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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 Five

A Quarterly Report

to

AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE

December 20, 1966

THE INSTITUTE OF PAPER CHEMISTRY

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TABLE OF CONTENTS

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SUMMARY

The efficiency of starch xanthide retention is affected by the ionic strength of the system at the time starch xanthate is oxidized to starch xanthide with hypochlorous acid (sodium hypochlorite adjusted to pH 5.5 to 6.5) and by the fiber consistency. Higher ionic strengths and higher fiber consistencies (3% vs. 1%) improve the retention of starch xanthide. The starch xanthate concentration does not affect retention efficiency in $1\underline{M}$ sodium chloride.

The control experiment at ambient ionic strengths shows the retention efficienty to improve as the ambient ionic strength, or xanthate concentration, increases. This contrasts with work covered in the preceding report in which retention efficiency is a negative function of the ambient ionic strength, or xanthate concentration. In the earlier experiment, 1% sodium hypochlorite was used at its normal pH of 11.2 to 11.4 rather than being adjusted to pH 5.5 to 6.5 before addition to the system. The implication is that cross-linking and sorption effects must be separated in order to study xanthide retention.

An attempt to measure the retention rate of starch xanthide at 15°C. produced no interpretable changes in xanthide retention over 15 to 120 seconds. Retention efficiency was lower than would be anticipated from the results of similar preparations.

INTRODUCTION

This is the fifth 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 and Marketing Act of 1946. The purpose of this project is to provide information for use in increasing the utilization of cereal starches in paper and paper products. This is to be done by determining the factors governing the adsorption or complexing of starch xanthates and xanthides with pulp fibers under the range of conditions encountered in papermaking.

One of the major objectives of the work planned for this project is the determination of the kind of adsorption involved in the retention of starch xanthates and xanthides in a sheet of paper. The earliest experiments established that starch xanthate is not adsorbed in quantities sufficient to be significant in the starch xanthide retention mechanism. Most of the work done subsequently has been devoted to attempts to isolate the rate-controlling step and to establish reproducible procedures for making starch xanthide in the presence of kraft fibers with the precision needed for this work.

AN EVALUATION OF THE EFFECT OF IONIC STRENGTH UPON
STARCH XANTHIDE RETENTION

INTRODUCTION

Starch xanthide retention efficiency, in Report Four, appears to be an inverse function of the concentration of starch xanthate in the aqueous phase. Reasonable straight line fits are obtained when either the xanthate concentration or the retention efficiency is plotted on the linear scale of semilogarithmic graph paper. Fiber concentration (1.5 and 5.0%) does not appear to be involved.

Relatively large amounts of soluble salts are introduced into the fiber suspension with the xanthate solution and with the sodium hypochlorite used to effect cross-linking. Since the amount of salt introduced is proportional to the amount of starch xanthate being used, what appears to be a function of starch xanthate concentration, instead may be a function of the salt concentration.

The experiment described here is an attempt to isolate the effect of the salt concentration, or ionic strength, from the effect of starch xanthate concentration. If the ionic strength of the xanthate-fiber system is raised sufficiently, variations in the salt concentration due to using increasing amounts of starch xanthate become negligible. In this way, it should be possible to study the effect of varying the xanthate concentration independently of changes in the salt concentration.

If ionic strength is not affecting xanthide retention, then there should be little difference between retention efficiencies observed with and without salt added to "drown out" the effects of the salts accompanying starch xanthate. Conversely, if ionic strength or salt concentration does have a

role in xanthide retention, the retention efficiency should follow different

patterns in the two systems.

The greatest starch xanthate concentration of interest (0.7 g./100 ml.)

represents a salt concentration in excess of 0.04$\underline{M}$. A hundredfold excess of salt

is usually recommended. However, procedural limitations restrict the practical

concentration. A salt concentration of 1.0$\underline{M}$ was selected as a reasonable compro-

mise. The total salt loading thus varies between slightly less than 1.01$\underline{M}$ and

a little more than 1.04$\underline{M}$. This compares with a four- or fivefold variation in

the control block of the experiment.

Sodium chloride was chosen to raise the ionic strength of the system.

This salt is already present in the system — it is introduced with sodium

hypochlorite — and does not disturb the pH, as would the alternative choice

of sodium acetate.

DESIGN OF THE EXPERIMENT

A 2 x 4 block design is used with two levels of fiber (1 and 3%) and

four concentrations of starch xanthate in the system (0.1, 0.3, 0.5, and 0.7

g./100 ml.). The block is repeated with and without 1.0$\underline{M}$ sodium chloride in

deionized water. All concentrations are based on the volume of water in the

system.

PROCEDURE

Starch xanthate from Run Number 449 (D.S. 0.12) was reduced to a

concentration of 1.0 g./100 g. solution with deionized water each day. Portions

of this solution were diluted to about 2 liters with part of the water needed to

give xanthate starch concentrations of 0.1, 0.3, 0.5, or 0.7% in 2.5 liters.

Where used, sodium chloride (146 g.) was dissolved in the dilute xanthate

solution so that a 1M concentration would be achieved after the final dilution.

Bleached kraft fiber, beaten to 700 Schopper-Riegler freeness before classifica-

tion (see Report One, et seq.), is then dispersed in this solution for one minute

in a British disintegrator. Either 25.0 g. or 75.0 g. fiber on a dry basis is

used per 2500 ml. water in the suspension, which includes water added with the

reagents and the dewatered pulp. The concentrations designated as 1 and 3%

represents grams of fiber per 100 grams of water, rather than the usual grams per

100 grams of suspension.

Alum (5 ml. 10 g./100 ml. solution) is added to the stock suspension

before it is adjusted to pH 5.5 with 20% acetic acid and made up to 2.5 liters

with predetermined amounts of water.

Sodium hypochlorite, i.e. Hi-lex, is diluted with three parts deionized

water, adjusted to pH 5.5-6.5 with 20% acetic acid and made up to 1% hypochlorite

with an additional one part of water and thoroughly blended. Part of the hypo-

chlorous acid solution is added immediately to the suspension of fiber in starch

xanthate at a rate of 10 ml. per gram of xanthate starch. This is a little more

than twice the amount required to give a blue color in the presence of potassium

iodide. Vigorous agitation with a laboratory model Lightnin' mixer is maintained

for five minutes after adding the oxidant. The stock is then diluted to 0.5%

consistency for making the 2.5-g. Noble and Wood handsheets. The uncontrolled

temperature of the stock ranged from 18 to 22°C. throughout the procedure.

The handsheets are not pressed but are drum dried between blotters for

two minutes with the couch blotter on top. The top blotter is removed and drying

is continued for two more minutes, whereupon the sheets are heated another two minutes in direct contact with the steam drum. If this procedure was not followed, the dry handsheets made at the higher xanthate concentrations could not be separated from the blotters. Omitting pressing was not important since strength tests were not part of this experiment.

DETERMINATION OF RETENTION EFFICIENCY

One-inch strips, cut from the center of each of 8 handsheets, were ground and blended. This powder was dried over P_2O_5. Two samples were treated with hot $1\underline{N}$ NaOH and then hydrolyzed for 1 hour in $0.93\underline{N}$ HCl. The reducing power of the hydrolyzates is expressed as glucan in the sample and is displayed in Table I. The analytical procedure is discussed further in the next section.

MODIFICATION OF XANTHIDE ANALYTICAL PROCEDURE

The analytical method outlined in Report Four, page 7, was modified by reducing the acid hydrolysis step to one hour instead of four. This modification is justified on the basis of the reducing power from ex situ starch xanthide hydrolyzates heated 1 to 2-1/2 hours after swelling in hot alkali according to the established procedure (Table II).

