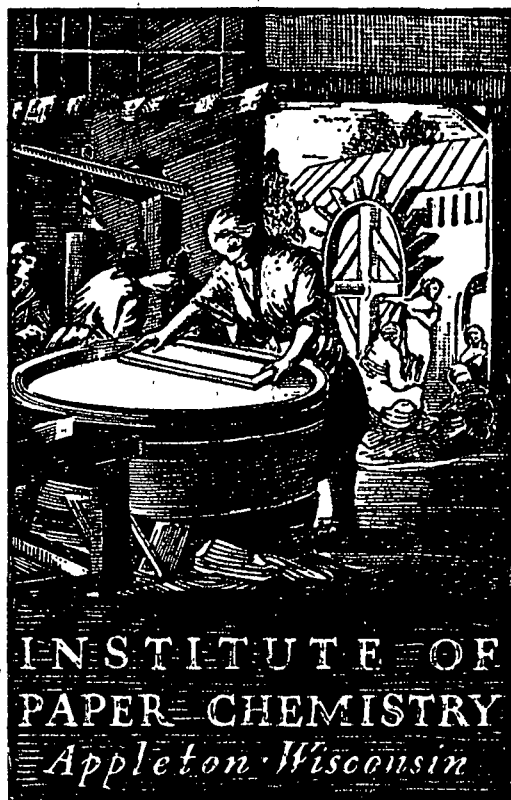


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**STUDIES ON THE FACTORS GOVERNING  
RETENTION AND EFFECTIVENESS OF  
STARCH XANTHATES AND XANTHIDES  
BY WOOD PULP IN PAPERMAKING**

Project 2580

Report Four

A Quarterly Report

to

AGRICULTURAL RESEARCH SERVICE  
UNITED STATES DEPARTMENT OF AGRICULTURE

September 15, 1966

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Analysis of the xanthide content of portions of the same handsheets by the cooperator's laboratory and at the Institute were essentially in good agreement. Only a little more work is needed to optimize and calibrate the procedure for our use. The concentration of the starch xanthate in the aqueous phase of the fiber suspension has a greater effect upon xanthide retention efficiency than the fiber consistency or the xanthate-to-fiber ratio. However, the present data are insufficient for distinguishing between the effects of the xanthate concentration and the effects of the salts that accompany the starch xanthate.

More evidence is presented implicating potassium iodide as an active participant in the cross-linking reaction.

## EVALUATION OF XANTHIDE ANALYSIS

### INTRODUCTION

The objective of this phase of the project is to deduce the mechanisms involved in the sorption of starch xanthide by papermaking fibers. This is done by observing sorption as a function of time under a number of conditions. The amount of starch xanthide adsorbed is best determined by direct analysis of mats of the fibers isolated after exposure to aqueous starch xanthide for several periods of time.

A method for determining the starch xanthide content of paper has been developed by the cooperator. This method involves steeping the paper sample in hot alkali and then hydrolyzing the swollen material with acid before determining the reducing power of the sugars produced. The reducing power is expressed as percent glucan on the weight of the oven-dry samples. This is a simplification since the basic method includes the determination of the sulfur content and the fiber residue. It is considered adequate for our purposes merely to follow the sorption of the starch portion of the starch xanthide.

When we attempted to use this method, it was difficult for us to obtain reproducible values for the blank (handsheets formed without exposure to starch xanthide). This forced some modifications in the way the samples are manipulated and may have affected the results.

In view of the importance of this determination, an evaluation of our technique was necessary. Arrangements were made with the cooperator to have xanthide analyses run on portions of the same handsheets at Peoria and at the Institute.

## DESIGN OF EXPERIMENT

A 2 x 2 factorial experiment was set up to evaluate the proposition that the starch xanthate concentrations rather than the starch xanthate-to-fiber ratio affects retention of starch xanthide. This provided us with handsheets for checking xanthide analysis and furthered our effort to understand the cross-linking reaction.

The initial design called for 1.5% and 6.0% fiber and for 0.25 and 0.75 gram xanthate starch per 100 ml. fiber suspension. After the experiment was underway, it was found that the stock could not be blended at 6% consistency. Dilution to 5% consistency produced a workable mass but distorted the symmetry of the design. However, this had no serious consequence.

## HANDSHEET PREPARATION

The preparation of the paper handsheets has been described in earlier reports. A brief description follows for convenience.

A portion of the Rayonier paper stock aside for this project was beaten <sup>700</sup> *on 10-12-66 St Lautbach* to 200-ml. Schopper-Riegler freeness by a Valley beater before being processed by a Bauer-McNett classifier to remove the portion accepted by the 150-mesh screen. The dewatered fiber was passed through a breaker, blended, and stored under refrigeration without a preservative.

The starch xanthate was from the *Chemical* *Co.* *Product* *440* (D.S. 0.13). It was diluted with deionized water to a starch concentration of 1.0% by weight.

Sodium hypochlorite, obtained from the commercial laundry bleach, Hi-lex, was diluted one volume to five volumes with deionized water. The concentration of the sodium hypochlorite used for cross-linking is thus about 1.0-1.1 grams per 100 ml.

