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

Project 2580

Report Six

A Quarterly Report

to

AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE

March 15, 1967

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

A procedure has been developed to prepare starch xanthide separately from the fiber and the aging stability of the preparation has been determined. Between 5 and 60 minutes after cross-linking is completed, xanthide retention efficiencies and wet and dry tensile strengths of handsheets are reasonably constant. With further aging, retention efficiencies increase while handsheet tensile strengths decrease. This suggests that a critical particle size distribution range controls the performance of starch xanthide in paper.

Ex situ starch xanthide is not retained by 0.15% consistency bleached kraft fibers in deionized water at 15 to 35°C. over a pH range of 5 to 10. When alum is present (i.e., 0.0002 molar), retention rates can be measured at 25°C. The data obtained follow both semilog and double log plots.

The age of the starch xanthate used to make ex situ starch xanthide did not have a profound effect upon retention efficiency or handsheet performance over the range of 3 to 31 days. The freshest xanthate did show the best xanthide retention efficiency at longer contact times but was not much better than that of samples 17 and 31 days old which were indistinguishable.

Xanthide-treated handsheets resuspended in water before drying and then reformed at intervals show progressive losses of wet tensile strength with the length of time they were soaked. However, the xanthide content does not change significantly. This suggests that the physical form of the xanthide on the fiber is important to improving paper strength.

Starch xanthate is sorbed by bleached kraft fibers at 35° to the extent of 4 to 6% of the total xanthate added if 0.0002M alum is present at pH 5 or 7 but is not sorbed at pH 10. In the absence of alum, no xanthate sorption is seen. Lower sorption with increasing pH values suggests that the free aluminum ion is the controlling factor. The low retention efficiencies observed under rather special conditions do not indicate direct sorption of starch xanthate is a major factor in the overall mechanism of starch xanthide retention.

INTRODUCTION

This is the sixth quarterly report submitted to the Agricultural Research Service concerning the work done for Contract 12-14-100-8303(71) issued under authority of the Research Marketing Act of 1946. The purpose of our cooperative Project 2580 is to expand the uses of cereal starches in paper-making by determining the factors governing the sorption of starch xanthate and xanthide by wood fibers in dilute aqueous suspensions.

One of the major objectives of this project is the deduction of the kind of sorption process responsible for retaining starch xanthide in paper. The earliest experiments (Reports One and Two) failed to demonstrate any sorption of starch xanthate by fiber suspensions at 15°C., with or without alum present, and under widely varying conditions of concentration, pH, and contact time. These observations eliminated direct sorption of starch xanthate as a significant step in the process leading to starch xanthide retention in paper. The rate-controlling process must occur after starch xanthide formation by oxidative cross-linking begins with the addition of sodium hypochlorite.

Whether sorption is significant during the cross-linking reaction or not remains to be determined. Several attempts to observe xanthide retention rates using the introduction of hypochlorite as the reference point in time have been inconclusive. The results in some cases have been incongruous with preceding experiments. It is fairly obvious that significant factors affecting retention have not been identified and defined.

The goal of the work covered in this report is to establish procedures whereby xanthide retention rates may be observed. This problem was approached

by isolating the cross-linking reaction from the xanthide sorption process. Starch xanthide was formed under controlled conditions separately from the fiber. In this way such variables as temperature, ionic strength, polyvalent ion concentration, fiber concentration, xanthide concentration, pH, and possibly other variables can be assessed for pertinency.

The role of direct sorption of starch xanthate by the fiber is reassessed at higher temperatures than used previously.

MATERIALS AND PROCEDURES

The fiber used in this report is from the same lot of Rayonier bleached western softwood kraft pulp set aside for this project. It was beaten to 700 cc. S.-R. freeness in distilled water and classified to remove fines as described previously. The fines-free pulp was washed with distilled water, filtered, and stored at least 2 weeks under refrigeration at about 70-80% moisture before use. As required, portions were resuspended in deionized water for 300 counts (2-1/2 minutes) in a British disintegrator.

The xanthate samples were shipped from Peoria and are identified by run number in the body of the report. The degree of substitution was about 0.12.

The analytical procedures have been described previously. Xanthate retention was measured by the iodine colorimetric procedure discussed in Reports One and Three. Xanthide content of the handsheets reported is the average of the results from two separate samples of paper. The acid hydrolysis was for one hour and no correction is made for incomplete accounting of xanthide by this procedure (see page 9, Report Five). Deionized or distilled water was used throughout the program except for pulp classification.

PREPARATION OF EX SITU STARCH XANTHIDE

INTRODUCTION

The preparation of starch xanthide to be added to fiber suspensions was not the prime objective of this report. A simple, reproducible method was all that was desired. In order to avoid a study of the effects of temperature upon cross-linking, oxidative coupling with sodium hypochlorite was carried out in a water bath set at 20°C. This temperature is typical of those encountered in previous experiments. As far as the concentration of starch xanthate is concerned, 0.33% was selected on the basis of convenience in measuring and handling the quantities desired and being in the range of 0.1 to 0.5% used at Peoria in their experiments with ex situ starch xanthide on the experimental paper machines (1).

Cross-linking has been most easily controlled at pH values below 7 (Report Three). Since pH 5.5 is specified in the basic procedure developed at N.U.R.D.D. this value was chosen for this study. Further consideration was given to whether the pH of the sodium hypochlorite solution should also be adjusted to this value. A minimum change in pH upon cross-linking is observed when both the hypochlorite solution and the xanthate are adjusted to pH 5.5 (p. 16, Report Three). This in itself is desirable from the standpoint of reproducibility. However, for simplicity, adjusting only one component would be more desirable.

The concentration of the hypochlorite used for cross-linking in the ex situ system at Peoria ranges from 2.5 to 5.0% (1). However, 1% hypochlorite (that is, one part Hi-lex diluted to 5 parts by volume) was chosen for this

study since most earlier work on this project has used this concentration. In this way maximum use of previous experience is possible.

PRELIMINARY INVESTIGATION

Three qualitative experiments were run at 20.0°C. to determine if stable starch xanthide suspensions can be prepared from 0.33% starch xanthate and to determine the need to have both reagents adjusted to pH 5.5. The starch xanthate was at (A) pH 5.5, (B) pH 5.5, and (C) pH 11.5 when the hypochlorite was (A) pH 11.0, (B) pH 5.5, and (C) pH 5.5. Earlier experience eliminated the combination of both reagents at about pH 11 from consideration.