About 80% of the starch in the starch xanthide is accounted for. Extending the hydrolysis time of the alkali-swollen xanthide does not increase the yield of measurable glucose. Autoclaving one hour apparently destroys more glucose than heating in the boiling water bath.

TABLE I

EFFECT OF IONIC STRENGTH UPON RETENTION EFFICIENCY

Set Number	Xanthate Starch Concentration, g./100 ml.	Xanthate to Fiber Ratio, %	Fiber Consistency, g./100 ml.	NaCl, 1M	pH After Cross-linking	Glucan, g./100 g. sheet	Xanthate (Sample-Blank), g./100 g. sheet	Xanthide, g./100 g. fiber	Retention Efficiency, %
1	0	0	1.0	+	−	5.52	−	−	−
						5.48	−	−	−
Mean						5.50	−	−	−
Standard deviation						0.04	−	−	−
2	0.1	10	1.0	+	5.0	9.31	3.81	3.96	39.60
						9.62	4.12	4.30	42.97
Mean							4.0	4.1	41.3
Standard deviation							0.27	0.30	3.0
3	0.3	30	1.0	+	4.9	23.14	17.64	21.42	71.40
						23.04	17.54	21.27	70.90
Mean							17.6	21.3	71.2
Standard deviation							0.09	0.13	0.44
4	0.5	50	1.0	+	4.8	25.69	20.19	25.30	50.60
						25.57	20.07	25.11	50.22
Mean							20.1	25.2	50.4
Standard deviation							0.11	0.17	0.34
5	0.7	70	1.0	+	5.0	36.00	30.50	43.88	62.69
						36.30	30.80	44.51	63.59
Mean							30.6	44.2	63.1
Standard deviation							0.27	0.56	0.80
6	0.1	3.3	3.0	+	5.1	8.47	2.97	3.06	91.89
						8.25	2.75	2.83	84.98
Mean							2.9	2.9	88.4
Standard deviation							0.19	0.19	6.11
7	0.3	10.0	3.0	+	5.0	11.55	6.05	6.44	64.40
						12.16	6.66	7.14	71.35
Mean							6.4	6.8	67.9
Standard deviation							0.54	0.62	6.16
8	0.5	16.7	3.0	+	5.0	17.33	11.83	13.42	80.50
						17.17	11.67	13.22	79.30
Mean							11.8	13.3	79.9
Standard deviation							0.14	0.18	0.71
9	0.7	23.3	3.0	+	4.9	20.13	14.63	17.14	73.47
						20.54	15.04	17.70	75.87
Mean						4.98	14.8	17.4	74.7
Standard deviation						0.11	0.36	0.49	2.13

TABLE I (Continued)

EFFECT OF IONIC STRENGTH UPON RETENTION EFFICIENCY

Set Number	Xanthate Starch Concentration, g./100 ml.	Xanthate to Fiber Ratio, %	Fiber Consistency, g./100 ml.	NaCl, 1M	pH After Cross-linking	Glucan, g./100 g. sheet	Xanthate (Sample-Blank), g./100 g. sheet	Xanthide, g./100 g. fiber	Retention Efficiency, %
10	0	0	1.0	0	5.5	5.89	—	—	—
						5.92	—	—	—
Mean						5.90	—	—	—
Standard deviation						0.03	—	—	—
11	0.1	10	1.0	0	5.1	9.59	3.69	3.83	38.31
						10.09	4.19	4.37	43.73
Mean							3.9	4.10	41.0
Standard deviation							0.44	0.48	4.8
12	0.3	30	1.0	0	5.1	12.29	6.39	6.83	22.75
						12.00	6.10	6.50	21.65
Mean							6.2	6.7	22.2
Standard deviation							0.26	0.29	0.97
13	0.5	50	1.0	0	5.2	18.75	12.85	14.74	29.49
						19.23	13.33	15.38	30.76
Mean							13.1	15.1	30.1
Standard deviation							0.43	0.56	1.12
14	0.7	70	1.0	0	5.3	36.67	30.77	44.45	63.49
						37.63	31.73	46.48	66.40
Mean							31.2	45.5	64.9
Standard deviation							0.85	1.80	2.58
15	0.1	3.3	3.0	0	5.3	6.87	0.97	0.98	29.43
						7.07	1.17	1.18	35.44
Mean							1.1	1.1	32.4
Standard deviation							0.18	0.18	5.32
16	0.3	10	3.0	0	5.2	10.60	4.70	4.93	49.32
						10.58	4.68	4.91	49.10
Mean							4.7	4.9	49.2
Standard deviation							0.02	0.02	0.19
17	0.5	16.7	3.0	0	5.2	14.12	8.22	8.96	53.73
						14.57	8.67	9.49	56.95
Mean							8.4	9.2	55.3
Standard deviation							0.40	0.48	2.85
18	0.7	23.3	3.0	0	5.3	17.33	11.43	12.90	55.32
						18.05	12.15	13.80	59.28
Mean					5.21		11.8	13.4	57.3
Standard deviation					0.07		0.64	0.82	3.51

Note: Standard deviation is based on the range of the duplicate determinations.

TABLE II

GLUCAN CONTENT OF EX SITU XANTHIDE

Hours Heated in 0.93N HCl	Glucan, %			
	Test 1	Test 2	Mean	Std. Dev.
1.0 (boiling water bath)	79.0	76.5	77.8	2.2
1.5 (boiling water bath)	79.0	77.8	78.4	1.1
2.0 (boiling water bath)	77.0	78.3	77.6	1.2
2.5 (boiling water bath)	79.2	77.9	78.5	1.2
1.0 (autoclave, 120°C.)	72.9	74.1	73.5	1.1

Note: Standard deviation is based on 0.886 times the range.

Preparation of ex situ Starch Xanthide

Starch xanthate (Run 449, about 4 weeks old) was diluted to contain 20 grams xanthate starch per 400 g. solution. Hi-lex (40 ml.) was diluted to 160 ml., adjusted to pH 6.5 with 20% acetic acid, and diluted to 200 ml. These solutions were combined rapidly with a magnetic stirrer (obtaining a pH of 4.3 after blending). The coagulum was agitated 2 minutes in a Waring Blendor and allowed to settle. The xanthide was separated by decantation and resuspended twice in deionized water with the Blendor. Two treatments with methanol, followed by soaking overnight in fresh methanol, preceded filtration and drying over calcium chloride in a vacuum desiccator — yield 6.57 g. xanthide, 0.38% ash (500°C.), and 2.2% sulfur on a dry basis. The sulfur content for a xanthide based on D.S. of 0.12 xanthate should be about 4.1% if no dexanthation occurs and xanthate groups have not been lost after the original xanthate analysis.

DISCUSSION OF RESULTS

The analyses for starch xanthide in the handsheets, presented in Table I, have standard deviation estimates (based on the range) of similar magnitude to those obtained in the most recent previous report (Report Four, page 9). The mean is 0.32% xanthide in the handsheet with the maximum and minimum (0.02 and 0.85%) both occurring in the control block of experiments, i.e., ambient ionic strength. These data are based on the reducing power of duplicate hydrolyzates rather than on two reducing power determinations on a single hydrolyzate, as in the earlier report. Shortening the hydrolysis time to one hour does not contribute unduly to the range of the duplicates and does make a significant contribution in reducing the time required for analysis.

