate[a], log 100 Δw/sec.
205446	15	3	Blank	11.6	0.44	1.58
47			1/4	18.6	1.16	
48			1/2	18.2	1.24	
49			1	19.2	1.40	
50			4	21.5	1.89	
51			16	24.1	2.16	
52			32	21.7	2.10	
205439	15	4	Blank	12.2	0.42	0.99
40			1/4	14.7	0.64	
41			1/2	13.6	0.64	
42			1	15.0	0.78	
43			4	17.2	1.05	
44			16	17.8	1.20	
45			32	18.0	1.12	
205432	15	5	Blank	12.1	0.44	0.11
33			1/4	12.4	0.44	
34			1/2	12.8	0.48	
35			1	12.6	0.49	
36			4	11.6	0.52	
37			16	14.5	0.54	
38			32	14.2	0.66	
205418	25	4	Blank	12.3	0.42	1.11
19			1/4	14.4	0.64	
20			1/2	15.4	0.72	
21			1	17.2	0.98	
22			4	16.0	0.96	
23			16	16.8	1.16	
24			32	17.4	1.18	
205425	35	4	Blank	11.9	0.44	1.51
26			1/4	16.1	0.95	
27			1/2	17.8	1.16	
28			1	17.8	1.26	
29			4	18.1	1.37	
30			16	21.0	1.74	
31			32	19.9	1.74	

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[a] Apparent rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE IX

SORPTION OF D.S. 0.12 XANTHIDE BY 300 ML. S.-R. FREENESS FIBERS

Sample File No.	Temp., °C.	Alum 2 x 10^{-N} M, N	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate[a], log 100 Δw/sec.
205575	25	3	Blank	17.2	0.68	1.89
76			1/4	27.7	1.93	
77			1/2	27.8	2.14	
78			1	27.9	2.72	
79			4	31.8	3.64	
80			16	31.5	3.88	
81			32	32.6	4.26	
205582	25	4	Blank	16.9	0.62	1.70
83			1/4	23.2	1.45	
84			1/2	25.3	1.82	
85			1	26.4	2.12	
86			4	23.6	2.91	
87			16	30.6	3.50	
88			32	31.8	3.83	
205589	25	5	Blank	15.4	0.62	0.31
90			1/4	16.8	0.68	
91			1/2	16.3	0.70	
92			1	17.4	0.78	
93			4	19.0	0.95	
94			16	20.2	1.16	
95			32	19.2	1.00	

---

[a] Apparent sorption rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE X

SORPTION OF D.S. 0.12 XANTHIDE BY 500 ML. S.-R. FREENESS FIBERS

Sample File No.	Temp., °C.	Alum 2 x 10^{-N} M, N	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate[a], log 100 Δw/sec.
205554	25	3	Blank	14.5	0.56	1.82
55			1/4	21.5	0.68(?)	
56			1/2	21.7	1.52(?)	
57			1	24.3	1.98	
58			4	25.9	2.82	
59			16	28.2	3.18	
60			32	25.8	2.84	
205561	25	4	Blank	13.2	0.48	1.50
62			1/4	18.4	1.04	
63			1/2	21.2	1.35	
64			1	22.6	1.58	
65			4	24.6	2.36	
66			16	26.0	2.83	
67			32	28.6	2.97	
205568	25	5	Blank	17.2	0.54	0.89
69			1/4	16.0	0.67	
70			1/2	17.4	0.77	
71			1	17.8	0.89	
72			4	19.6	1.02	
73			16	21.8	1.26	
74			32	19.2	1.22	

(?) (There was slippage of the line clamp during these determinations.)

[a] Apparent rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE XI

SORPTION OF D.S. 0.12 XANTHIDE BY 700 ML. S.-R. FREENESS FIBERS

Sample File No.	Temp., °C.	Alum 2 x $10^{-N}M$, N	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate[a], log 100 Δw/sec.
205533	25	3	Blank	11.2	0.41	1.49
34			1/4	18.0	1.04	
35			1/2	17.6	1.32	
36			1	21.4	1.51	
37			4	23.0	2.17	
38			16	21.7	2.56	
39			32	25.9	2.62	
205540	25	4	Blank	12.4	0.45	1.27
41			1/4	14.2	0.81	
42			1/2	14.4	1.06	
43			1	19.6	1.44	
44			1/4	21.0	2.10	
45			16	24.0	2.35	
46			32	22.2	2.56	
205547	25	5	Blank	11.9	0.42	0.75
48			1/4	14.2	0.55	
49			1/2	14.2	0.58	
50			1	15.0	0.64	
51			4	16.0	0.80	
52			16	16.8	0.93	
53			32	17.3	1.08	

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[a] Apparent sorption rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE XII

SORPTION OF D.S. 0.12 XANTHIDE BY 700 ML. S.-R. FREENESS FIBERS at 25°C. AT VARYING CONCENTRATIONS

File No.	Xanthide, ml.	Xanthide Added, g./100 g. fiber	Fiber Consistency, g./100 ml	Alum $2 \times 10^{-N}\underline{M}$, $\underline{N}$	Contact Time, min.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Sorption Rate[a], log 100 $\Delta\underline{w}$/sec.
505596	600	31.25	0.15	4	Blank	11.6	0.40	1.89
97					1/4	19.4	1.65	
98					1/2	22.5	2.05	
99					1	24.3	2.80	
600					4	24.8	2.88	
601					16	27.4	3.26	
602					32	27.9	4.33	
505603	50	2.60	0.15	4	Blank	11.2	0.41	1.08
604					1/4	14.8	0.56	
605					1/2	14.1	0.65	
606					1	15.2	0.72	
607					4	16.8	1.03	
608					16	18.2	1.26	
609					32	18.8	1.26	
505610	200	10.42	0.04	4	Blank	10.8	0.41	0.83
611					1/4	15.7	0.76	
612					1/2	16.2	0.76	
613					1	17.4	0.92	
614					4	19.4	1.28	
615					16	23.4	1.84	
616					32	25.2	2.05	

---

[a] Apparent rate at 1 second based on increase in wet tensile strength. By graphic analysis.