Stock suspensions were made up in the British disintegrator according to the proportions shown in Table I. Deionized water, starch xanthate and alum were combined before the fiber was introduced. The suspension was then made up to the specified volume. Following agitation for one minute in the disintegrator, the pH was adjusted to about 5.5 with dilute acetic acid or sodium hydroxide as required. Sodium hypochlorite (200 to 250% the amount required to produce a permanent blue color in the presence of potassium iodide) was added rapidly from a graduate at the beginning of 4 minutes agitation in the British disintegrator.

Manual blending of the hypochlorite into the 5% stock preparations was necessary since poor mixing was obtained mechanically. This defeated the purpose of using the British disintegrator. It had been hoped that reasonable reproduction of shear rates between sets could be obtained in the disintegrator in case the xanthide retention rate is diffusion controlled. However, the results do not indicate differences in the handsheets large enough for the variation in mixing to be important here.

The stock was diluted to 0.5% consistency before making 2.5-g. handsheets in an 8 by 8-inch Noble and Wood sheet mold equipped with a 100-mesh Monel wire. Groups of four handsheets were pressed between blotters at 50 pounds per square inch for 5 minutes. The handsheets were dried on single blotters on a drum containing steam at 3.5 pounds per square inch.

TABLE I  
 COMPOSITION OF HANDSHEET STOCKS

Set no.	I	II	III	IV	V	VI
Fiber/water, %	1.5	1.5	5.0	1.5	5.0	5.0
Xanthate/water, %	0	0.25	0.21	0.75	0.62	0
Xanthate/fiber, %	0	16.6	4.2	50.0	12.5	0
Deionized water, ml.	1500	1000	1000	0	0	1500
1% Xanthate, ml.	0	500	500	1500	1500	0
10% Alum, ml.	5	5	5	5	5	5
Fiber (o.d.), g.	30	30	150	30	150	150
Total volume, ml.	2000	2000	2400	2000	2400	2400
Adjusted pH	5.5	5.3	5.3	5.4	5.5	5.5
1% Hypochlorite, ml.	50	50	50	150	150	150
0.5% Consistency, pH	8.0	5.8	6.1	8.3	7.1	7.8

Selection of Handsheets for Xanthide Analysis

The third, fourth, and fifth handsheets of each set of eight were cut in half. One section was retained for our own analysis and the other sent to Peoria. The right and left halves of each sheet were labeled and intermingled according to the pattern shown in Table II. This was done to reduce the significance of nonuniform formation due to irregularities in the structure of the sheet mold. We have no indications that this sheet mold is not "square" but this factor has not been evaluated recently.



TABLE II  
RESULTS OF INTERLABORATORY DETERMINATION OF XANTHIDE CONTENT

Set No.	Sheet No.	Side No.	N.U.P.D.D. Data			I.P.C. Data			Mean	Standard Dev. <sup>a</sup>
			Glucan, %	Xanthide, %	Standard Dev. <sup>a</sup>	Glucan, %	Xanthide, % <sup>b</sup>	Standard Dev. <sup>a</sup>		
I	3	L	--	--	--	6.60	--	(6.56)	(0.04)	
	4	R	--	--	--	6.53	--			
	5	L	--	--	--	6.54	--			
II	3	L	--	7.60	0.28	12.69	6.13	6.18	0.10	
	4	R	--	7.31	0.28	12.63	6.07			
	5	L	--	7.79	0.28	12.80	6.24			
III	3	L	--	2.45	0.34	9.20	2.64	2.90	0.34	
	4	R	--	2.55	0.34	9.80	3.24			
	5	L	--	3.03	0.34	9.39	2.83			
IV	3	L	--	5.55	0.26	11.60	5.04	5.26	0.31	
	4	R	--	5.99	0.26	12.13	5.57			
	5	L	--	5.83	0.26	11.72	5.16			
V	3	L	--	1.93	0.40	8.63	2.07	2.20	0.20	
	4	R	--	2.33	0.40	8.96	2.40			
	5	L	--	2.63	0.40	8.70	2.14			
VI	3	L	--	--	--	6.20	--	(6.17)	(0.07)	
	4	R	--	--	--	6.02	--			
	5	L	--	--	--	6.30	--			

<sup>a</sup>Standard deviation based on range.

<sup>b</sup>Sample less mean of Set I.

#### ANALYTICAL PROCEDURE USED AT THE INSTITUTE OF PAPER CHEMISTRY

The following steps in the procedure evolved from the procedure of M. A. Buchanan (1) as our analyst, L. G. Borchardt, strove for improved precision:

1. Grind sample in a Wiley mill equipped with a 40-mesh screen.
2. Place a 0.5-gram sample (analytical balance) in a 29 x 200 mm. test tube provided with a cover to reduce evaporation loss (e.g., an inverted 25-ml. Erlenmeyer flask).
3. Weigh out samples for moisture determinations over  $P_2O_5$ .
4. Add 15 ml. 1N NaOH to sample in test tube and heat 30 minutes in a boiling water bath. Mix occasionally.
5. Add 50 ml. water and 15 ml. 6N HCl without removing sample tube from water bath.
6. Continue heating in the boiling water bath for 2.5 hours with occasional mixing.
7. Remove sample tube from water bath and cool to room temperature.
8. Transfer contents of test tube to a 150-ml. beaker and add 3.5 ml. 50% NaOH and cool.
9. Neutralize to pH 6.0-7.0 with 8% NaOH (pH meter).
10. Transfer neutral suspensions to a 100-ml. volumetric flask and dilute to mark.
11. Centrifuge about 15 ml. of the suspension in a 15-ml. conical centrifuge tube. (Table-top centrifuge.)
12. Pipet  $3/8$  ml. of the clear supernatant into a 10-ml. volumetric flask. (A 1-ml. syringe equipped with a Chaney adaptor may be used to measure  $3/8$  ml. accurately.)