The control of pH was better than had been obtained previously. A pH value of 5.5 was desired throughout the cross-linking reaction. After adding the acidified hypochlorite, the pH was 5.0 ± 0.1 in $1\underline{M}$ sodium chloride and 5.2 ± 0.1 under ambient salt conditions. Previously, the pH rose from 5.5 to about 7 when unacidified hypochlorite was used. As it will be seen, controlling the reaction pH by acidifying the sodium hypochlorite solution before it is added to the xanthate solution may change the overall cross-linking reaction. Neutralizing the excess alkali in the reagent, in effect, changes the reagent. At the normal pH of the hypochlorite solution, about pH 11, hypochlorite ion is the oxidant added, whereas at pH 5.5 to 6.5, hypochlorous acid is the dominant form of the oxidant. It is thought that hypochlorous acid, rather than the hypochlorite ion, is the agent producing starch xanthide.

The raw analytical data are corrected for glucan due to hydrolysis of the fiber components and then reexpressed in grams of starch xanthide per 100 grams

fiber. The ratio of the xanthide found in the handsheet to the xanthate added,

in percentage units, is the retention efficiency. These data are also given in

Table I.

Xanthide retained in the handsheets increases with the xanthate concen-

tration (Fig. 1). The amount retained is a linear function of the xanthate

concentration at high ionic strength but is not linear at low or ambient ionic

strength. It is different for 1 and 3% fiber consistencies for both salt concen-

trations. This observation conflicts with the findings covered in the previous

report.

Xanthide retention efficiency (Fig. 2) is a nonlinear function of

xanthate concentration and seems different for the two fiber levels at low ionic

strength. In 1M sodium chloride, xanthide retention efficiency apparently is

not affected by the xanthate concentration but is improved by increasing the

fiber consistency (Fig. 3).

In Fig. 4, the log of the xanthate concentrations is plotted as a

function of the xanthide retention efficiency. At low ionic strength (Fig. 4A)

a linear relationship is observed with 3% fiber as was found in the previous

report. However, it is a positive function and not the negative function observed

earlier. The relationship at 1% fiber is nonlinear and does not fit a recognized

pattern. While low efficiencies are found for 0.3 and 0.5% xanthate at 1% fiber,

the overall trend is toward higher efficiency as the xanthate concentration

increases. This pattern is more like that found in the work done for Report Three

when unacidified hypochlorite is added more slowly (from a buret rather than a

graduated cylinder) and in the presence of a small amount of potassium iodide (see

page 31, Report Four, for a plot of these data). It is thought that potassium

A. Ambient Salt Concentration
<u>ca.</u> 0.01 to 0.04<u>M</u>

B. 1<u>M</u> NaCl
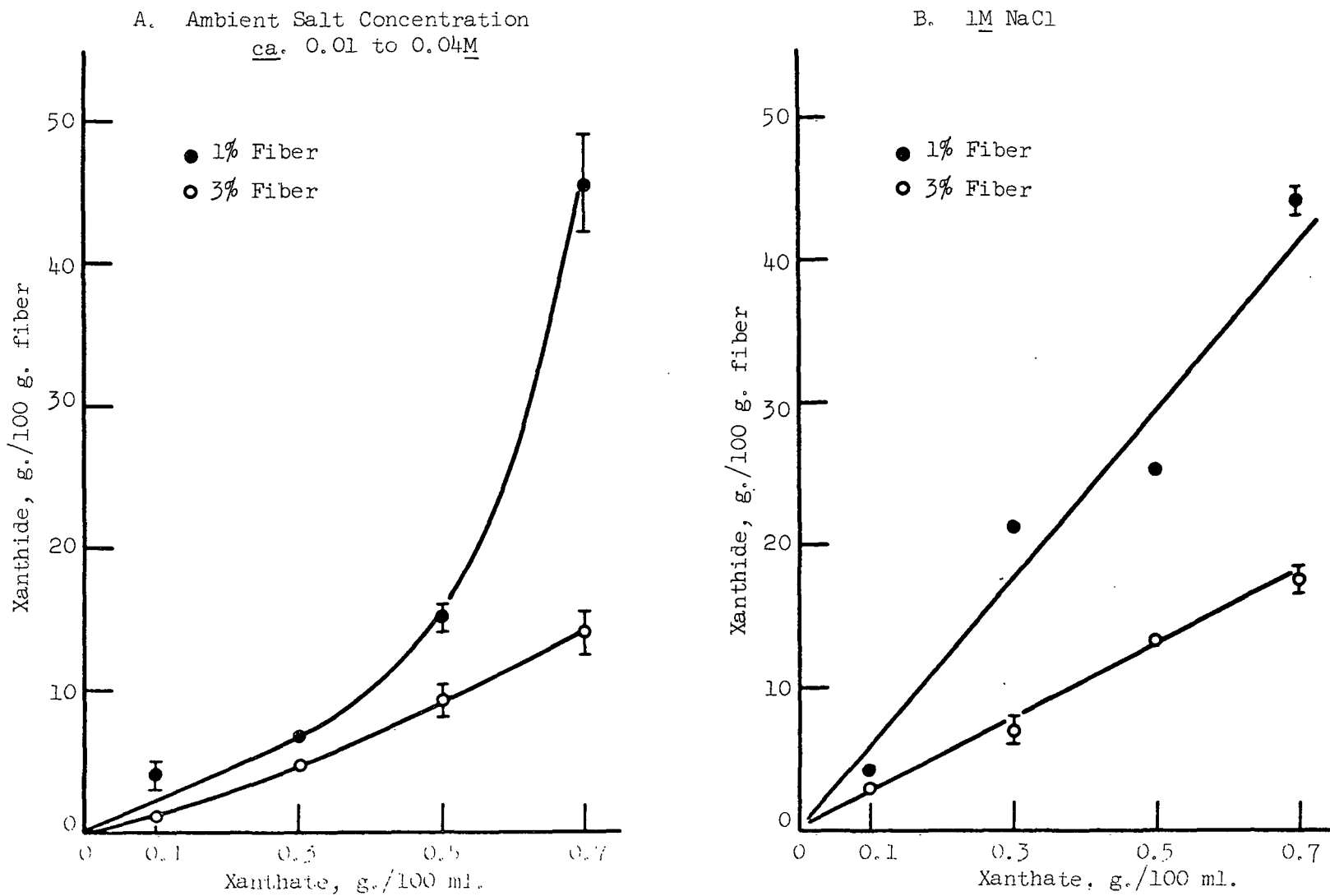
Figure 1. Xanthide Retained <u>versus</u> Xanthate Concentration at Low and High Ionic Strength
95% Confidence Limits shown