Five grams of xanthate starch (Run No. 472, 9.46%, 0.12 D.S., 4 days old) was diluted with 1450 ml. deionized water in a 2-quart fruit jar. The mixture was blended by means of a magnetic stirrer driven from beneath the 20° water bath. Potassium iodide solution (5 ml., 10%) was added after pH adjustment. The bleach solution was run in from a buret until the blue endpoint persisted. Then the milky suspension was diluted to 2000 ml. (0.25%), returned to the water bath, and allowed to stand over the weekend.

Both preparations from pH 5.5 xanthate had a layer of coagulated xanthide on the bottom of the jar after standing 3 days. The supernatant looked like watered milk. No precipitate formed from the opalescent, nearly colorless preparations made from pH 11 xanthate and pH 5.5 hypochlorite. The appearance of this preparation (which was made at pH 11 to 7.6) did not suggest that a useful starch xanthide had been prepared. It appeared more like dilute starch than starch xanthide and had consumed about 3 times as much hypochlorite as the other preparations during cross-linking.

In spite of the fact that precipitates formed in 3 days with Preparations A and B, no settling was seen during the 5 to 6 hours of observation on the first day. The preparation using both reagents at pH 5.5 appeared to be best for the purposes of this study. The least amount of hypochlorite was needed and the pH during cross-linking stayed within 5.5 to 5.9. When unacidified hypochlorite was used in Preparation A, the pH rose to 10 during the appearance of a fugitive endpoint color reaction. Additional hypochlorite was required to produce a permanent blue color after the pH of the preparation was restored to 5.5.

EVALUATION OF THE USEFUL LIFE OF STARCH XANTHIDE SUSPENSIONS

Starch xanthate from Run No. 472 was diluted to give 1500 ml. at 0.33 g./100 ml. and brought to 20.0°C. in the water bath. A magnetic stirrer placed underneath the glass aquarium used for the bath provided agitation in the 2-quart fruit jar containing the starch xanthate solution. The stirrer was operated at the maximum rate possible under these conditions throughout temperature equilibration, neutralization, cross-linking, and storage of the xanthide suspension. Dilute acetic acid (20% v/v) was used to bring the pH to 5.5.

Fifty milliliters of Hi-lex was diluted to 200 ml. and brought to pH 5.5 with 20% acetic acid before being diluted to a final volume of 250 ml. After adding 5 ml. of 10% w/v potassium iodide to the starch xanthate, the acidified hypochlorite (actually mostly hypochlorous acid) was added from a 50-ml. buret to the starch xanthate until the blue color of the endpoint reaction persisted. The starch xanthide suspension was made up to 2000 ml. in a graduated cylinder and returned to the water bath.

Portions of the milk-white xanthide suspension (450 ml. at 0.25% or 1.125 g. xanthide starch) were added to 2000 ml. of pH 5.5 stock suspensions containing 25.0 g. of fines-free bleached kraft fiber and 5 ml. of 10% alum (0.00031M $Al_2SO_4 \cdot 18H_2O$ in 2450 ml.) at intervals of 5 min., 1 hr., 4 hr., and 24 hr. after the blue color appeared at the end of oxidative cross-linking. The mixture of xanthide and fiber was blended mechanically for 5 minutes at 20°C. and diluted to 0.5% fiber consistency for handsheet making. Eight 2.5-gram 8 by 8 in. Noble and Wood handsheets were prepared, dried, and evaluated for xanthide content and wet (30-min. soak) and dry (50% R.H.) M.I.T. tensile strength. The handsheets were not pressed in order to avoid having the sheets stick to the blotters if the xanthide retention efficiency was high. Two xanthide preparations were tested this way when the xanthate was 7 and 8 days old, respectively.

The data are shown in Table I and plotted as semilogarithmic functions in Fig. 1.

Wet and dry tensile strength responses are unchanged between 5 and 60 minutes and decrease linearly with the logarithm of the xanthide age in minutes. Wet tensile is proportionally more affected than dry tensile.

The xanthide content of the handsheets increases with the age of the preparation. Variations in the data from the two runs make a more specific statement difficult but it appears that retention is fairly constant for the first hour. The fact that retention increases as the strength properties decrease is unexpected. This may be a consequence of a specific xanthide particle size range being effective in improving handsheets while larger particles formed by

TABLE I
EFFECT OF AGE OF EX SITU XANTHIDE PREPARATION UPON HANDSHEETS

No. Determinations	Xanthide Age, min.	Glucan, %	Xanthide, (sample blank) g./100 g. sheet	Xanthide, g./100 g. fiber	Retention Efficiency, %	Dry Tensile M.I.T., lb./in.	Wet Tensile ^a M.I.T. lb./in.
Blank	--	5.88	--	--	--	20.7	0.7
Run 1	5	6.92	1.04	1.05	23.3	30.9	3.7
	60	7.28	1.40	1.42	31.5	31.5	3.4
	240	7.60	1.72	1.75	38.9	27.5	2.2
	1440	7.92	2.04	2.32	51.3	24.0	1.3
Run 2	5	6.88	1.00	1.01	22.4	32.4	3.3
	60	6.43	0.55	0.55	12.2	31.3	3.5
	240	8.10	2.22	2.27	50.4	28.6	2.3
	1440	7.62	1.74	1.77	39.4	23.5	1.1

^a Soaked 30 minutes in distilled water at 72°F.