13. Follow the colorimetric procedure of Saeman and others to relate reducing power to the weight of sugar (2). Optical density is read in duplicate.
14. Report as grams glucan per 100 grams of dry sample.

#### RESULTS OF XANTHIDE ANALYSES

The results of the work done in the Northern Utilization Research and Development Division (N.U.R.D.D.) laboratories were reported by telephone on August 16, 1966. These data are presented as percent xanthide in Table II along with the data produced at the Institute.

#### DISCUSSION OF RESULTS

The precision of analysis, as shown by the estimate of the standard deviation, is nearly the same in both laboratories. This suggests that both analysts have the techniques of the procedure well in hand. However, the xanthide levels for Set II are quite different between laboratories. This difference is greater than three standard deviations. Nonetheless, we reject the hypothesis that these samples are different since each laboratory received specimens from the same handsheets.

In Table III, a comparison of means and estimates of standard deviation is made sheet by sheet. This emphasizes the existence of a problem in the case of Set II. Set IV displays a tendency toward lower results by the Institute procedure. However, no distinction between sheets or between laboratories is warranted statistically except for Set II.

TABLE III

COMPARISON OF DEVIATION WITHIN SET AND BETWEEN LABORATORIES

Set No.	Laboratory	Xanthide in Handsheet Handsheet Number, %			Intra- Laboratory Mean, %	Standard Deviation	St. Dev. as Percent of Mean
		3	4	5			
II	N.U.R.D.D.	7.60	7.31	7.79	7.57	0.28	18.0
	I.P.C.	6.13	6.07	6.24	6.18	0.10	
	Interlaboratory Mean	6.87	6.69	7.02	6.86	0.79 <sup>a</sup>	
	Standard Deviation	1.11	1.24	1.37		1.23 <sup>b</sup>	
III	N.U.R.D.D.	2.45	2.55	3.03	2.68	0.34	7.1
	I.P.C.	2.64	3.24	2.86	2.90	0.34	
	Interlaboratory Mean	2.54	29.0	29.4	2.79	0.24 <sup>a</sup>	
	Standard Deviation	0.17	0.61	0.15		0.20 <sup>b</sup>	
IV	N.U.R.D.D.	5.55	5.99	5.83	5.79	0.26	8.5
	I.P.C.	5.04	5.57	5.16	5.26	0.31	
	Interlaboratory Mean	5.30	5.78	5.50	5.52	0.28 <sup>a</sup>	
	Standard Deviation	0.45	0.37	0.59		0.47 <sup>b</sup>	
V	N.U.R.D.D.	1.95	2.33	2.63	2.30	0.40	4.0
	I.P.C.	2.07	2.40	2.14	2.20	0.20	
	Interlaboratory Mean	2.01	2.36	2.38	2.25	0.22 <sup>a</sup>	
	Standard Deviation	0.11	0.06	0.45		0.09 <sup>b</sup>	

Standard Deviation is based on range of data entering the mean.

<sup>a</sup><sub>n</sub> 3.  
<sup>b</sup><sub>n</sub> 2.

Figure 1 displays the good correlation of the data from the two laboratories (except for the highest value which corresponds to Set II). If all the points are connected, a curve is produced which suggests either overdetermination at N.U.R.D.D. or underdetermination at the Institute.

When the interlaboratory standard deviation is plotted against the grand mean of each set (Fig. 2), the standard deviation increases more rapidly