TABLE XIII

SUMMARY 0.12 D.S. XANTHIDE SORPTION AS A FUNCTION OF CONCENTRATION AT 25°C. IN 2 X 10^{-4} MOLAR ALUM (BASED ON INCREASE IN WET TENSILE)

Set	File Number	Beaten Freeness, ml. S.-R.	Consistency, [F] g./100 ml.	Surface Area,[a] [A] cm.^{2}/ml.	Xanthide Added X/F, g./100 g. fiber	Xanthide Added [X], mg./ml.	[A][X] Alum, g./100 g. fiber	Log Rate[b]
A	540-546	700	0.15	17.76	10.42	15.63	278	1.27
B	561-567	500	0.15	21.22	10.42	15.63	361	1.50
C	582-588	300	0.15	26.92	10.42	15.63	420	1.70
D	596-602	700	0.15	17.76	31.25	46.80	827	1.89
E	603-609	700	0.15	17.76	2.60	3.90	69	0.83
F	610-616	700	0.04	4.74	10.42	4.17	20	1.08

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[a] cm.^{2}/g. x g./ml.

[b] Based on graphic analysis of wet tensile data. Log apparent rate at 1 sec. = log [100 Δw] at log t = 0.

THE EFFECT OF AGING DILUTE STARCH XANTHATE BEFORE CROSS-LINKING

The usual procedure for preparing starch xanthide _ex situ_ was varied by lengthening the interval between diluting to 0.167 g./100 ml. and acidifying to pH 5.5. The intervals used were 5 min. (control), 1 hr., 4 hr., and 19 hr. After aging for the specified periods of time at 20.0°C., the solutions (Run No. 546, D.S. 0.12) were acidified to pH 5.5 and oxidized to the iodine end point with acidified sodium hypochlorite and diluted to 0.125 g. starch per 100 ml. solution.

Starch xanthide (1430 ml.) was added to 10.00 liters of stock containing 17.14 g. 700 S.-R. Freeness kraft fiber and 2×10^{-4} molar (after blending) alum at 25.0°C. The mixture was blended 15 minutes before making 4, 2.4 g. (1600 ml. stock) 8 in. x 8 in. handsheets. These sheets were not pressed but were dried between blotters as described in Reports Six and Seven (Table XIV).

TABLE XIV

EFFECT OF AGING DILUTE D.S. 0.12 XANTHATE AT 20°C. BEFORE CROSS-LINKING

Sample File No.	Xanthate Aged, hr.	Instron Dry Tensile, lb./in.	Instron Wet Tensile, lb./in.	Glucan, %	Xanthide, %	Xanthide, g./100 g. fiber
205617	1/12	19.8	1.96			
	1	19.4	1.66			
	4	20.3	1.60			
	19	15.2	0.73			

Handsheet Conditions:

25°C., 700 ml. S.-R. Freeness fiber, 2×10^{-4} _M_ alum, 15 minutes contact.