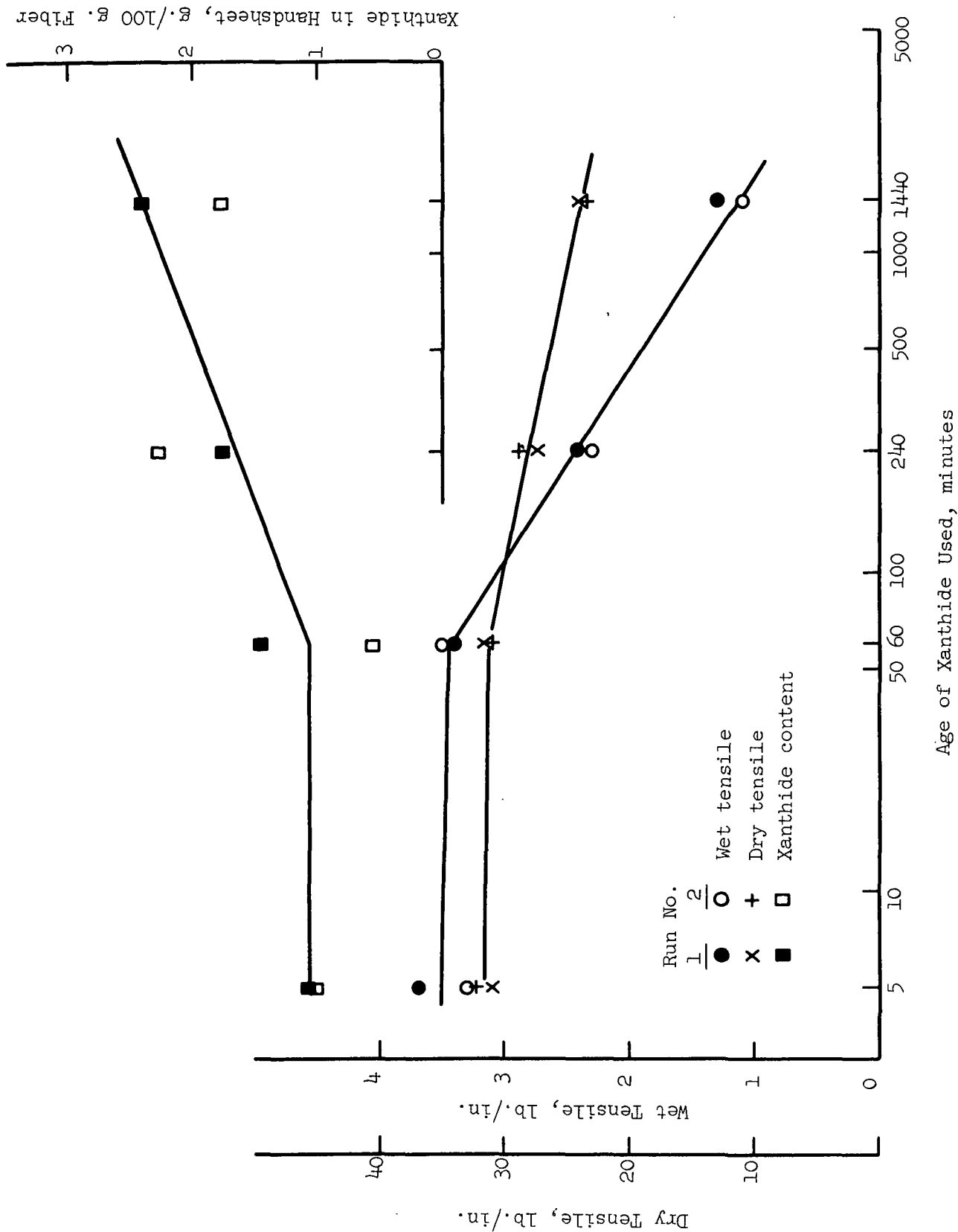


Figure 1. Effect of Age of Ex Situ Xanthide Preparation Upon Handsheets

coalescence during aging are better retained by filtration mechanisms. A certain amount of rapidly settling particles are present in the 24-hour xanthide preparations.

Handsheet properties and xanthide retention efficiencies change after storing ex situ starch xanthide more than about one hour at 20°C. Consequently, a single preparation is not satisfactory for each work day.

STUDY OF EX SITU STARCH XANTHIDE SORPTION RATES

The object of this experiment was to observe the rate of xanthide sorption on papermaking fibers as a function of temperature and pH. This information would be used to estimate the sorption activation energy, and thereby gain some insight into the sorption mechanism. A second objective was to compare the sorption rates of starch xanthide prepared from starch xanthates of different ages. This aspect was forced upon this experiment by certain circumstances.

When this experiment was started, xanthate Run No. 479 had just been received. However, when this xanthate was used to form ex situ xanthide, only a coagulum was obtained under the cross-linking conditions used in the two preceding sections. Consequently, it was decided to proceed with the older xanthate preparation (Run 472), which could be used to prepare ex situ starch xanthide by the procedure already developed.

Concurrent investigations showed that satisfactory xanthide preparations could be made from Run No. 479 if the cross-linking concentration were cut in half. That is, with 0.167% starch xanthate instead of 0.333%. The block of experiments was then repeated with the fresher xanthate.

The only difference between Runs 472 and 479 that is shown on the run data sheets and which could account for the differences in behavior, is the viscosity. Run 472 had a Brookfield viscosity of 65.0 c.p.s. compared with 86.4 c.p.s. for a 5% solution of Run 479. The age of the xanthate runs was not a significant factor since 472 was 2 to 3 days old when first used to set up the procedure for making starch xanthide separately.

The basic procedure for making starch xanthide separately has been described in preceding sections. For this study and those subsequent, the intervals for equilibration to 20°C. and while at pH 5.5 before cross-linking, were limited to $5 \pm 1/4$ minutes each. It was hoped dexanthation occurring during these intervals would be reproduced and that dissolved H₂S and other by-products would reach about the same level from preparation to preparation. In this way the salt concentration from using sodium hypochlorite and the oxidation of by-products would also have a minimum variability. The only change in the procedure to adapt it to Run No. 479 xanthate was to use 2950 ml. water instead of 1450 ml. and, of course, a larger container. These quantities give total volumes of 3000 and 1500 ml. when the volume of 10% xanthate added is included. Since the stability data discussed in the preceding section were not completed at the time of this experiment, it was necessary to establish an aging interval by intuition. For this study, the xanthide preparations were aged about 1 hour before use. The actual age of the xanthide preparation when used is shown in Table II with the other data for this section.

The experiment consisted of exposing 1500-ml. portions of a fiber suspension made up to contain 16 grams per 10,000 ml. to 100 ml. of 0.25% starch xanthide for 15 sec., 1 min., 4 min., 16 min., or 32 min. The contact time was terminated by dumping the mixture from 2-quart fruit jars into the Noble and Wood sheet mold as the valve was tripped. After pressing with the couch roll, the handsheets were dried on blotters on a steam drum without further pressing.