Figure 2. Retention Efficiency at Low Ionic Strength
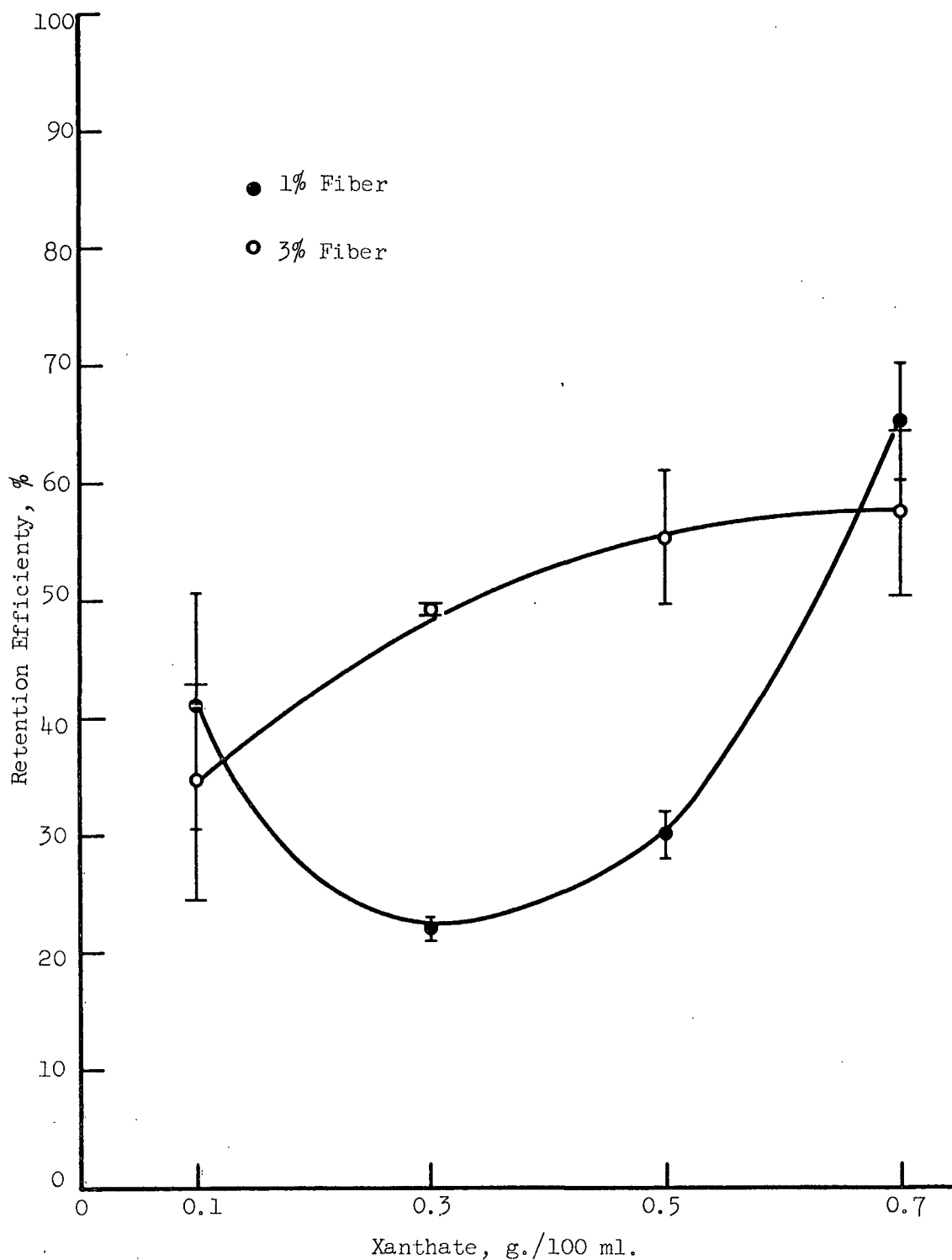(Ambient Salt Concentration) 95% Confidence
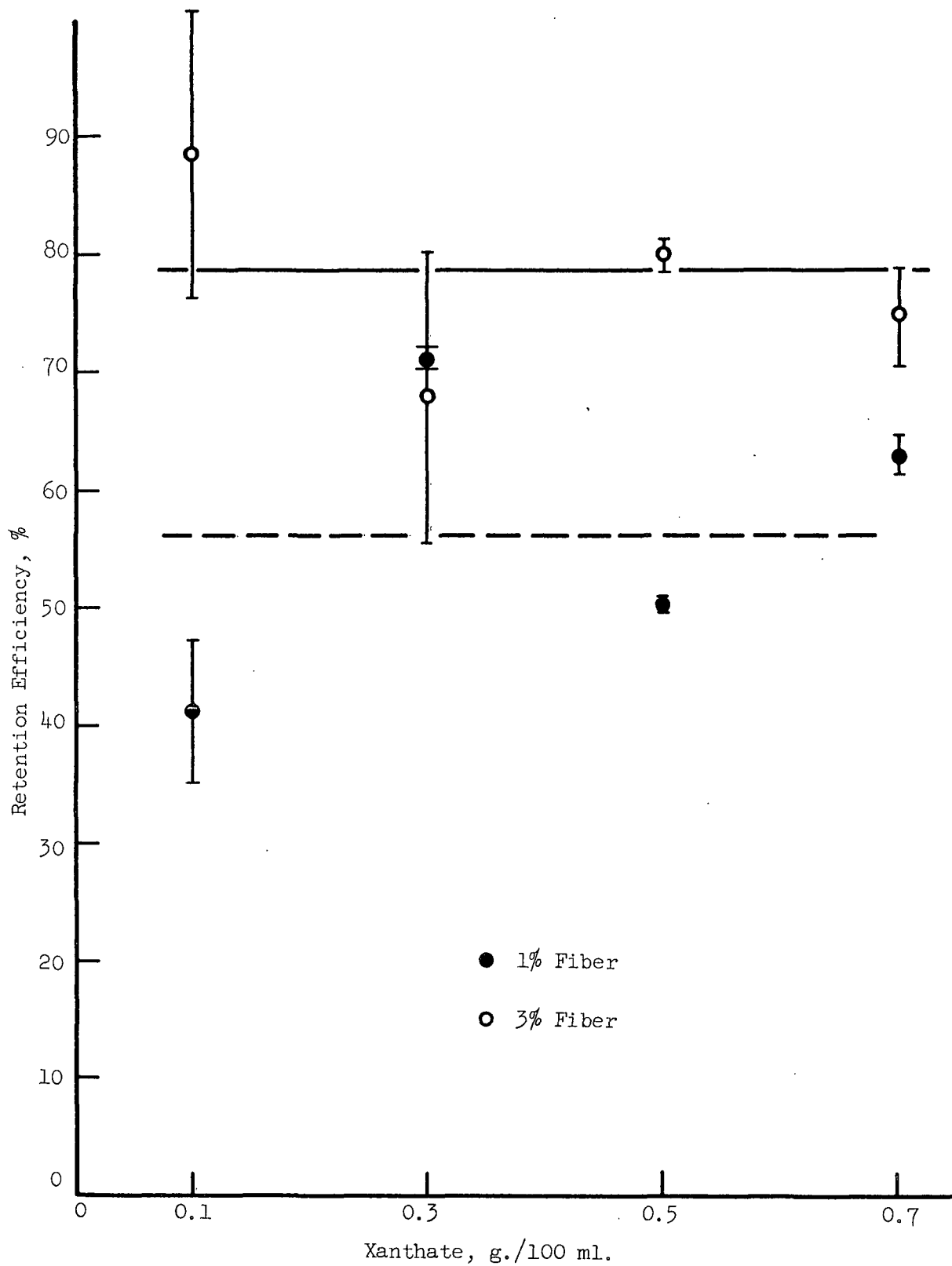Limits Shown