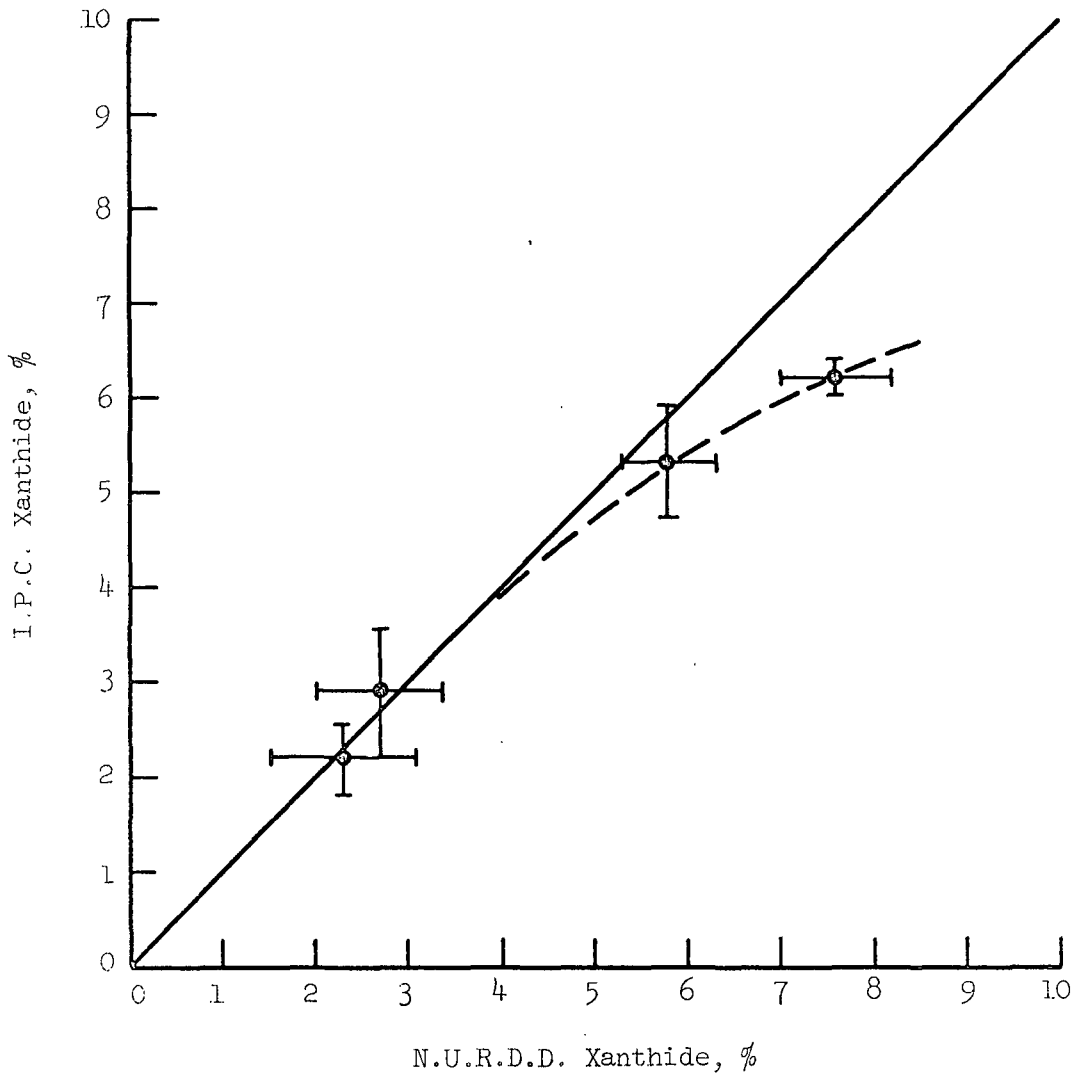


Figure 1. Xanthide Content I.P.C. Data vs. N.U.R.D.D. Data; 2s Limits (Based on Table II)