DISCUSSION

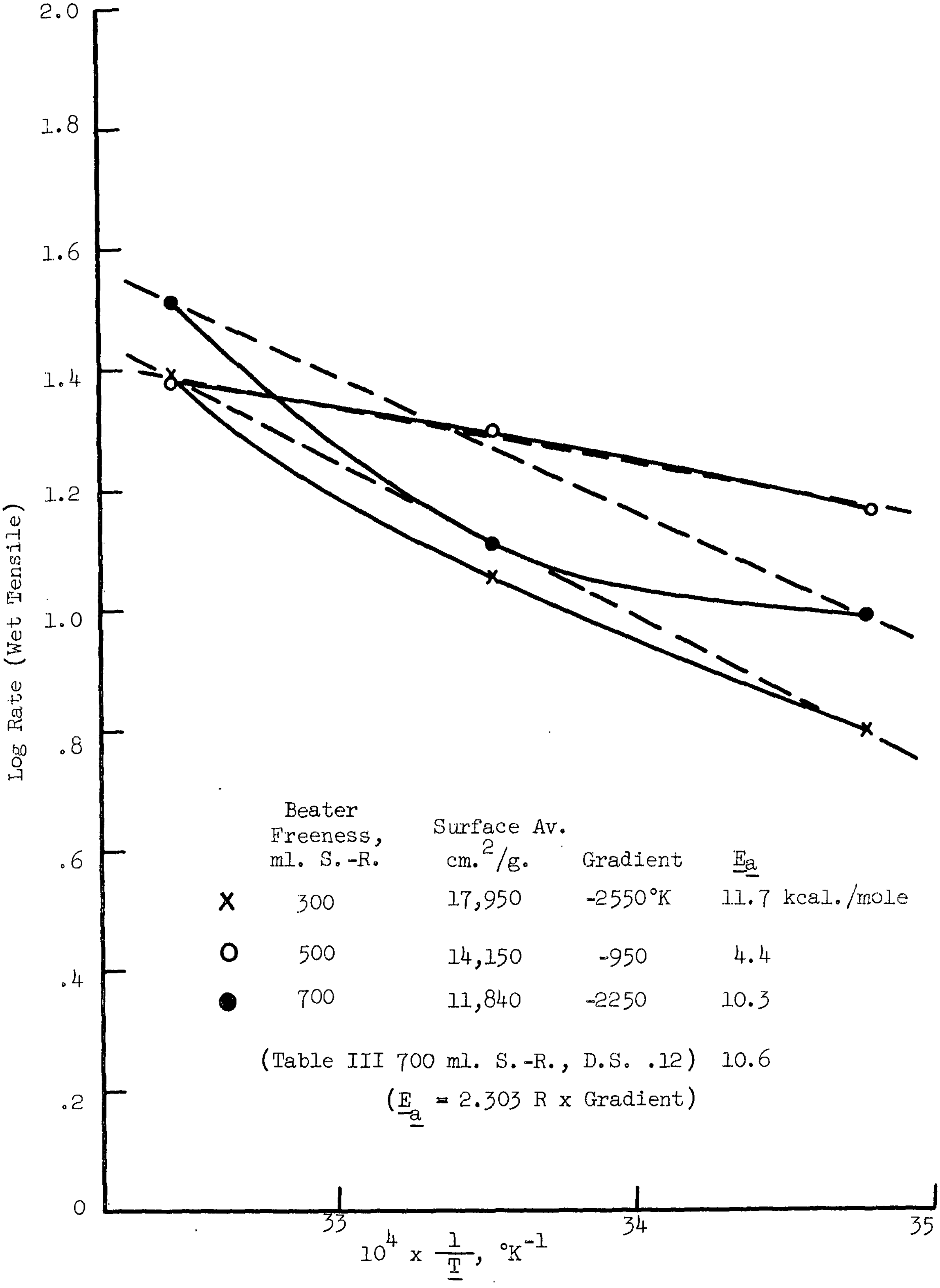
INTRODUCTION

The discussion of the results of the experimental work done during this reporting period will be limited to a preliminary analysis of the wet tensile data. It has been shown (Fig. 4, Table IV) that a reasonably good correlation between wet tensile strength and starch xanthide content exists for sorption carried out at 25°C. Much of the new work was done at that temperature. A more extensive evaluation will be undertaken after the analyses for xanthide sorption are completed.

XANTHIDE FROM D.S. 0.08 XANTHATE

A direct comparison of the effect of the degree of substitution of the parent starch xanthate must be postponed since the sorption studies were carried out at different xanthide-to-fiber ratios as mentioned previously. The lower wet tensile strengths seen with the 0.08 D.S. xanthide are expected since less xanthide was added.

The Arrhenius plot of 0.08 D.S. xanthide sorption in 2×10^{-4} $\underline{M}$ alum (Fig. 6) is based on apparent rates at 1 second derived graphically by extrapolating the wet tensile data to log $\underline{t} = 0$ using the relationship shown in Equation (3) and replotting according to Equation (2). It is not expected that the activation energy should go through a minimum as the fiber surface area increases (Fig. 6). This presents the possibility of an optimum surface area-to-alum relationship. If this is the case then alum could encourage xanthide sorption by being itself adsorbed by the fiber or xanthide to neutralize part of the surface charge as well as by reducing the diffuse double layer surrounding the surface charge.



	Beater Freeness, ml. S.-R.	Surface Av. $cm.^2/g.$	Gradient	E_a
X	300	17,950	-2550°K	11.7 kcal./mole
O	500	14,150	-950	4.4
●	700	11,840	-2250	10.3

(Table III 700 ml. S.-R., D.S. .12) 10.6

(E_a = 2.303 R x Gradient)

Figure 6. Arrhenius Plot of 0.08 D.S. Xanthide Sorption in 2 x 10^{-4} M Alum based on Wet Tensile Strength

The similarity of activation energies for the experiments with 700 ml. S.-R. freeness fibers using D.S. 0.08 and D.S. 0.12 xanthide (Fig. 6) suggests comparable wet tensile strength capabilities for the two xanthides.

COMPARISON OF XANTHIDES FROM D.S. 0.08 AND 0.12 XANTHATES

Figures 7 and 8 compare sorption rates of D.S. 0.08 and D.S. 0.12 xanthides as functions of fiber surface area and alum concentration. There is a strong dependency upon the log of the alum concentration in both cases.

The intermediate refining level (500 ml. S.-R. freeness, 21.2 cm.^{2}/ml. in Fig. 7 and 8) shows maximum sorption at the lowest alum concentration. This is consistent with the low activation energy noted above.

CONCENTRATION DEPENDENCIES

In Table XIII the effects of varying fiber concentration, surface area and D.S. 0.12 xanthide concentration are summarized for 2 x 10^{-4} molar alum at 25°C. Where the number of fibers and the xanthide concentration are held constant, the log rate is proportional to the fiber surface area (Fig. 9). The log sorption rate is also proportional to the xanthide concentration (Fig. 10) when the surface area and fiber consistency are constant.

If xanthide sorption is a function of both surface area and xanthide concentrations, the logarithm of the rate should be proportional to the product of the concentrations for a second-order reaction. That this is not true is illustrated in Fig. 11. Apparently, there are other factors not being considered in the interpretation.

One factor of importance in a diffusional system is the number of fibers. This is reflected in the fiber consistency. For example, with