Figure 3. Retention Efficiency at High Ionic Strength (1M̲ NaCl)
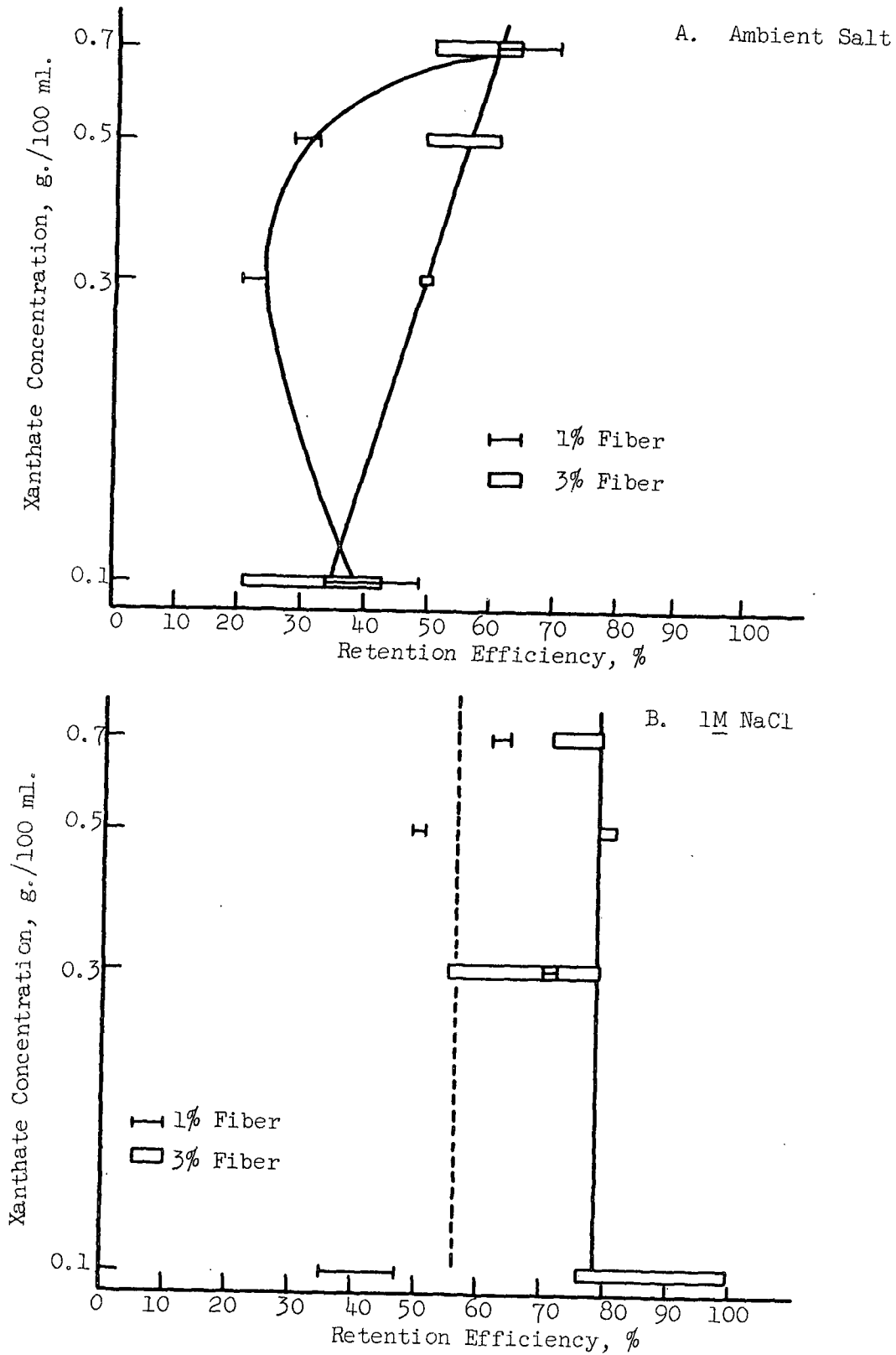The Limits Shown Are for the 95% Confidence Range

Figure 4. Xanthate Concentration as a Function of the 95%
Confidence Range of Retention Efficiency at Low
and High Ionic Strength

iodide increases the formation of starch xanthide and reduces the extent of the

dexanthation reactions proposed for the hypochlorite ion.

The retention efficiency at high ionic strength (Fig. 4B) apparently

is not affected by the xanthate concentration.

Plotting retention efficiency as a function of the xanthate-to-fiber

ratio (Fig. 5) shows no patterns not seen for xanthate-concentration as the

independent variable (Fig. 2 and 3).

In Fig. 6 and 7, retention efficiency is presented as a function of

the logarithm of the xanthate/fiber ratio with no distinction made for the

different fiber consistencies. Rather tenuously fitted straight lines suggest

retention efficiency decreases with the xanthide/fiber ratio at high ionic

strength and increases at low ionic strength.

Some of the data from Table I are summarized in Table III, which serves

as an aid for further examination of the effects of ionic strength, fiber consis-

tency, and xanthate concentration. Mean values of the retention efficiency are plot-

ted (Fig. 8 and 9) as logarithmic functions of the xanthate concentrations.

The means averaged over both ionic strengths indicate xanthide retention increases