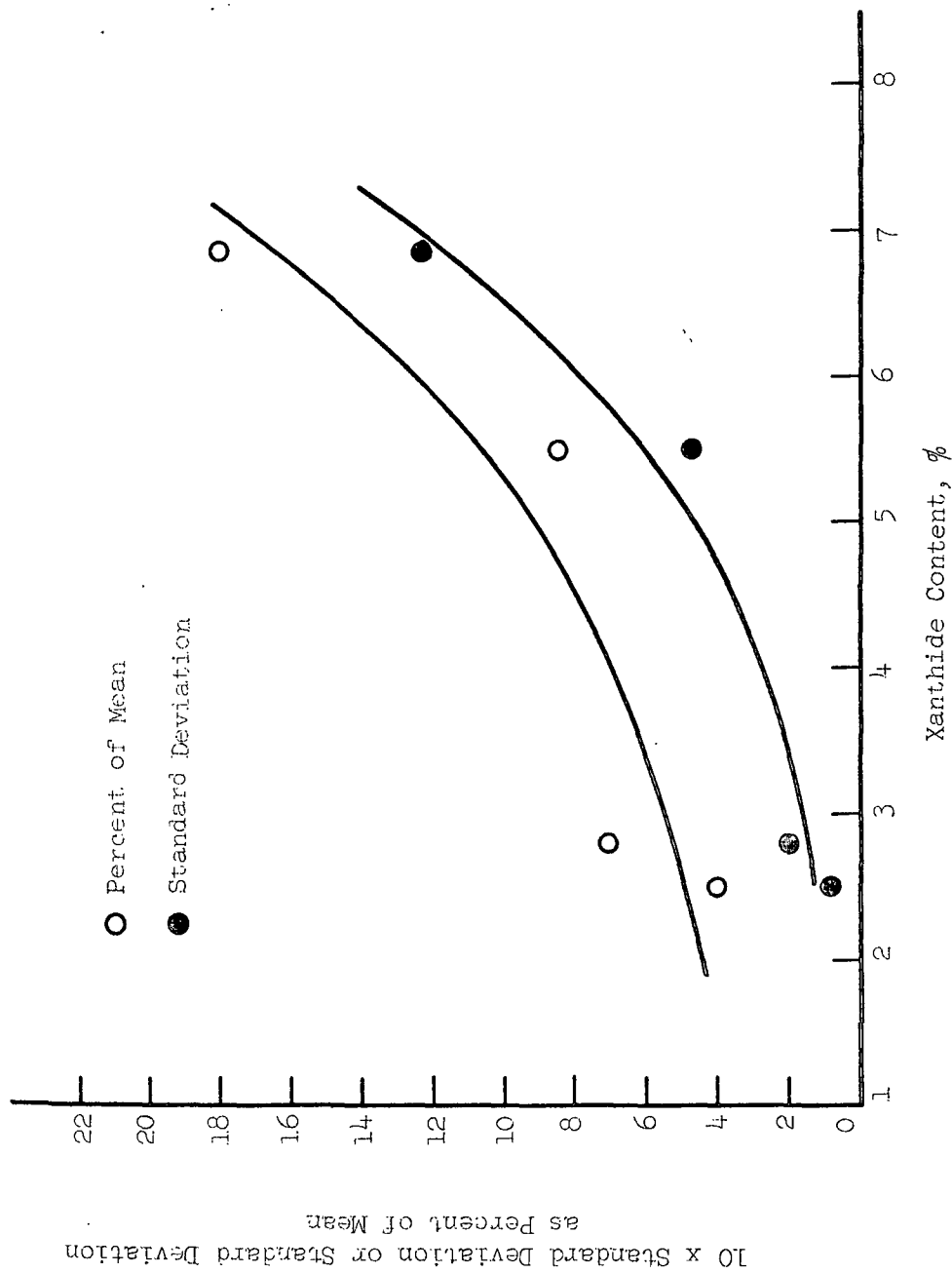


Figure 2. Interlaboratory Deviation as a Function of Xanthide Content

than the grand mean. If the standard deviation is expressed as percent of the mean and plotted against the mean (Fig. 2), a similar curve is obtained. Inter-laboratory agreement deteriorates as the xanthide content increases. This argues against the size of the blank determination being a critical factor. In general, precision, as a percent of the mean, decreases as the value of the sample and blank determinations converge.

When considering the Institute modifications of the procedure, less than optimum conditions for the alkaline steep and acid hydrolysis may be contributing to underdetermination of the xanthide content. Since these conditions have not been examined, it is recommended that such an evaluation be undertaken.

#### EFFECT OF BLANK UPON THE DETERMINATION

The quantity of hypochlorite in relation to the fiber present varies with the xanthate concentration at the time cross-linking is undertaken. Two controls were prepared for this experiment which correspond to the two intermediate hypochlorite-to-fiber ratios (Tables I and II). The values of the blank determination for the xanthide analysis differ by 0.39% glucan or about 6% of the lower value. The blank was lower for the higher level of hypochlorite. Since the difference between means of the blanks is about one standard deviation for the samples, either blank leads to the same general conclusions revealed in the preceding section.

#### INDIRECT ASSESSMENT OF RETENTION BY PHYSICAL PROPERTIES OF HANDSHEETS

The handsheets not used for xanthide analysis were subjected to physical tests as an indirect means of assessing starch xanthide content. These

tests were carried out at 50% relative humidity and 73°F. according to accepted procedures (see Report Three). The results of the tests are shown in Table IV.

The test responses should vary with the amount of starch xanthide retained in the handsheet. If the xanthide analysis is in error, that point should give a poor fit to a curve relating the physical property to xanthide content.

Figures 3 to 6 relate bursting strength, Instron tensile strength, apparent density, and opacity to the xanthide content as determined in both laboratories.

The figures for burst and tensile strengths suggest the point corresponding to Set II may be high in the case of the data from N.U.R.D.D. However, there is no easy distinction to be made from the plots of density and opacity.

It does appear that there are no great differences in the properties of the xanthide actually retained in spite of the rather large range of the cross-linking correlations.



TABLE IV  
PHYSICAL PROPERTIES OF THE HANDSHEETS

Set No.	Fiber Consistency, %	Xanthate on Water, %	Added on Fiber, %	Xanthide in Sheet, N.U.R.D.D., I.P.C., %	Basis Weight, lb. $\frac{c}{c}$	Apparent Density, lb./mil	Instron Tensile, lb./in.	Burst, pt./100 lb.	Opacity, %
I	1.5	0	0	--	44.1	(1/5)	(5)	(10)	(5)
II	1.5	0.25	16.6	7.6	44.5	10.3	30.8	156	60.2
III	5.0	0.21	4.2	2.7	45.5	9.7	24.0	125	69.5
IV	1.5	0.75	50.0	5.8	44.9	10.2	30.9	154	62.2
V	5.0	0.62	12.5	2.3	43.4	9.4	25.2	132	68.5
VI	5.0	0	0	--	46.0	9.4	20.3	98	72.0