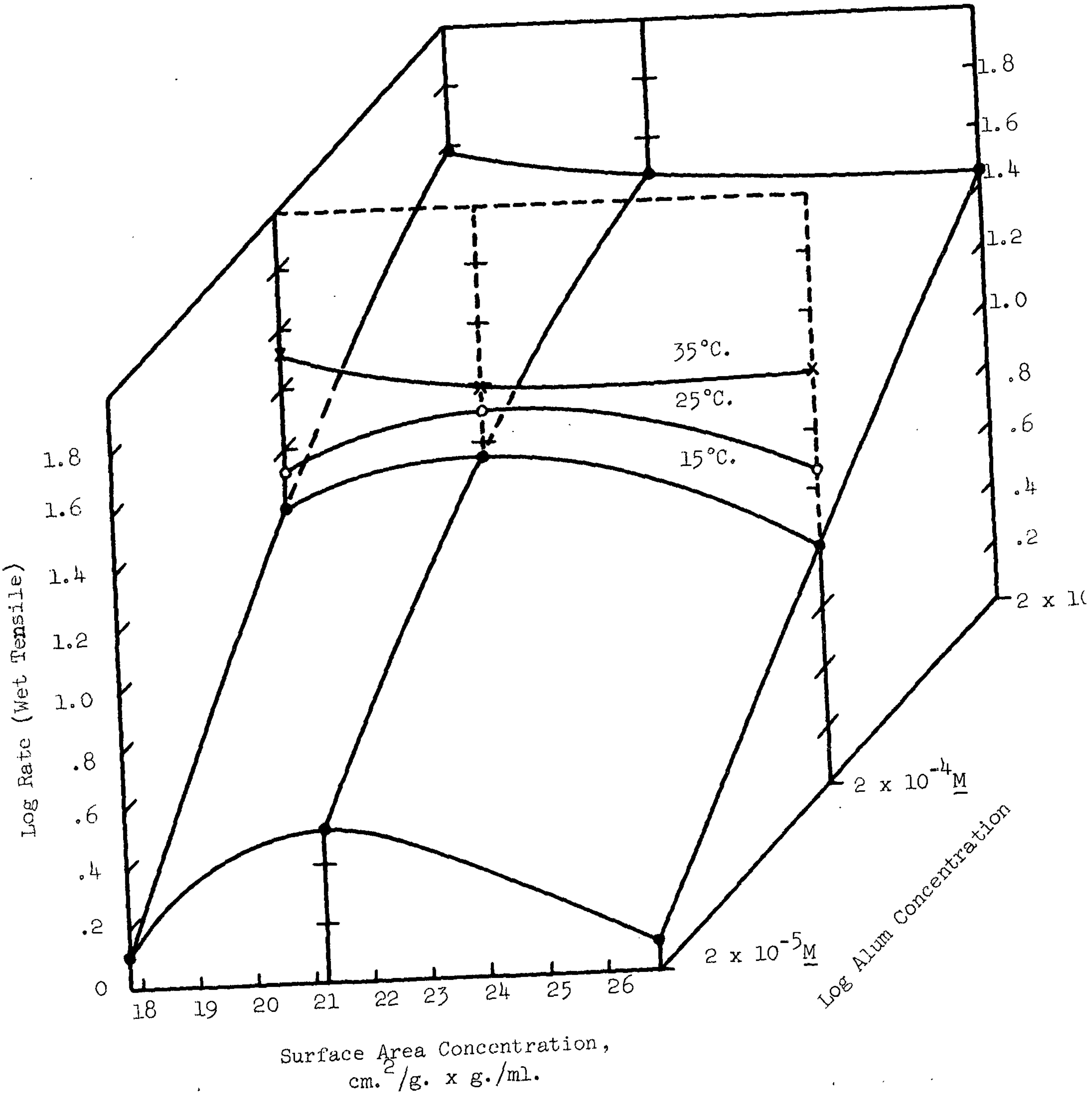


Figure 7. D.S. 0.08 Xanthide Sorption as a Function of Fiber Surface Area and Alum Concentration at 0.15% Fiber Consistency. 8.7 g. Xanthide Added per 100 g. Fiber