The materials present after combining the fiber and xanthide were 0.15% fiber (^{2.4 gcs.}~~1.6 gcs.~~) and 0.0156% starch xanthide at a level of 10.4 g. per 100 grams fiber plus whatever organic and inorganic salts were introduced by adjusting

TABLE II

EX SITU STARCH XANTHIDE SORPTION WITHOUT ALUM

Set Number	Contact Time, min.	Xanthate Run Number	Age of Xanthate, days	Xanthide Preparation Age, hr.	Sorption Temp., °C.	Sorption pH	Dry Tensile M.I.T., lb./in.	Wet Tensile M.I.T., lb./in.	Glucan, %	Xanthide. (Sample-5.19) g./100 g. sheet
2	Blank	--	--	--	--	7	19.4	0.68	4.83 5.64 5.51	-- -- --
6	Blank	--	--	--	--	10	23.6	0.76	4.87 5.09 5.19	-- -- --
Mean of blanks							21.5	0.72	5.19	--
1	1/4	472	21	1/3	15	5	13.3	0.59	5.67	0.58
	1						21.2	0.80	5.56	0.37
	4						20.6	0.68	5.72	0.53
	16						20.9	0.82	5.77	0.58
	32						20.0	0.84	5.33	0.14
	Mean						19.2	0.75	--	0.44
2	1/4	472	21	1/3	15	7	22.5	0.75	5.28	0.09
	1						18.6	0.72	5.42	0.23
	4						22.1	0.81	5.35	0.16
	16						19.1	0.82	5.90	0.71
	32						22.2	0.78	5.88	0.69
	Mean						20.9	0.78	--	0.38
3	1/4	472	21	1-1/3	15	10	26.4	0.78	5.36	0.17
	1						20.8	0.80	5.34	0.15
	4						23.8	0.82	5.42	0.23
	16						23.0	0.78	5.31	0.12
	32						23.2	0.80	5.40	0.21
	Mean						23.0	0.80	--	0.14
4	1/4	472	22	1	25	5	23.3	0.47	5.30	0.11
	1						22.7	0.71	5.36	0.17
	4						21.0	0.65	4.88	-0.31
	16						20.4	0.66	5.54	0.35
	32						20.4	0.78	5.48	0.29
	Mean						21.6	0.65	--	0.12
5	1/4	472	22	2	25	7	22.6	0.69	5.11	-0.08
	1						23.2	0.72	5.39	0.20
	4						23.6	0.85	5.29	0.10
	16						24.6	0.77	5.33	0.14
	32						22.8	0.76	5.62	0.43
	Mean						23.4	0.76	--	0.16
6	1/4	472	22	3	25	10	16.3	0.74	5.58	0.31
	1						20.2	0.75	5.30	0.11
	4						22.0	0.74	5.30	0.11
	16						21.4	0.80	5.41	0.22
	32						23.2	0.76	5.36	0.16
	Mean						20.6	0.76	--	0.18
7	1/4	472	23	1-1/2	35	5	11.4	0.52	5.44	0.25
	1						19.3	0.67	5.58	0.39
	4						19.4	0.67	5.78	0.59
	16						19.5	0.79	5.74	0.55
	32						20.9	0.78	5.76	0.57
	Mean						18.1	0.69	--	0.45

TABLE II (Continued)

EX SITU STARCH XANTHIDE SORPTION WITHOUT ALUM

Set Number	Contact Time, min.	Xanthate Run Number	Age of Xanthate, days	Xanthide Preparation Age, hr.	Sorption Temp., °C.	Sorption pH	Dry Tensile, M.I.T., lb./in.	Wet Tensile M.I.T., lb./in.	Glucan, %	Xanthide, (Sample-5,19) g./100 g. sheet
8	1/4	472	23	2-1/2	35	7	19.5	0.76	5.64	0.45
	1						20.6	0.73	5.93	0.74
	4						18.4	0.68	5.40	0.21
	16						23.0	0.72	6.00	0.81
	32						21.0	0.70	6.06	0.87
	Mean									
9	1/4	472	23	3-1/2	35	10	21.4	0.68	6.03	0.84
	1						22.0	0.72	6.19	1.00
	4						19.4	0.74	6.14	0.95
	16						22.0	0.77	5.88	0.69
	32						20.4	0.71	6.08	0.89
	Mean									
10	1/4	479	10	1	35	5	14.8	0.68	6.10	0.91
	1						18.0	0.72	5.08	-0.11
	4						16.9	0.68	5.30	0.11
	16						17.1	0.76	5.34	0.15
	32						21.1	0.74	5.24	0.05
	Mean									
11	1/4	479	10	2	35	7	20.5	0.66	4.67	-0.52
	1						19.1	0.66	4.52	-0.67
	4						18.4	0.72	4.95	-0.24
	16						19.2	0.70	4.84	-0.35
	32						20.1	0.66	5.00	-0.19
	Mean									
12	1/4	479	10	1-1/6	35	10	17.7	0.60	4.86	-0.33
	1						21.6	0.70	5.01	-0.18
	4						19.0	0.67	5.00	-0.19
	16						19.6	0.68	5.04	-0.15
	32						20.0	0.71	4.74	-0.45
	Mean									
13	1/4	479	11	1	25	5	20.4	0.70	5.14	-0.05
	1						21.5	0.69	5.32	0.13
	4						20.4	0.74	5.41	0.22
	16						19.7	0.75	5.84	0.65
	32						18.2	0.79	6.00	0.81
	Mean									
14	1/4	479	11	2	25	7	21.6	0.64	5.02	-0.17
	1						19.2	0.72	5.36	0.17
	4						18.5	0.73	4.89	-0.30
	16						21.4	0.76	4.94	-0.25
	32						18.0	0.65	5.14	-0.05
	Mean									

TABLE II (Continued)