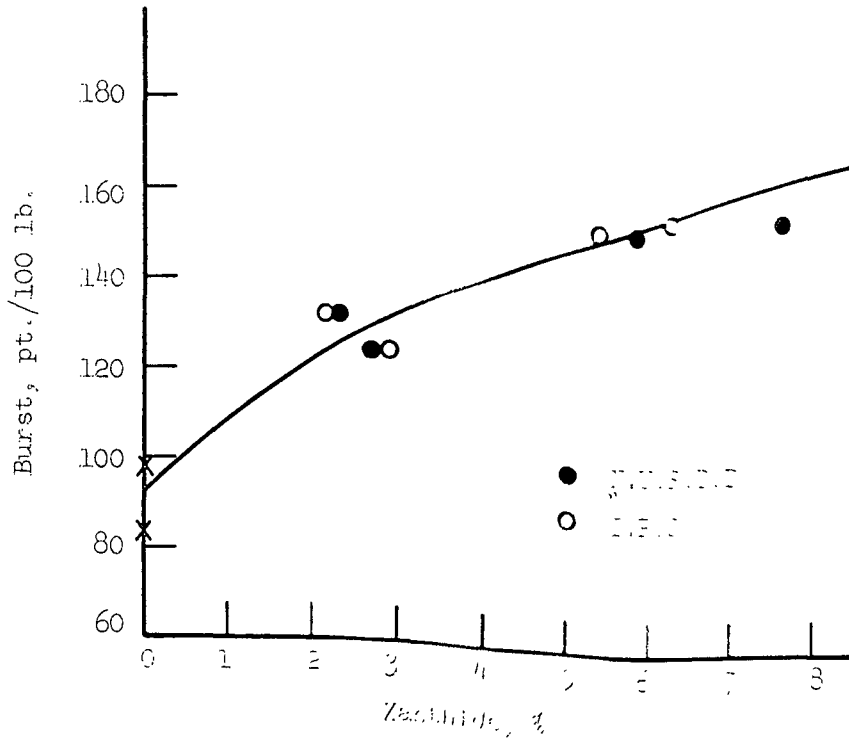


Figure 3. Burst vs. Xanthide Content

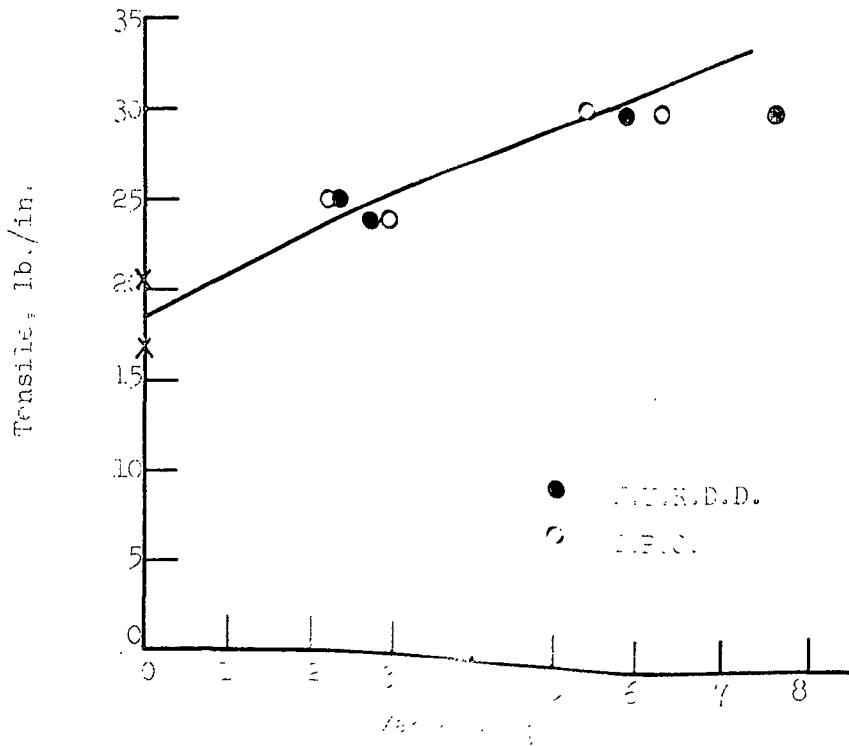


Figure 4. Tensile vs. Xanthide Content

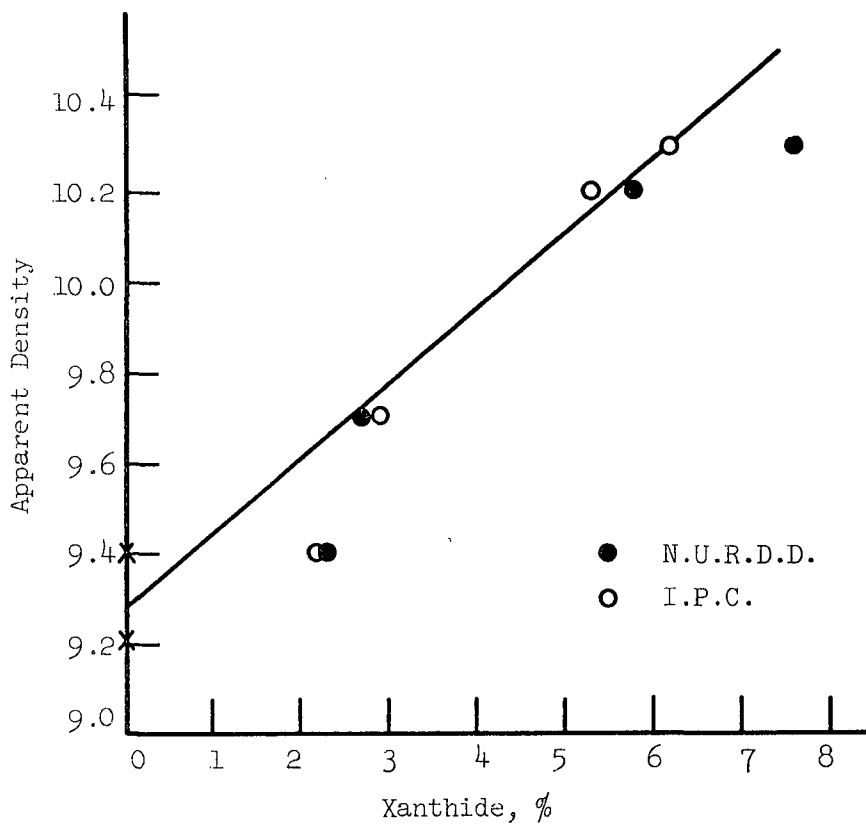


Figure 5. Apparent Density vs. Xanthide Content

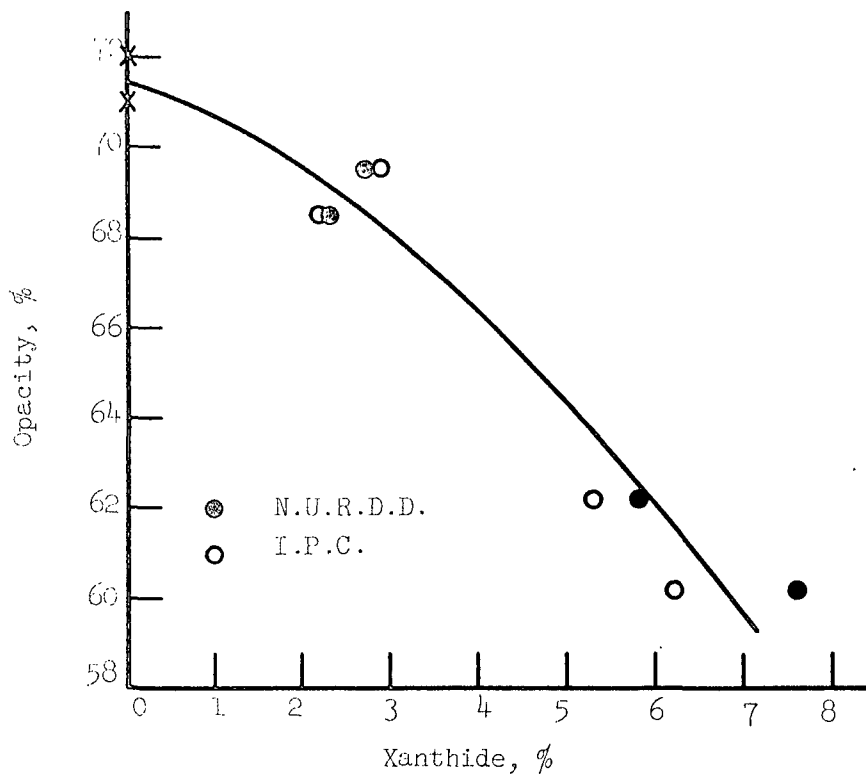


Figure 6. Opacity vs. Xanthide Content

## EFFECTS OF CROSS-LINKING CONDITIONS UPON RETENTION EFFICIENCY

### INTRODUCTION

The oxidation of starch xanthate to starch xanthide appears to fit the reaction scheme proposed for disulfide displacement reactions discussed in reviews by Pryor (3) and Foss (4). It is a two-step nucleophilic reaction. If this is true, then the concentration of the starch xanthate in the aqueous phase of the stock system is an important factor. Thus:

$$-\frac{d[\text{xanthate}]}{dt} = k [\text{xanthate}]^2 [\text{ClOH}].$$

In addition, dexanthation reactions can be proposed which involve  $\text{ClO}^-$  or  $\text{HO}^-$  ions. Following dexanthation, eight hypochlorite ions would be consumed in oxidizing the two sulfur atoms formerly present in one xanthate group to sulfate ions. The extent to which this series of reactions occurs would thus be dependent upon the concentration of hypochlorite ions and the starch xanthate concentration.

By experience, a pH of 5.5 has been established as one favorable for cross-linking starch xanthate. Ionization of hypochlorous acid is thereby suppressed so that the ~~reactive heating~~ <sup>reaction leading</sup> to starch xanthide is favored over dexanthation. <sup>corr. 10-12-66 S.E. Paulsen</sup> The desirability of preventing elevation of the pH during the reaction is also understandable.