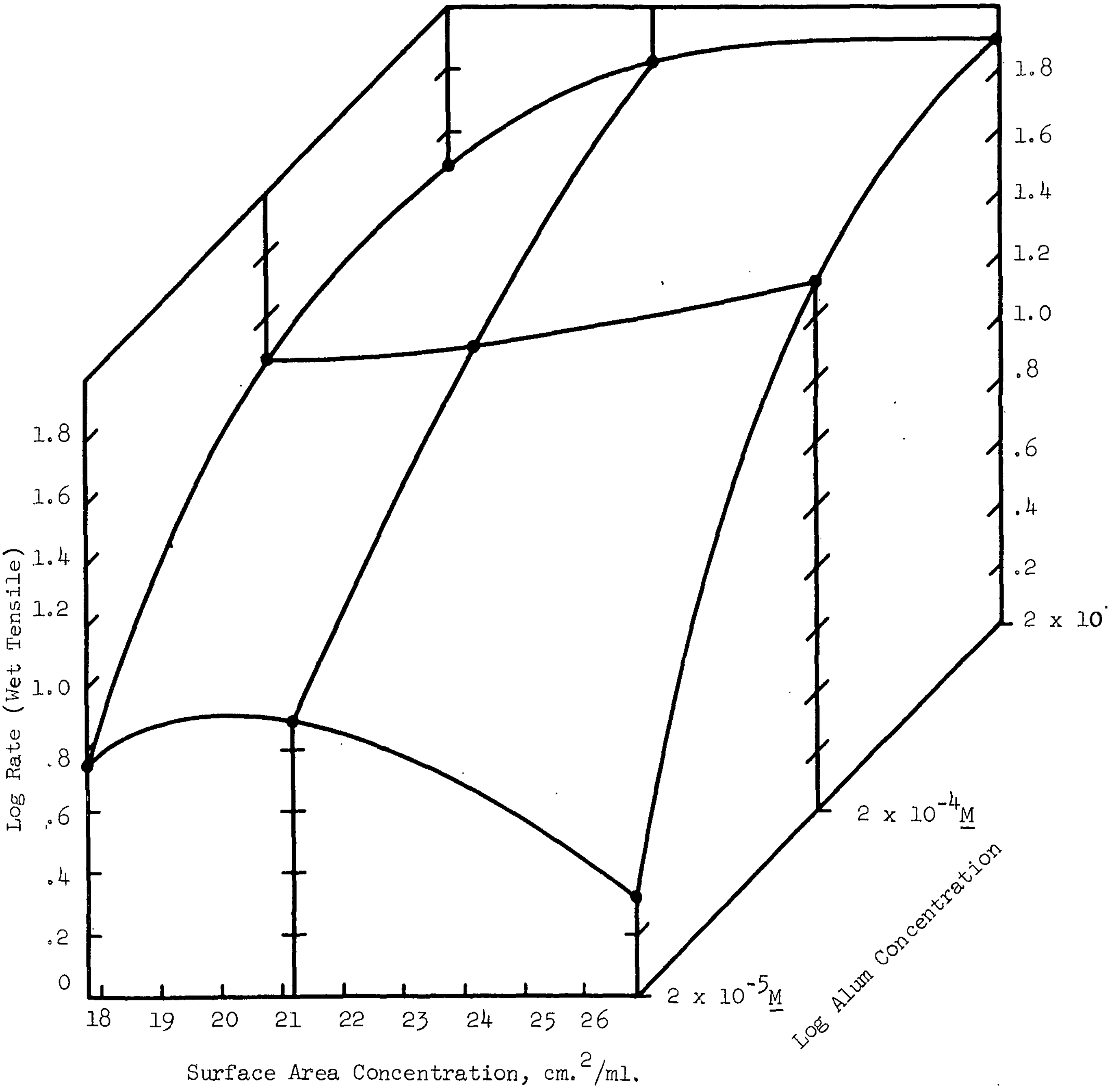


Figure 8. D.S. 0.12 Xanthide Sorption as a Function of Fiber Surface Area and Alum Concentration at 25°C. and 0.15% Fiber Consistency. 10.42 g. Xanthide Added per 100 g. Fiber

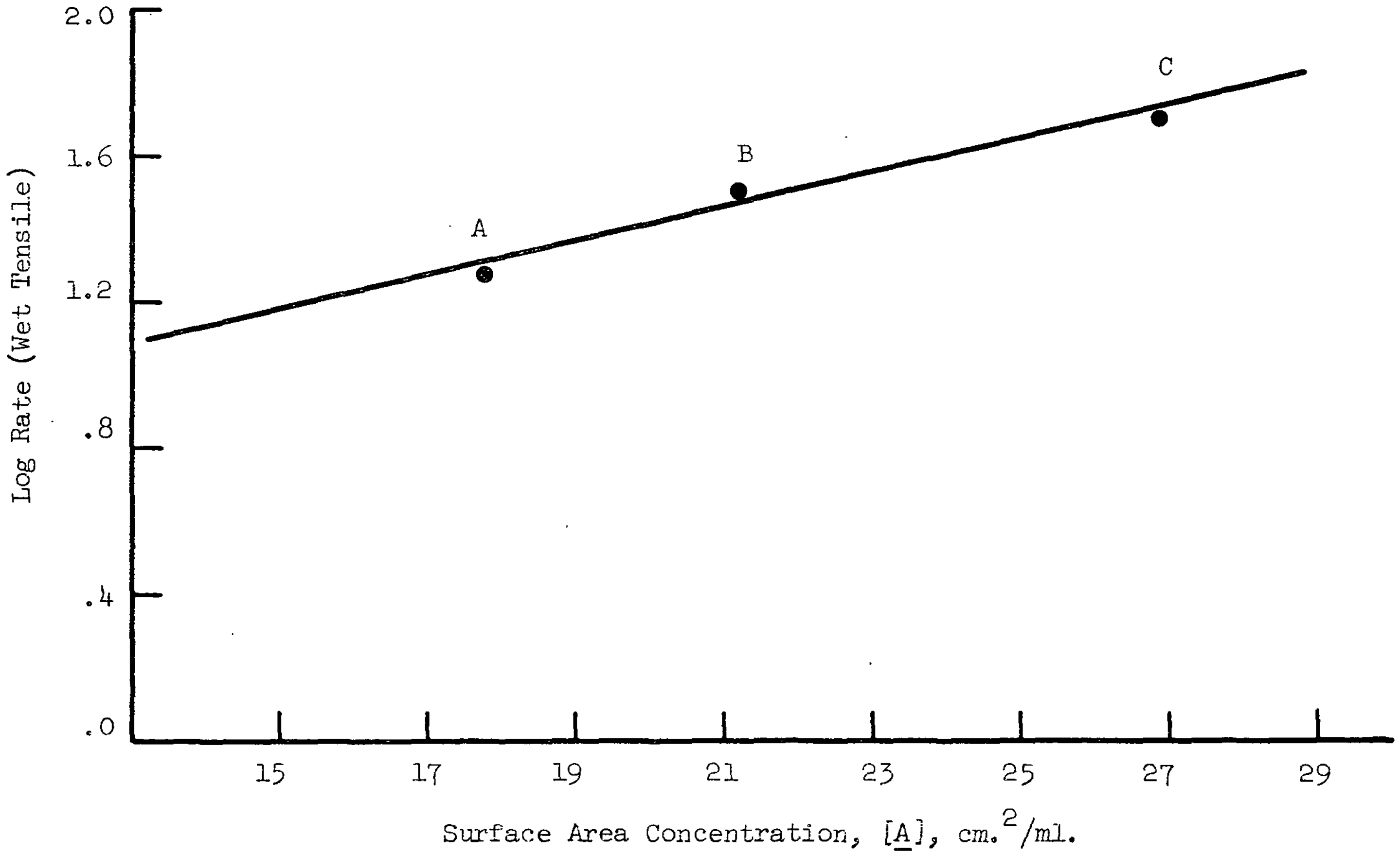


Figure 9. D.S. 0.12 Sorption Rate as a Function of Fiber Surface Area at 25°C. in 0.15% Consistency Fiber Using 10.42 g. Xanthate per 100 g. Fiber