EX SITU STARCH XANTHIDE SORPTION WITHOUT ALUM

Set Number	Contact Time, min.	Xanthate Run Number	Age of Xanthate, days	Xanthide Preparation Age, hr.	Sorption Temp., °C.	Sorption pH	Dry Tensile, M.I.T., lb./in.	Wet Tensile M.I.T., lb./in.	Glucan, %	Xanthide, (Sample-5.19) g./100 g. sheet
15	1/4	479	11	3	25	10	22.0	0.73	4.82	-0.37
	1						19.6	0.64	5.02	-0.17
	4						16.2	0.74	4.92	-0.27
	16						19.7	0.70	5.34	0.25
	32						21.8	0.66	5.16	-0.03
	Mean						19.9	0.69	--	-0.12
16	1/4	479	12	1	15	5	17.8	0.70	5.32	0.13
	1						18.2	0.76	5.42	0.23
	4						19.6	0.79	5.61	0.42
	16						22.0	0.82	5.58	0.39
	32						19.7	0.80	5.84	0.65
	Mean						19.5	0.78	--	0.36
17	1/4	479	12	2	15	7	19.6	0.67	4.78	-0.41
	1						21.8	0.72	5.60	0.41
	4						19.6	0.68	5.48	0.29
	16						20.1	0.76	5.46	0.27
	32						20.3	0.72	5.68	0.49
	Mean						20.7	0.71	--	0.21
18	1/4	479	12	3	15	10	20.8	0.70	5.47	0.28
	1						19.6	0.74	5.30	0.19
	4						20.4	0.70	5.68	0.49
	16						19.4	0.66	5.75	0.56
	32						16.8	0.70	5.66	0.47
	Mean						19.4	0.70	--	0.40

Dry tensile was measured at 50% R.H. at 72°F.

Wet tensile was measured after soaking 16 hours in distilled water at 72°F.

the pH (acetic acid, H_2SO_4 , NaOH) or from the hypochlorous acid and xanthate by-products. These proportions were preserved with the Run 479 xanthide.

The sorption temperatures of 15.0, 25.0, and 35.0°C. were maintained by immersing the jars of fiber in a water bath. Equilibration to the desired temperature was hastened by preconditioning the fiber suspension in a jacketed container in which adjustments to pH 5, 7, or 10 were made with dilute sulfuric acid or sodium hydroxide. The xanthide preparation was adjusted to the same pH as the stock and held 10 minutes more at 20°C. before being used. The xanthide temperature was not changed from 20°C. This produced a small departure from the stated sorption temperature but was judged to be preferable to investigating possible changes in the xanthide preparation at this time. The 15-sec. and 1-min. sorption periods were thus at 15.3, 24.6, and 33.0°C. since they were not in the water bath long enough to compensate for this departure from stated conditions.

The mixtures of fiber and xanthide were stirred mechanically with the bent-rod stirrers used in Report One during the long sorption periods. Agitation for the 15-sec. and 1-min. samples was done manually - cocktail shaker style. The sequence in which the xanthide was introduced into the fiber was into the 32-min., 16-min., 4-min., and 15-sec. samples as rapidly as was possible to measure four 100-ml. portions and into the 1-min. sample after the 15-sec. and 4-min. intervals had been terminated. The total lapsed time was never more than 8 minutes.

The data for wet and dry tensile and xanthide content, shown in Table II, show no temporal progression either in xanthide content or tensile strength. It is quite doubtful that significant quantities of xanthide were absorbed at all. While

the experience at Peoria indicates that alum improves xanthide retention it was not expected that no measurable sorption would occur in the absence of alum.

STUDY OF SORPTION RATES WITH 0.0002M ALUM AS
AFFECTED BY THE AGE OF THE XANTHATE

An evaluation of the effect of aging the starch xanthate was combined with a study of alum as a retention aid for starch xanthide. This was a single condition evaluation to try to pin down the experimental conditions needed to study xanthide retention rates. The experiment followed the procedure described in the preceding section. All of the xanthides were prepared at a xanthate concentration of 0.167% and were diluted to 0.125% before aging 1 hour at 20°C. Alum was added to the fiber in quantities that would give a concentration of 0.0002M after the xanthide and fiber were combined. This amount of alum lies in the optimum range for maximum retention of pigments such as TiO_2 (2). [About 0.00009M is the mean flocculation value for aluminum ions in acidic solution giving maximum flocculation rates (3).] The quantity used represents a loading of about 9% $Al_2(SO_4)_3 \cdot 18H_2O$ on the weight of the fiber at 0.15% consistency. The stock was subsequently adjusted to pH 5.5 and equilibrated to 25.0°C. In this experiment the handsheets were pressed for 5 minutes at 50 p.s.i. before drying.

The starch xanthide preparations were made using xanthate Runs No. 472, 479, and 481, whose ages are stated in Table III along with the xanthide retention and tensile strength.

Temporal variances in xanthide content are observed in this experiment at 25°C. with 0.0002M alum adjusted to pH 5.0. The general trend is linear with either a semilog or double log plot (Fig. 2 and 3). As far as age of the xanthate

TABLE III
EX SITU STARCH XANTHIDE RETENTION RATES WITH ALUM AT PH 5.5 AND 25°C.

Evaluation of Xanthate Age

Set No.	Contact Time, min.	Xanthate Run Number	Age of Xanthate, hr.	pH	Temp., °C.	Alum, M	Dry Tensile M.I.T., lb./in.	Wet Tensile M.I.T., lb./in.	Glucan, %	Xanthide, (Sample-519) g./100 g. sheet	Xanthide, g./100 g. fiber
16A	1/4	472 (31 days old)	1	5.0	25.0	0.0002	23.0	2.1	6.17	0.98	0.99
	1						27.8	2.8	6.76	1.57	1.60
	4						26.2	2.8	6.88	1.69	1.82
	16						28.2	3.2	7.41	2.22	2.27
	32				31.4	3.2	7.10	1.91	1.95		
16B	1/4	479 (17 days old)	1	5.0	25.0	0.0002	23.4	2.4	6.22	1.23	1.24
	1						25.9	3.0	6.52	1.33	1.35
	4						26.8	3.0	6.61	1.42	1.44
	16						28.7	3.4	7.30	2.11	2.16
	32				26.6	3.6	7.65	2.46	2.52		
17C	1/4	481 (3 days old)	1	5.0	25.0	0.0002	22.8	2.0	6.42	1.23	1.24
	1						25.0	2.6	6.70	1.51	1.53
	4						29.4	3.1	7.48	2.29	2.34
	16						29.0	3.6	7.95	2.76	2.84
	32				29.2	3.2	7.90	2.71	2.78		