At this point we do not know whether the rates of the chemical reactions involved in the oxidation of starch xanthate or the rates of physical sorption of the starch xanthide formed by oxidation control xanthide retention in paper. However, the concentration of starch xanthate in the aqueous phase in either case can be an important variable if retention is not controlled by the number of receptive sites on the fiber.

This experiment is designed to detect the influence of the starch xanthate concentration upon starch xanthide retention. If there is relatively little effect, the amount of starch xanthide retained should be a function of the amount of starch xanthate added with respect to the fiber. If starch xanthate concentration is important, then retention efficiency should be a function of this variable.

#### DATA

The data representing the xanthide content of the handsheets were reexpressed as grams xanthide per 100 grams fiber in order to relate the amount of xanthide retained to the xanthate added (Table V).

#### DISCUSSION

A single curved line connects the data points when retention efficiency is plotted as a function of xanthate concentration (Fig. 7). However, two lines are required when the same factor is plotted against the xanthate-to-fiber ratio (Fig. 8). Here retention appears to be a function of the fiber concentration as well as the xanthate-to-fiber ratio. This is reasonable if the xanthate concentration is the significant factor since it changes as the xanthate-to-fiber ratio is varied while the stock consistency remains constant.

The shape of the curve in Fig. 7 suggests an exponential function. Plotting the logarithm of the retention efficiency against the xanthate concentration (Fig. 9) yields a straight line passing through 100% retention efficiency at zero xanthate concentration.