with xanthate concentrations and with the fiber consistency (Fig. 8). When

averaged over both fiber consistencies, retention efficiency increases with the

xanthate concentration at ambient ionic strength and is independent of xanthate

concentration in 1M sodium chloride (Fig. 9). The mean efficiencies for all salt

and fiber concentrations show higher retention as the xanthate concentration

increases, as would be expected from combining a constant with a variable.
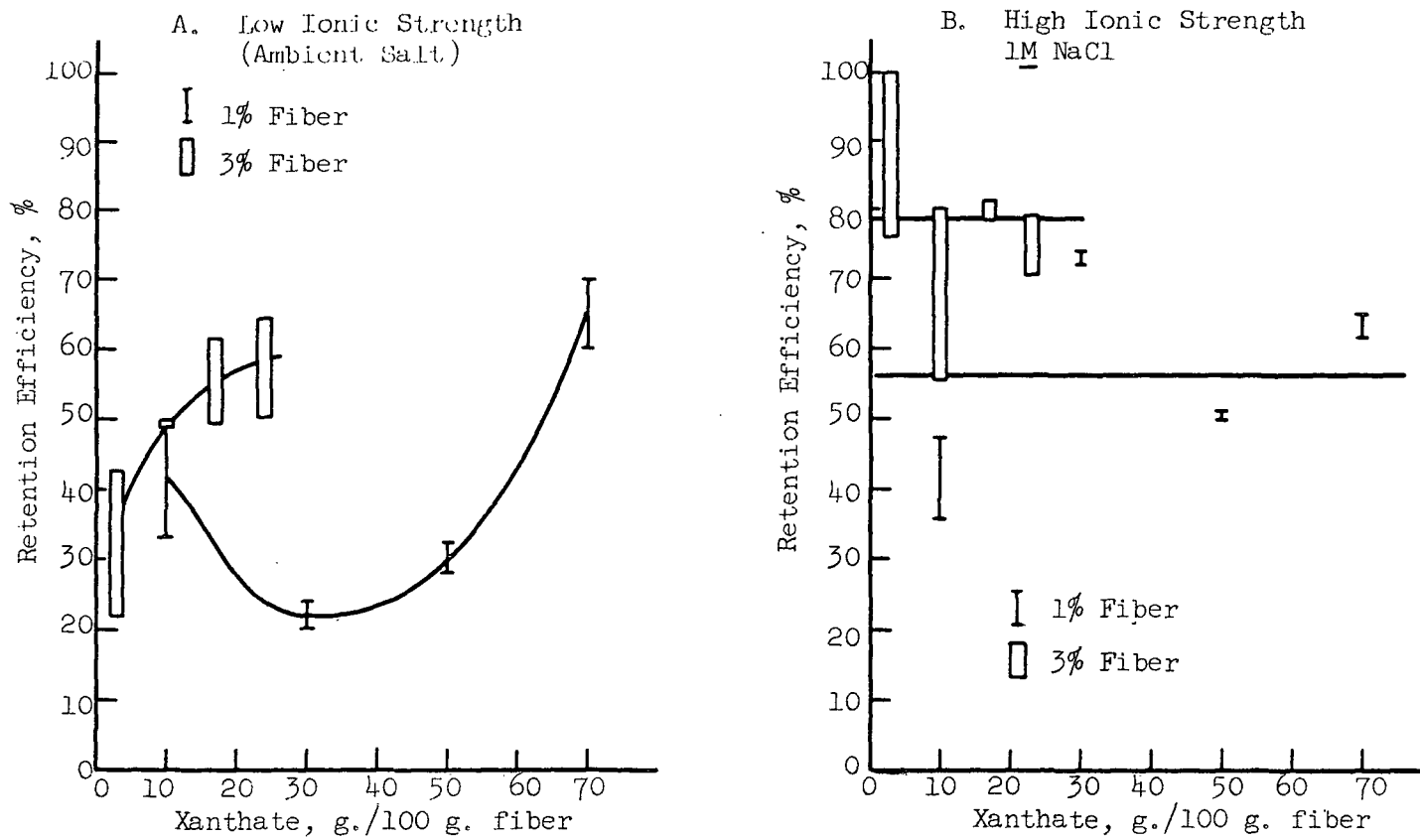
Figure 5.   Retention Efficiency as a Function of the Xanthate to Fiber Ratio
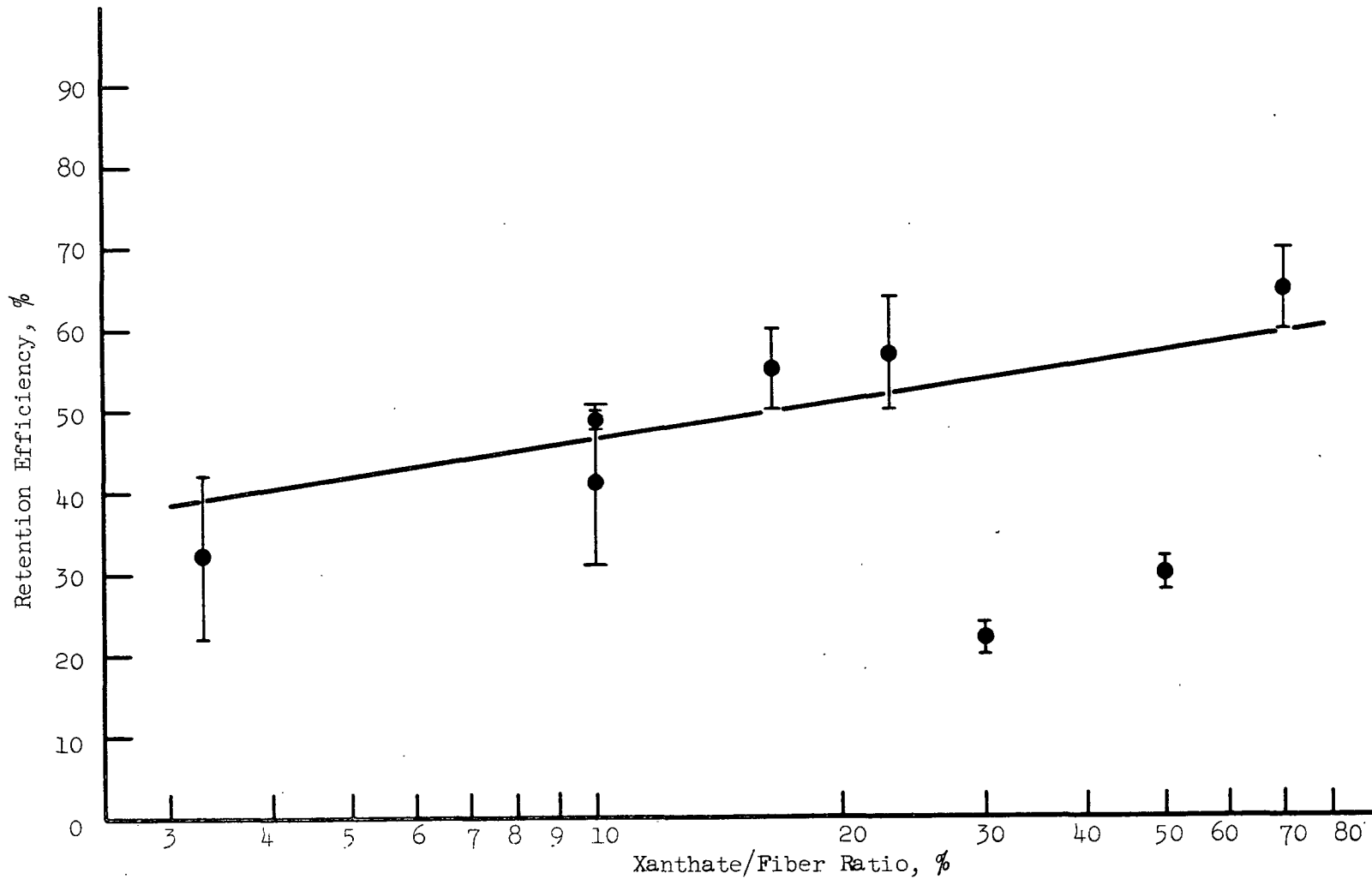(95% Confidence Range)

Figure 6. Low Ionic Strength Retention Efficiency versus Log Xanthate/Fiber Ratio
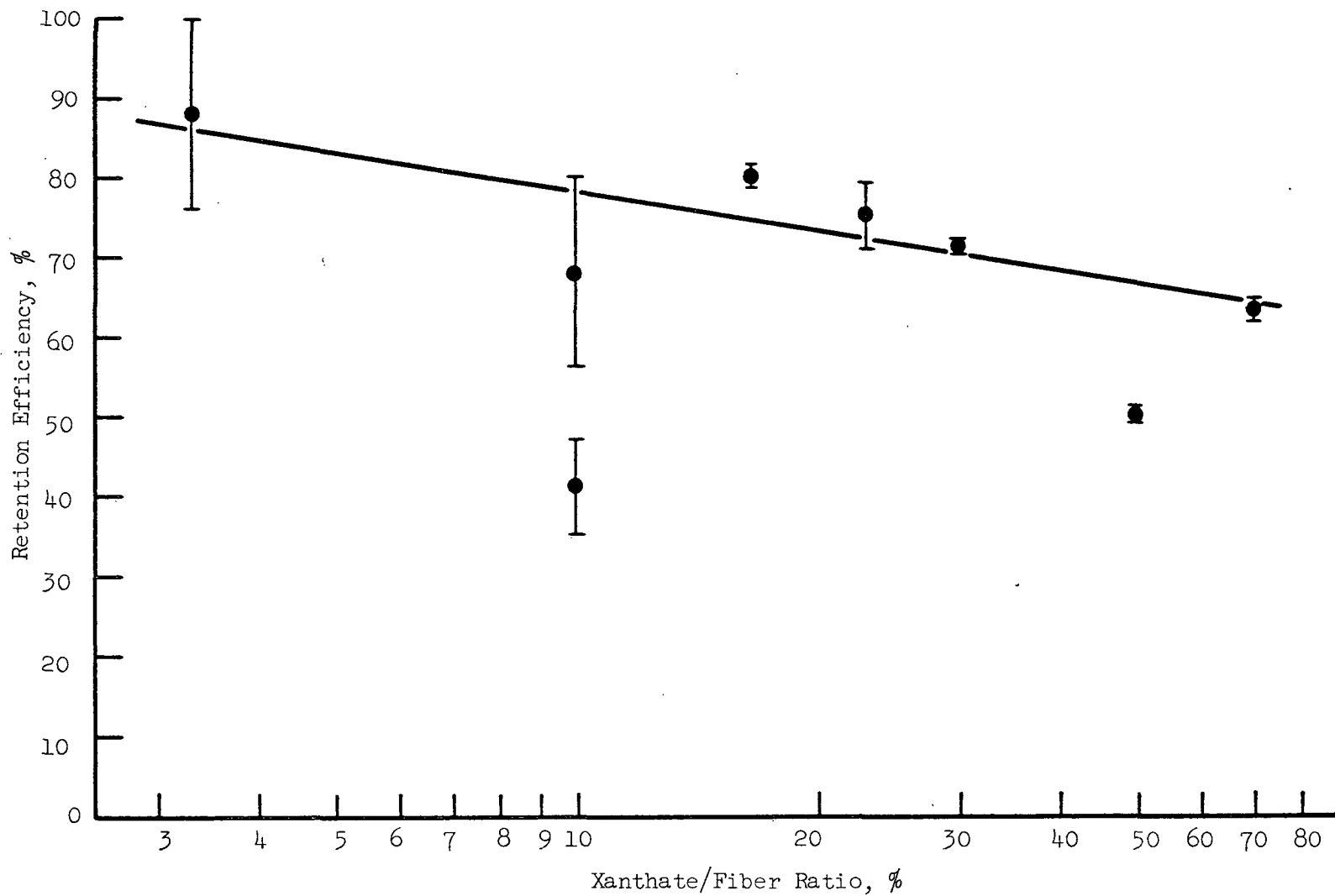The 95% Confidence Range is Indicated