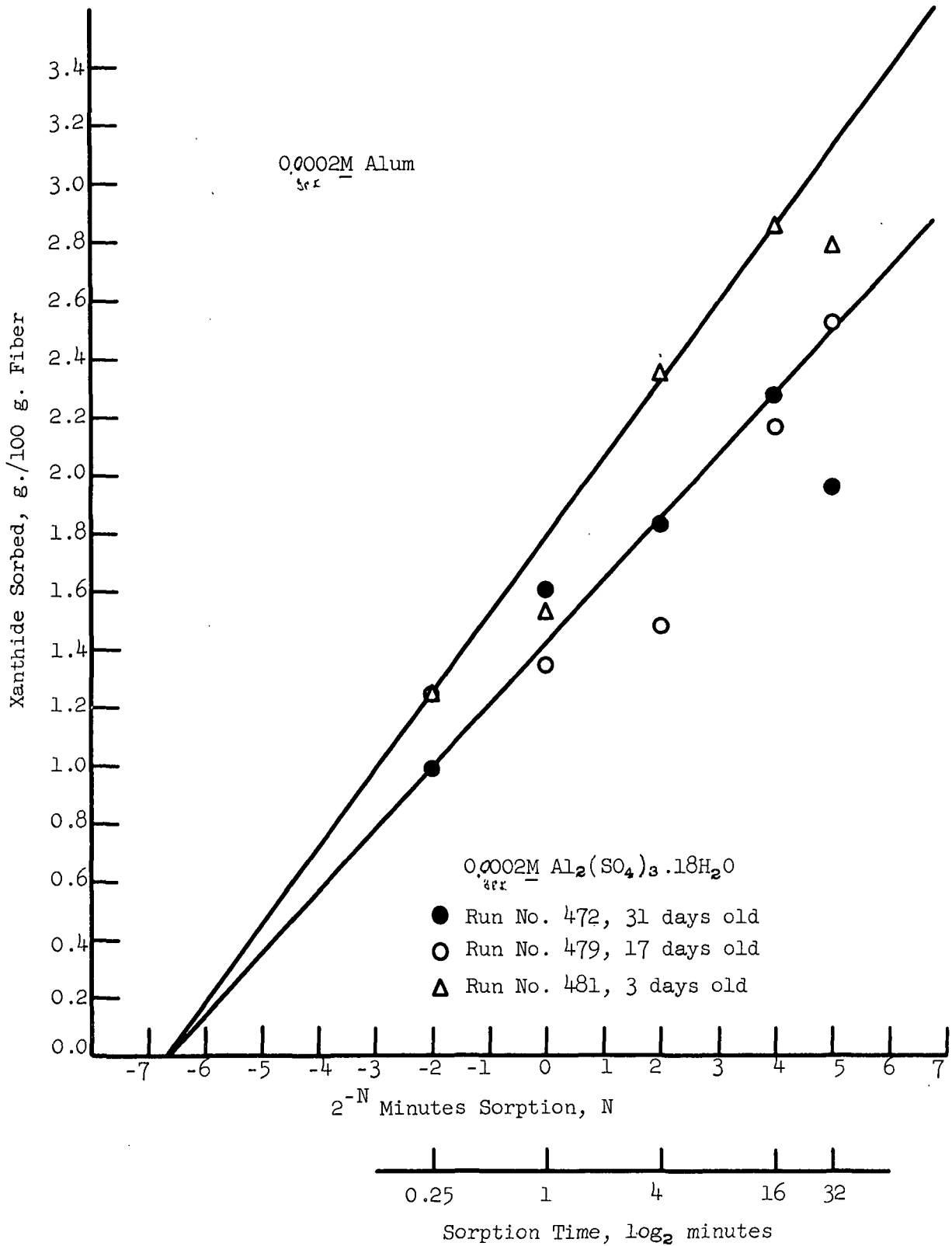


Figure 2. Ex Situ Starch Xanthide Sorption, Semilog Plot

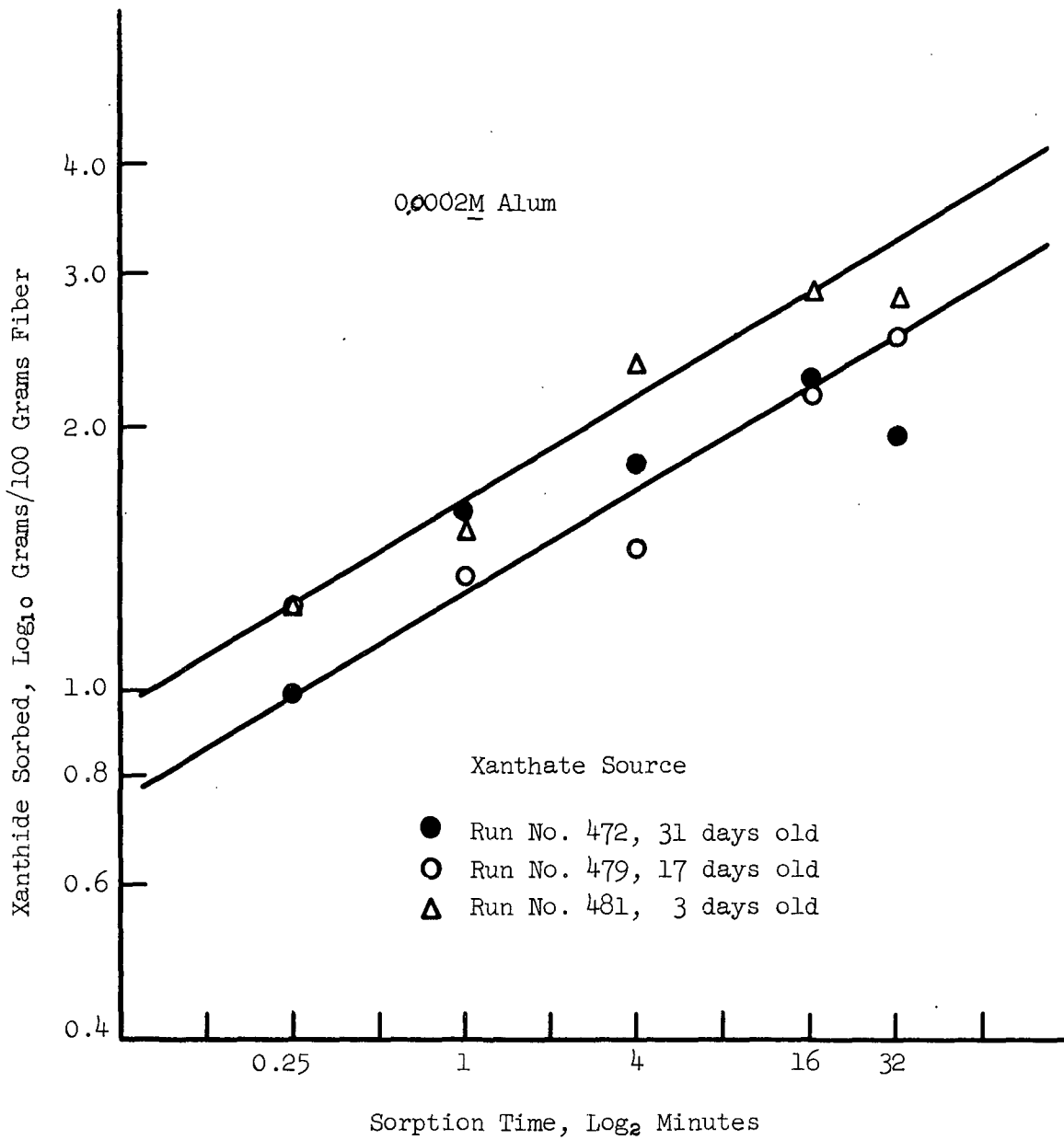


Figure 3. Ex Situ Starch Xanthide Sorption, Double Log Plot

is concerned, the freshest sample (Run 481, 3 days old) produced xanthide having a tendency toward higher retention at longer contact times. There is no distinctive difference between xanthate 17 days old (Run 479) and xanthate 31 days old (Run 471). Both were almost as useful as the freshest sample in producing effective starch xanthide.

It is evident that aluminum, or perhaps other trivalent ions, is required for xanthide retention. Further work should evaluate the role of aluminum ion concentration both upon ex situ xanthide retention and upon the formation of the starch xanthides. Particle size distribution control is likely involved in the overall mechanisms.

Experimental conditions have been established under which starch xanthide sorption rates can be measured. Data necessary for a major portion of this project are now obtainable.

REVERSIBILITY OF STARCH XANTHIDE SORPTION

Starch xanthide was prepared from xanthate Run No. 481 at 20°C. and a concentration of 0.167% at pH 5.5 After diluting to 0.125% and aging 1 hour, 1000 ml. of the preparation were added to 30 grams of fiber in 2000 ml. of water and 10 ml. of 10% alum (0.0005M in 3 liter) at pH 5.0 and 25°C. The mixture (1% fiber, 4.17 g. xanthide/100 g. fiber) was blended mechanically for 5 minutes at 25°C. and used to prepare 8-2.5 g., 8 by 8-in. Noble and Wood handsheets. Two handsheets were dried immediately. Each of the remaining undried handsheets was redispersed in 1500 ml. deionized water at 25° and stirred at that temperature for one of the intervals shown in Table IV. Vigorous agitation was not necessary to break up the wet handsheets. The agitation normally used in the sorption experiments was sufficient. That is, bent-rod stirrers driven at speeds just slow enough to avoid whipping air into the suspension. Two handsheets were reformed at each of the desorption intervals specified. The xanthide content and wet tensile strength of the original and reformed handsheets are shown in Table IV.

TABLE IV

REVERSIBILITY OF STARCH XANTHIDE SORPTION AT 25°C. IN DEIONIZED WATER

Desorption Interval, hr.	Wet Tensile, ^a lb./in.	Glucan, %	Xanthide (Sample-5.19), g./100 g. sheet	Xanthide, g./100 g. fiber	Retention ^b Efficiency, %
0	2.43	8.23	3.01	3.10	74
1/4	1.57	7.27	1.91	1.95	47
4	1.06	8.05	2.85	2.93	70
24	0.85	8.12	2.89	2.98	72

^aSoaked 16 hr. at 73°F. in distilled water.

^b4.17 g. Xanthide/100 g. fiber = 100% retention.