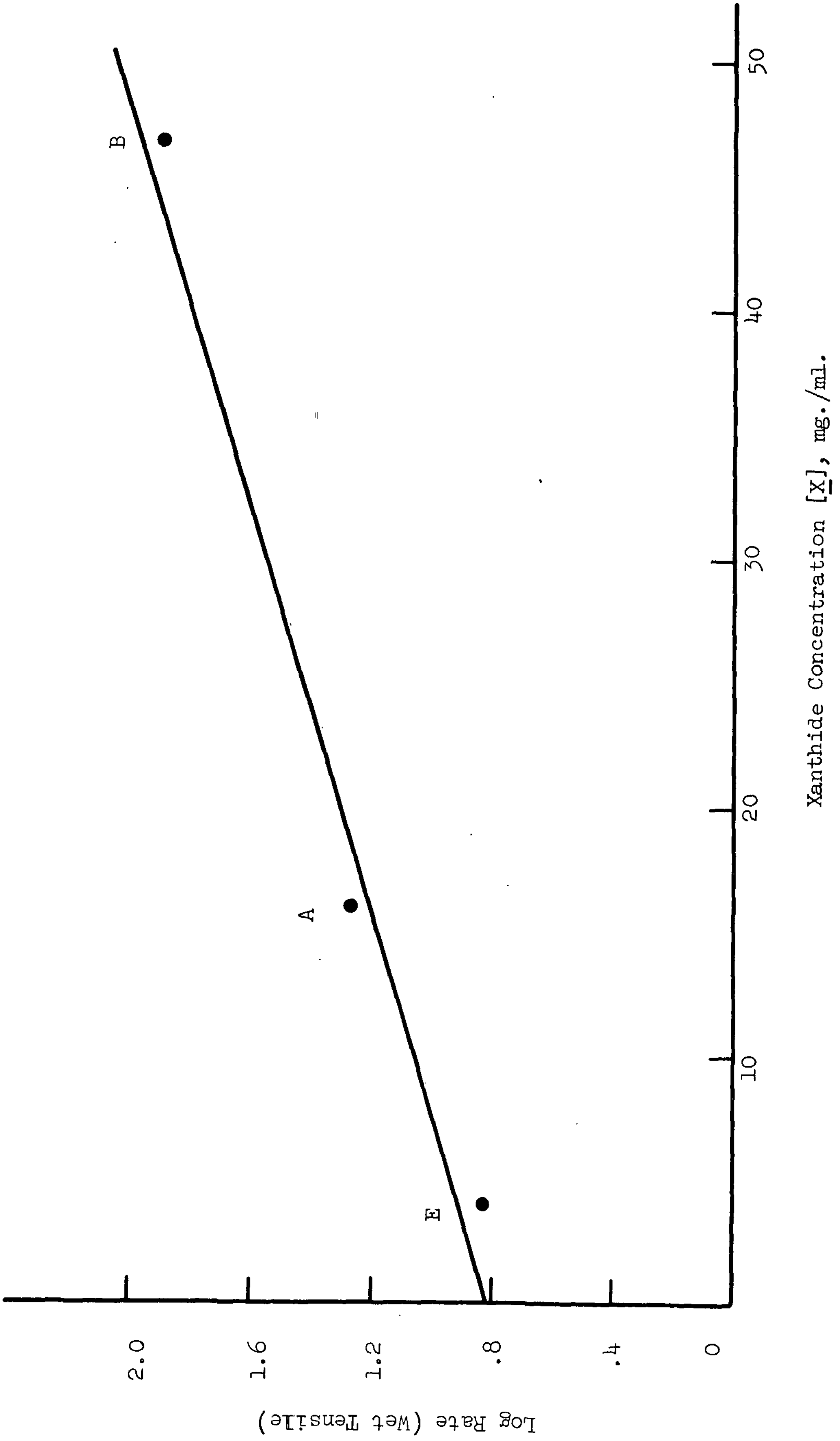
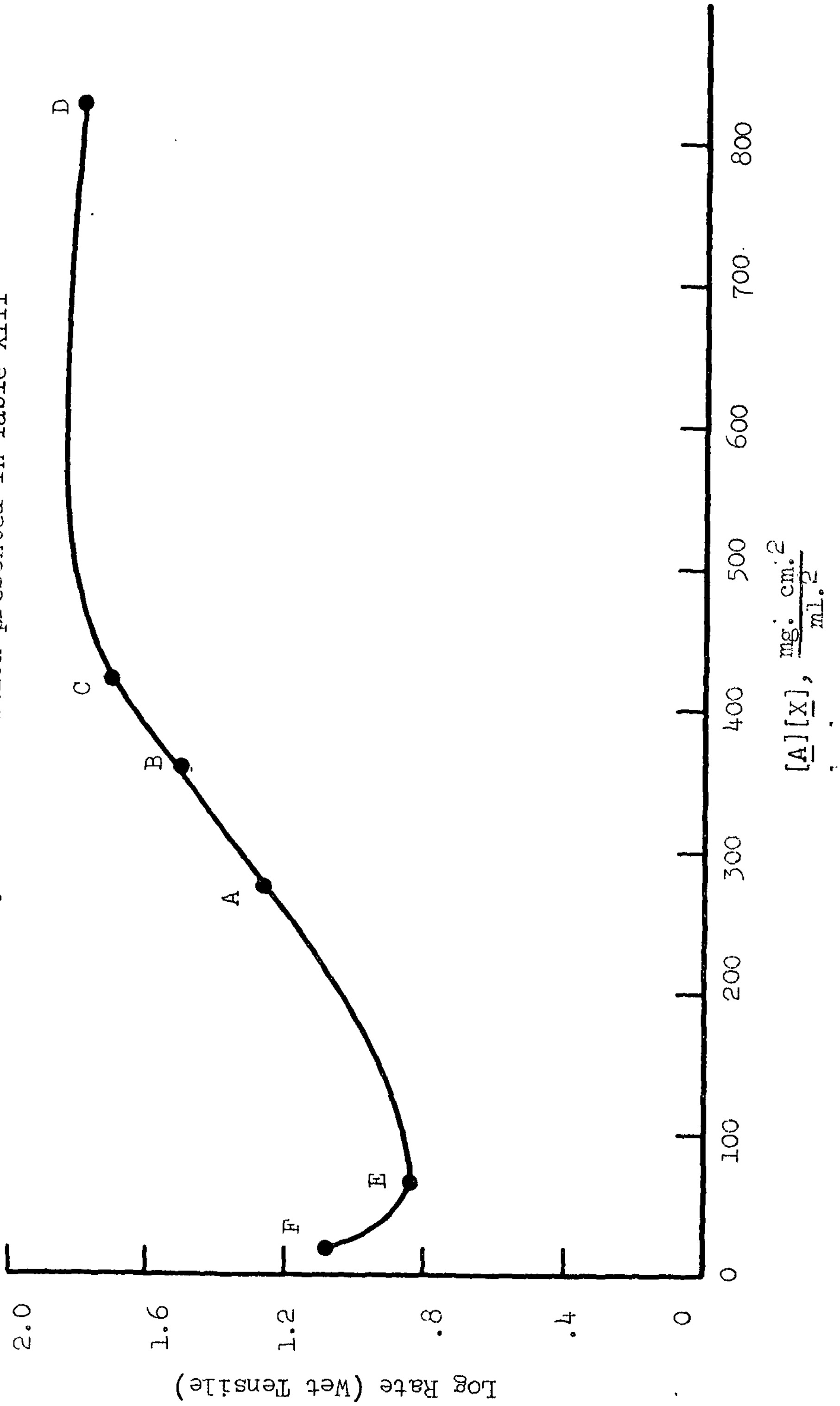