Figure 7.   High Ionic Strength Retention Efficiency <u>versus</u> Log Xanthate/Fiber Ratio
(95% Confidence Limits)

TABLE III

RETENTION EFFICIENCY MEANS

Summary of Data from Table II

Fiber Consistency	NaCl, 1M	Xanthate, g./100 ml.				Mean
		0.1	0.3	0.5	0.7	
1	0	41.0	22.2	30.1	64.9	39.6
3	0	32.4	49.2	55.3	57.3	48.6
1	+	41.3	71.2	50.4	63.1	56.5
3	+	88.4	67.9	79.9	74.7	77.7
1	0	41.2	46.7	40.2	64.0	48.0
3	0	60.4	58.6	67.6	66.0	63.2
0	0	36.7	35.7	42.7	61.1	44.0
0	+	64.8	69.6	65.2	68.9	67.1
0	0	50.8	52.6	53.9	65.0	55.6

The means for each cross-linking condition are summarized in Table IV. By inspection, retention efficiency is a function both of the fiber consistency and ionic strength. Higher fiber consistencies and high ionic strength favor maximum retention of starch xanthide.

TABLE IV

COMPARISON OF MEAN RETENTION EFFICIENCIES WITH
CROSS-LINKING CONDITIONS. SUMMARY FROM TABLE II

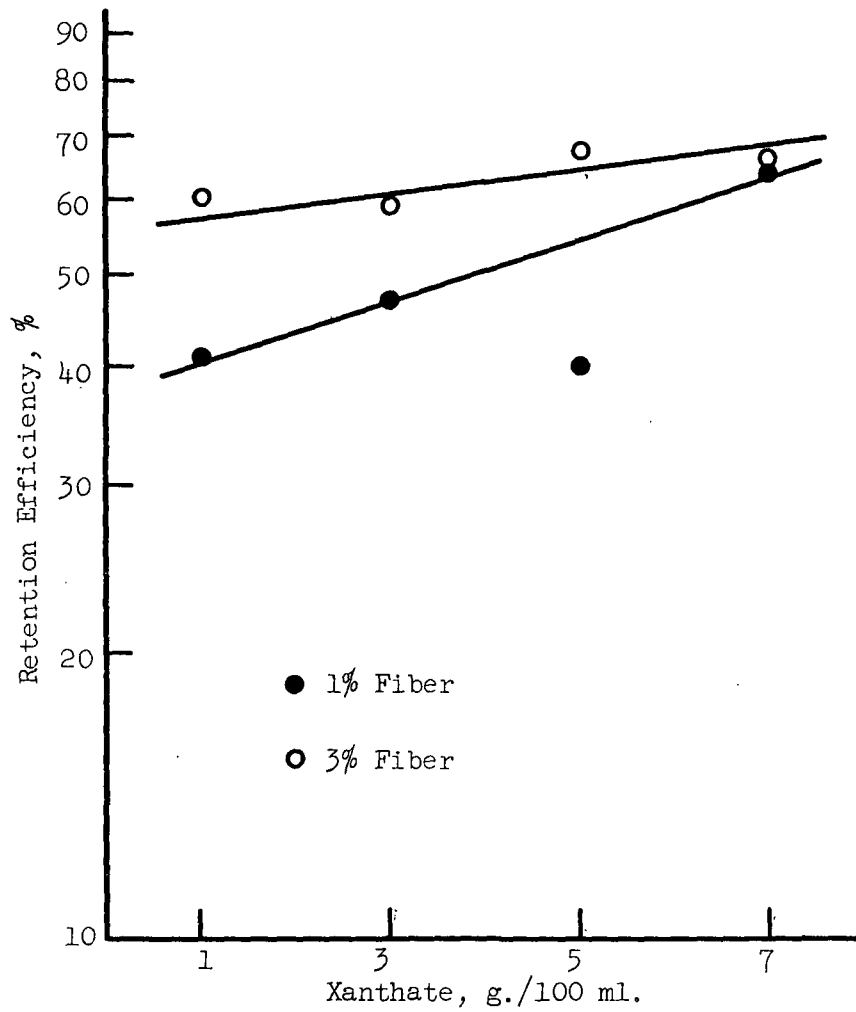| Fiber Consistency, %	Retention Efficiency, %		
	1M NaCl		
	0	+	Mean
1	39.6	56.5	48.0
3	48.6	77.7	63.2
Mean	44.1	67.1	55.6

Figure 8. Ionic Strength Mean Retention Efficiency
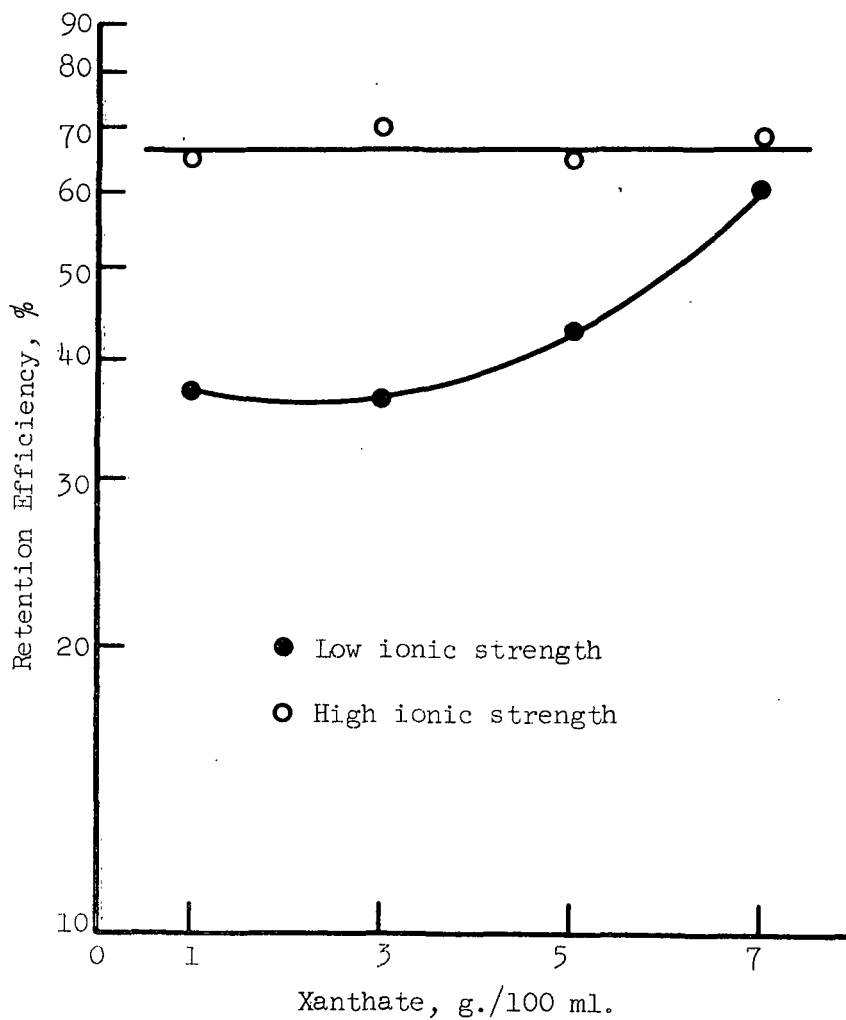as a Function of Xanthate Concentration