Wet tensile strength decreases as the soaking time increases. However, the xanthide content is relatively unaffected. The sample soaked 15 minutes has lost about 1/3 of the xanthide originally present and the wet tensile is about 75% of that of the unsoaked specimen. This would indicate significant reversal of xanthide sorption if the 4-hour and 24-hour samples did not have almost as much starch xanthide as the control sample. We must set aside the low xanthide content of the 15-minute specimen as being due to some unexplained variation in the experiment. Resorption of desorbed starch xanthide in the case of the longer soaking times is not a tenable explanation since starch xanthide is not sorbed by these fibers at 25° in deionized water (see Table II).

Starch xanthide sorption is not reversible over a period of 24 hours at 0.167% fiber consistency at 25°C. in deionized water. Something does occur to the starch xanthide on the fiber since wet tensile strength is lost as the soaking time increases. After soaking 24 hours, the reformed handsheets have wet tensile strength similar to handsheets having no starch xanthide at all. Just what is happening to the sorbed starch xanthide is not known.

The retention efficiency is much higher in this experiment. Best retention has been obtained previously at fiber consistencies in the range of 1 to 2% and when larger batches of fiber are being treated. There is something about combining xanthide and fiber for single handsheets that is not conducive to obtaining the highest retention efficiency. This may have something to do with mixing rates or with the relative surface area of the container.

The alum concentration in the water system may be assisting improved retention. Only 3.3% alum is used on the fiber weight in this experiment compared with about 9% in the preceding section. However, the alum concentration is 0.0005M here and 0.0002M in the preceding section due to the difference in fiber consistency.

XANTHATE SORPTION AT 35°C. WITH AND WITHOUT ALUM

The earliest experiments of this project were designed to observe the direct sorption of starch xanthate at 15°C. at several pH values and alum concentrations. No sorption was observed through 64 minutes' exposure. These results focused attention upon starch xanthide retention in the work following. Xanthate sorption was reexamined here at 35°C. so that any significant aspect of the total problem might not be overlooked.

Five grams of starch xanthate (Run 481) were diluted to 2000 ml. and adjusted to pH 5.0, 7.0, or 10.0 at 20°C. with dilute acetic acid. Portions of these solutions (100 ml.) were added to 1500 ml. of fiber suspension (^{2.4 g}~~1.6~~ g. fiber) at 25°C. and at the same pH as the xanthate. The ensuing operations have been described for ex situ xanthide sorption with and without 0.0002M alum. Xanthate retained in the handsheets was estimated by the iodine colorimetric method described in Report One. These data and those for dry tensile strength are shown in Table V.