Figure 10. D.S. 0.12 Xanthide Sorption Rate as a Function of Xanthide Concentration at 25°C. in 2×10^{-4} $\underline{M}$ Alum with .15% Consistency. 700 ml. S.-R. Freeness Fiber



The letters identify the information presented in Table XIII

Figure 11. Sorption Rate as a Function of the Product of the Xanthide Concentration and Fiber Surface Area.

3×10^6 fibers per gram in a long fibered softwood kraft pulp, there will be about 4500 fibers per ml. at 0.15% consistency. Varying the number of large particles will of course vary the number of collisions between xanthide and fiber and hence the number of opportunities the xanthide has to remain on the fiber.

Theoretical models for the time dependency of polymer sorption by fibers are not well established. Müller (6) has presented a relationship for the sum of the number of large spherical particles and small spherical particles remaining in suspension as a function of time in a diffusional system:

$$N_t + n_t = \frac{N_o}{1 + \frac{t}{T_{N_o}}} \left[1 + \frac{\frac{V_r}{2}}{\left(\frac{V_r}{2} V_n + 1\right)\left(1 + \frac{t}{T_{N_o}}\right)^{V_r/2} - 1} \right]$$

where

N_o = original number of large particles

n_o = original number of small particles

N_t = number of large particles at time t

n_t = number of small particles at time t

V_n = N_o/n_o

V_r = radius of large particles/radius of small particles

T_{N_o} = half life for the coagulation of the large particles

For a system containing 4500 particles having the radius of the cross section of kraft fibers, T_{N_o} is of the order of 10 hours. While this equation is not readily applied to the xanthide sorption system, it is interesting as a model representing a similar system. It is worth noting that the ratio of the radii (V_r) is also the square root of the relative surface areas which would be: R^2/r^2. The physical meaning of the equation according to Müller is that the larger particles are disappearing according to the coagulatio process as if the little particles were not present. The smaller particles are deposited on the larger in a short time and disappear very rapidly according to the theory of Smoluchowski for monodisperse systems.

Another factor to be considered is that as the fiber consistency is changed at constant alum concentration, the alum-to-fiber ratio changes. If alum sorption is a factor, then lower fiber consistencies should have more of the ionic species of the alum system that are significant to this process and hence should show higher sorption rates at a given alum concentration and pH. This is observed with 0.04% fiber ("*F*" in Table XIII, Fig. 11).

THE EFFECT OF AGING DILUTE STARCH XANTHATE BEFORE CROSS-LINKING

The effect of aging dilute xanthate solutions for increasingly longer periods of time before forming starch xanthide is shown in Table IV. It appears that the dilute D.S. 0.12 xanthate (0.18%) can be stored 4 hours at 20°C. without significant loss of handsheet strength properties.

ACKNOWLEDGMENTS

Others who contributed to this report are Don Gilbert whose technical competence and assistance are greatly appreciated and Dr. Dale G. Williams who was involved in many discussions concerning the interpretation of the kinetic and thermodynamic data presented in this report.

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George E. Lauterbach

George E. Lauterbach, Research Associate
Colloid Chemistry Group
Physical Chemistry Section

Edward J. Jones, Research Associate
Group Leader, Colloid Chemistry Group
Physical Chemistry Section

John W. Swanson

John W. Swanson, Senior Research Associate
Chairman, Physical Chemistry Section

APPENDIX

TABLE IV, REPORT SEVEN, P. 30

XANTHIDE SORPTION AT 15.0°C.