Figure 9. Fiber Mean Retention Efficiency as a
Function of Xanthate Concentration

The foregoing observations support the conclusion that starch xanthide

retention is a function of ionic strength rather than a function of the xanthate

concentration. Apparently, the ionic materials introduced with the xanthate and

hypochlorite elevates the ionic strength to a critical range that affects either

the sorption of xanthide or the cross-linking reaction.

If the negative effect of increasing xanthate concentration upon reten-

tion efficiency found in Report Four is due to increasing ionic strength, then

the effect must be upon the cross-linking reactions. That is, the differences

between the experiments at ambient ionic strength in Report Four and in this

report are so small (pH 7 versus pH 5 after cross-linking), it is difficult to

assign the different sorption patterns to the sorption conditions. The fact

that the fiber concentration is a factor in this report and was not in the

earlier work also implicates the cross-linking reaction. Increasing the sub-

strate surface area by increasing the substrate concentration should increase

retention efficiency in both experiments. The differences in pH are not in a

range likely to have a strong effect on the fiber surface characteristics.

STARCH XANTHIDE RETENTION RATES

In an effort to measure retention rates, starch xanthide is formed at 15°C. by adding acidified hypochlorite to fiber suspended in dilute starch xanthate solutions. Timing of the contact period began as the hypochlorite solution (pH 5.5) was dumped into the stock and ended when the preparation was poured into a Noble and Wood sheet mold. The sheet mold valve was tripped as the stock was being poured into the deckle box partially filled with cold deionized water.

PROCEDURE FOR 0.1% FIBER

Twenty grams of fines-free kraft fiber are dispersed for 2 minutes in a British disintegrator and then made up to 20,000 ml. with cold deionized water. Four milliliters of 10% (w/v) alum is added to the 0.1% fiber suspension while it is being cooled to $15 \pm 1/2$°C. by means of a copper coil immersed in the stock. A portion of the dilute fiber (2.00 l.) is placed in a 3-liter stainless steel beaker which is immersed in a 15.0°C. thermostat. Starch xanthate (100 ml., 1%, Run No. 452), also at 15°C., is added. The mixture is adjusted to pH 5.5 with 20% acetic acid and reequilibrated to $15 \pm 1/2$°C. Acidified sodium hypochlorite solution 10 ml. (about 1.1 to 1.2%, pH 5.5-5.8) is added and dispersed manually with a spatula while the container remains in the 15°C. water bath. Intervals of 15, 30, 45, 60, and 120 sec. are allowed to lapse between the time the hypochlorite is added and the time the stock is poured into the partially filled sheet mold as the valve is tripped. Three handsheets are made for each interval. The drying procedure for the unpressed handsheets was described earlier.

PROCEDURE FOR 1.0% FIBER

Forty grams, dry basis, fines-free kraft fiber is dispersed in a British disintegrator, and made up to 2.00 liters with deionized water. The suspension is then cooled to 15°C. in a water bath. Four milliliters of 10% alum are added at this point. A portion of the stock (100 ml., 2%) is combined with an equal portion of 1% starch xanthate solution (Run No. 452) and adjusted to pH 5.5 with 20% acetic acid. This produces a 1% fiber suspension in 0.5% starch xanthate. After the mixture attains a temperature of 15°C. in the water bath, 10 milliliters of acidified hypochlorite are added and blended in with a magnetic stirrer. Three handsheets are made at each of the 15-, 60-, and 120-second intervals used in this experiment.

RESULTS AND DISCUSSION

The xanthide analysis was run on two of the three handsheets in each set. These samples were ground in the Wiley mill and the acid hydrolysis step was run for one hour in boiling water. These data for starch xanthide are listed in Table V.

There is no sign of a temporal sequence in the xanthide content of the handsheets, and the retention efficiency is quite low. Since total retention would show 33.3% xanthide on the weight of the fiber, retention efficiency is about 3%. There is no obvious reason for this low efficiency. Earlier, a retention efficiency of 22% was obtained under similar conditions (Table I) but at a slightly higher temperature and with a contact time of five minutes.

TABLE V
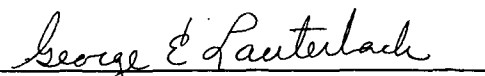
XANTHIDE RETENTION AS A FUNCTION OF TIME AT 15°C.

Fiber Consistency, %	Time Interval, sec.	Sheet Identification	Glucan, % Test 1	Test 2	Sheet Mean	Sample Mean	Xanthide, % Sample Mean	Block Mean
Blank	--	A	5.05	4.79	4.92		--	--
		B	5.03	4.80	4.92	4.92		
0.1	15	A	5.65	5.63	5.64			
		B	6.04	6.02	6.03	5.84	0.92	
0.1	30	A	5.92	5.87	5.90			
		B	5.91	5.91	5.91	5.90	0.98	
0.1	45	A	5.91	5.93	5.92			
		B	5.88	5.77	5.85	5.88	0.96	
0.1	60	A	5.34	5.33	5.34			
		B	5.42	5.44	5.43	5.38	0.46	
0.1	120	A	5.34	5.23	5.28			
		B	5.35	5.52	5.44	5.36	0.44	0.75
1.0	15	A	5.84	6.03	5.94			
		B	5.92	5.97	5.94	5.94	1.02	
1.0	60	A	6.14	5.93	6.04			
		B	6.09	6.04	6.06	6.05	1.13	
1.0	120	A	6.04	6.15	6.10			
		B	5.96	5.85	5.90	6.00	1.08	1.08

FUTURE WORK

Most of the work covered in Reports Two through Five has been devoted to finding reproducible cross-linking conditions in order to study xanthide sorption rates. It now appears that cross-linking and xanthide retention must be separated so that sorption may be observed independently of the variations in cross-linking. This would be done by oxidizing dilute solutions of starch xanthate. Fiber suspension would then be exposed to portions of this dispersion for several time intervals, addition levels, temperatures, and consistencies.

This proposal is in line with the current programs of the cooperating agency. In these programs, starch xanthide, formed continuously at 0.1 to 0.5% starch xanthate concentrations, is to be added to the stock line of a paper machine.

THE INSTITUTE OF PAPER CHEMISTRY

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