Starch xanthate is not sorbed when alum is not present and not at pH 10 when 0.^{3 g}0002M alum is present. Measurable sorption is detected at pH 5 and 7 with 0.0002M alum. Retention efficiencies approach 6% at pH 5 and 4% at pH 7. The semilog plots (Fig. 4) show rapid sorption between 0 and 4 minutes followed by a decrease in xanthate sorbed as the contact time is extended. Dry tensile strength is not affected by the starch xanthate sorbed by the fibers except perhaps to be lowered during the early stages of sorption. The different extents of sorption at pH 5 and 7 are probably due to the lower concentration of free aluminum ions at the higher pH.

TABLE V

STARCH XANTHATE SORPTION AT 35°C. WITH AND WITHOUT ALUM

Set No.	Contact Time, min.	pH	Alum, \underline{M}	Dry Tensile, lb./in.	% Starch, g./100 g. fiber	Retention Efficiency, %
Blank	--	5	0	20.0	a	--
18A	1/4	5	0	19.1	a	--
	1			20.2	a	--
	4			18.6	< 0.1	--
	16			20.6	a	--
	32			17.8	a	--
	Mean				19.3	
18B	1/4	7	0	19.2	a	--
	1			18.8	a	--
	4			14.8	a	--
	16			18.3	< 0.1	--
	32			21.8	a	--
	Mean				18.6	
18C	1/4	10	0	22.2	a	--
	1			22.2	a	--
	4			23.4	a	--
	16			22.2	< 0.1	--
	32			21.6	a	--
	Mean				22.3	
18D	1/4	5	0.0002	16.5	0.44	4.22
	1			21.8	0.54	5.18
	4			22.0	0.61	5.85
	16			21.4	0.53	5.09
	32			21.6	0.48	4.61
	Mean				20.7	
18E	1/4	7	0.0002	17.0	0.22	2.11
	1			18.8	0.34	3.26
	4			20.8	0.40	3.84
	16			19.5	0.40	3.84
	32			21.6	0.32	3.07
	Mean				19.5	
18F	1/4	10	0.0002	17.8	a	--
	1			21.8	a	--
	4			21.8	a	--
	16			20.2	< 0.1	--
	32			19.8	a	--
	Mean				20.3	
Control		10	0.0002	21.7	a	--

^aNegative qualitative iodine test for starch in paper.
 Alum on fiber = 8.875 g. $Al_2(SO_4)_3 \cdot 18H_2O$ /100 g. fiber.
 Fiber consistency = 0.150
 Xanthate concentration = 0.0156
 Xanthate added/100 g. fiber = 10.42

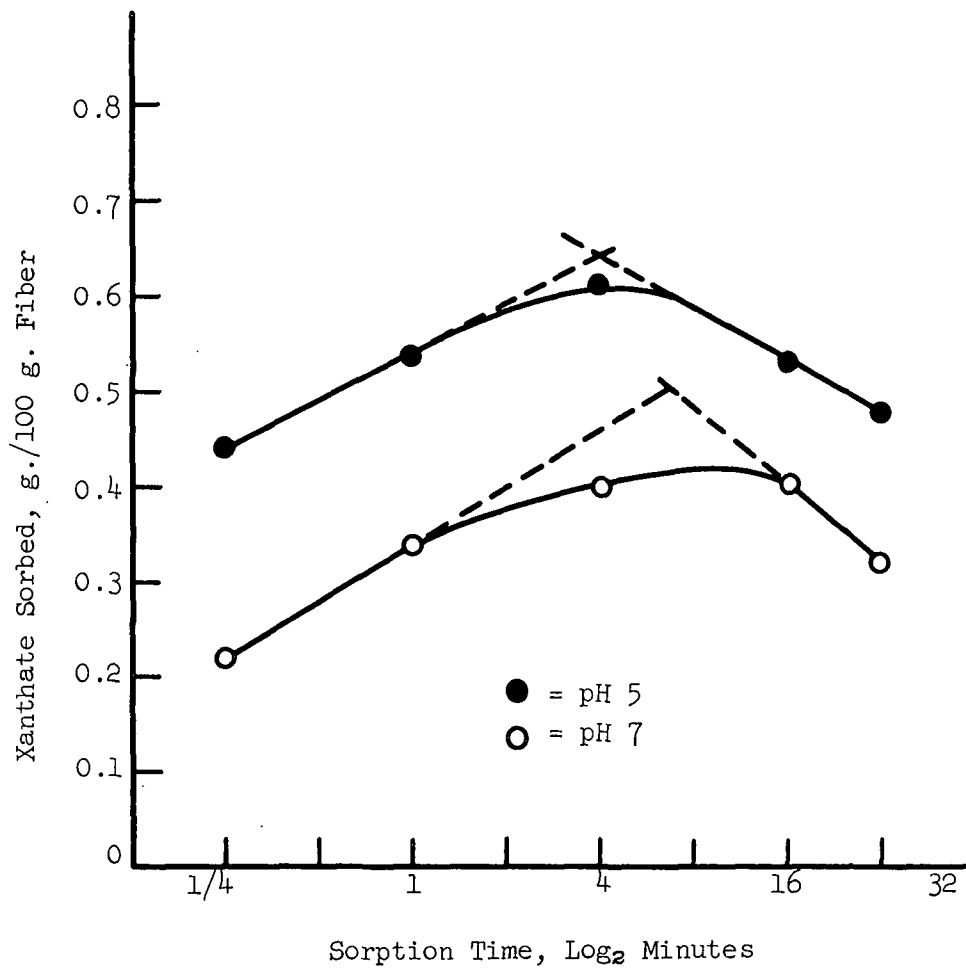


Figure 4. Starch Xanthate Sorption at 35°C. with 0.0002M Alum. Semilog Plot HCP

Contrary to earlier results at 15°C., a small amount of starch xanthate (6 to 4%) is absorbed by wood fibers at 35°C. This is true at pH 7 and 5 with 0.0002M alum but not true at pH 10 or at any of the pH levels tested when alum is not present. The small amount sorbed and the limited conditions for sorption do not indicate direct sorption of starch xanthate is a major factor in the overall retention mechanism for starch xanthide formed in the presence of the fiber.

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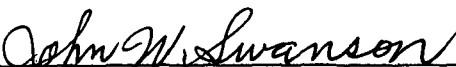
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