Set Number	Xanthide pH	Alum Concentration, molar	Stock, pH	Contact Time, min.	Dry[a] Instron Tensile, lb./in.	Wet[b] Instron Tensile, lb./in.	Glucan, %	Xanthide (Sample Blank[c]), %	Xanthide, g./100 g. fiber	Retention Efficiency, %
(No. Tests)					(2)	(2)	(2)			
15-3 (5)	5.0	2 x 10^{-3}	5.0 (NaOH)	1/4	--	--	6.45	1.43	1.45	13.9
				1/2	--	--	6.48	1.46	1.48	14.2
				1	--	--	6.71	1.69	1.72	16.5
				4	--	--	7.20	2.18	2.23	21.4
				16	--	--	7.80	2.78	2.86	27.5
				32	--	--	8.27	3.25	3.36	32.3
				Blank	--	--	4.98[c]	--	--	--
15-3	5.1	2 x 10^{-3}	3.3	1/4	20.8	1.41	6.68	1.66	1.69	16.2
				1/2	18.6	1.24	7.02	2.00	2.04	19.6
				1	23.0	1.88	7.28	2.26	2.31	22.2
				4	24.2	2.78	8.16	3.14	3.24	31.1
				16	23.9	3.36	9.34	4.32	4.52	43.4
				32	27.4	3.90	8.84	3.82	3.97	38.2
15-4	4.9	2 x 10^{-4}	4.0	1/4	16.0	0.75	5.78	0.76	0.76	7.3
				1/2	16.2	0.85	6.10	1.08	1.09	10.5
				1	17.6	1.10	6.63	1.61	1.64	15.8
				4	23.2	1.82	6.81	1.79	1.82	17.5
				16	23.6	2.44	7.37	2.35	2.41	23.2
				32	24.3	1.98	7.56	2.54	2.61	25.1
				Blank	13.0	0.43	5.06[c]	--	--	--
15-5	5.2	2 x 10^{-5}	4.6	1/4	13.4	0.54	5.26	0.24	0.24	2.3
				1/2	12.7	0.44	5.34	0.32	0.32	3.1
				1	13.1	0.52	4.87	(-0.15)	--	--
				4	14.6	0.68	5.37	0.35	0.35	3.4
				16	15.7	0.72	5.98	0.96	0.97	9.3
				32	17.6	0.78	6.29	1.27	1.29	12.4

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[a] 50% R.H. at 73°F.

[b] Soaked overnight in distilled water at 73°F.

[c] Average = 5.02.

TABLE V, REPORT SEVEN, P. 31

XANTHIDE SORPTION AT 25.0°C.

Set Number	Xanthide pH	Alum Concentration, molar	Stock, pH	Contact Time, min.	Dry[a] Instron Tensile, lb./in.	Wet[b] Instron Tensile, lb./in.	Glucan, %	Xanthide (Sample Blank), %	Xanthide, g./100 g. fiber	Retention Efficiency, %
(No. Tests)					(2)	(2)	(2)			
25-3	5.3	2×10^{-3}	3.4	1/4	17.2	1.12	6.50	1.19	1.20	11.5
				1/2	19.0	1.31	6.43	1.12	1.13	10.9
				1	19.6	1.36	6.62	1.31	1.33	12.8
				4	22.1	2.04	7.38	2.07	2.11	20.3
				16	21.2	2.96	8.45	3.14	3.24	31.1
				32	24.9	3.30	9.24	3.93	4.09	39.3
				Blank	10.5	0.35	5.31	--	--	--
25-4	5.1	2×10^{-4}	4.1	1/4	15.8	0.88	6.05	0.74	0.74	7.1
				1/2	17.2	1.08	6.40	1.09	1.10	10.6
				1	15.2	0.92	6.64	1.33	1.35	13.0
				4	21.2	1.68	7.20	1.99	2.03	19.5
				16	21.2	2.34	7.47	2.16	2.21	21.2
				32	25.8	2.76	7.45	2.14	2.19	21.0
25-5	5.1	2×10^{-5}	4.6	1/4	12.9	0.48	5.60	0.29	0.29	2.8
				1/2	13.6	0.54	6.01	0.70	0.70	6.7
				1	13.6	0.55	5.77	0.46	0.46	4.4
				4	16.2	0.79	5.78	0.47	0.47	4.5
				16	15.7	0.98	6.20	0.89	0.90	8.6
				32	15.0	0.88	6.02	0.71	0.72	6.9

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[a] 50% R.H., 73°F.

[b] Soaked overnight in distilled water at 73°F.

TABLE VI, REPORT SEVEN, P. 32

XANTHIDE SORPTION AT 35.0°C.

Set Number	Xanthide pH	Alum Concentration, molar	Stock, pH	Contact Time, min.	Dry[a] Instron Tensile, lb./in.	Wet[b] Instron Tensile, lb./in.	Glucan, %	Xanthide, %	Xanthide, g./100 g. fiber	Retention Efficiency, %
(No. Tests)					(2)	(2)	(2)			
35-3		2×10^{-3}	3.3	1/4	19.2	1.18	6.69	1.05	1.06	10.2
				1/2	18.3	1.32	6.86	1.22	1.24	11.9
				1	18.6	1.42	6.98	1.34	1.36	13.1
				4	24.3	2.12	7.34	1.70	1.73	16.6
				16	21.6	1.98	7.78	2.14	2.19	21.0
				32	24.2	2.26	7.96	2.32	2.38	22.9
				Blank	10.8	0.39	5.64	--	--	--
35-4		2×10^{-4}	4.4	1/4	17.6	1.24	6.58	0.78	0.79	7.6
				1/2	18.4	1.40	6.76	0.96	0.97	9.3
				1	22.3	1.71	7.07	1.27	1.29	12.4
				4	22.9	2.73	7.09	1.29	1.31	12.6
				16	23.6	2.61	7.34	1.54	1.57	15.1
				32	24.4	2.71	7.74	1.94	1.98	19.0
				Blank	13.2	0.36	5.80	--	--	--
35-5		2×10^{-5}	4.8	1/4	13.0	0.50	5.86	0.14	0.14	1.3
				1/2	13.4	0.59	5.76	0.04	0.04	0.4
				1	14.2	0.61	5.90	0.18	0.18	1.7
				4	14.3	0.67	5.62	(-0.10)	--	--
				16	16.2	0.69	5.60	(-0.12)	--	--
				32	14.8	0.62	5.62	(-0.10)	--	--
				Blank	11.6	0.38	5.72	--	--	--

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[a] 50% R.H., 73°F.

[b] Soaked overnight in distilled water at 73°F.