TABLE V  
 ESTIMATION OF RETENTION EFFICIENCY

Laboratory	Set No.	Xanthate Level g./100 ml.	Fiber Consistency, %	Xanthide Content g./100 g. sheet	Xanthide Content g./100 g. fiber	Retention Efficiency %	Retention Efficiency Mean	Std. Dev.
N.U.R.D.D.	II	0.25	1.5	7.60	8.22	49.3	49.1	2.0
					7.31	47.3		
					7.79	50.7		
	III	0.21	5.0	2.45	60.2	66.0	8.7	
				2.55	62.8			
IV	0.75	50.00	1.5	3.03	74.9	12.3	0.6	
				5.55	11.8			
V	0.62	12.50	5.0	5.99	12.7	18.9	3.4	
				5.83	12.4			
				1.95	15.9			
I.P.C.	0.25	16.67	1.5	2.33	19.1	71.1	9.0	
				2.63	21.6			
				6.13	39.2			
III	0.21	4.17	5.0	6.09	38.9	11.1	0.7	
				6.24	39.9			
				2.64	65.0			
IV	0.75	50.00	1.5	3.24	80.3	18.0	1.6	
				2.83	67.9			
V	0.62	12.50	5.0	5.04	10.6	41.7	1.6	
				5.57	11.8			
I.P.C. Blank	II			5.16	10.9	80.8	13.9	
				2.07	16.9			
Set VI	III			2.40	19.7	21.1	21.1	
				2.14	17.5			
IV								
V								

$$^a \frac{\text{Xanthide}}{100 \text{ g. Fiber}} \times \frac{100 \text{ g. Fiber}}{\text{Xanthate}}$$

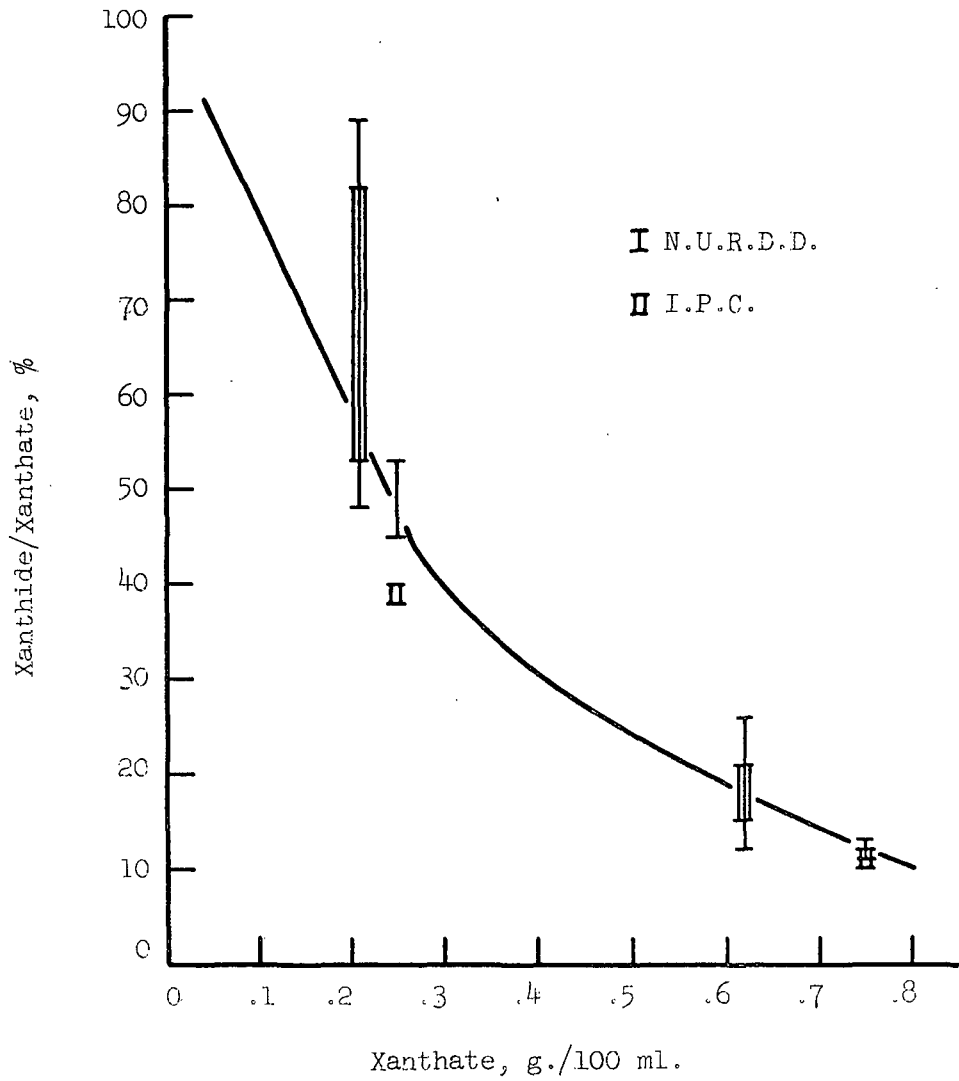


Figure 7. 95% Confidence Range of Retention Efficiency vs. Xanthate Concentration

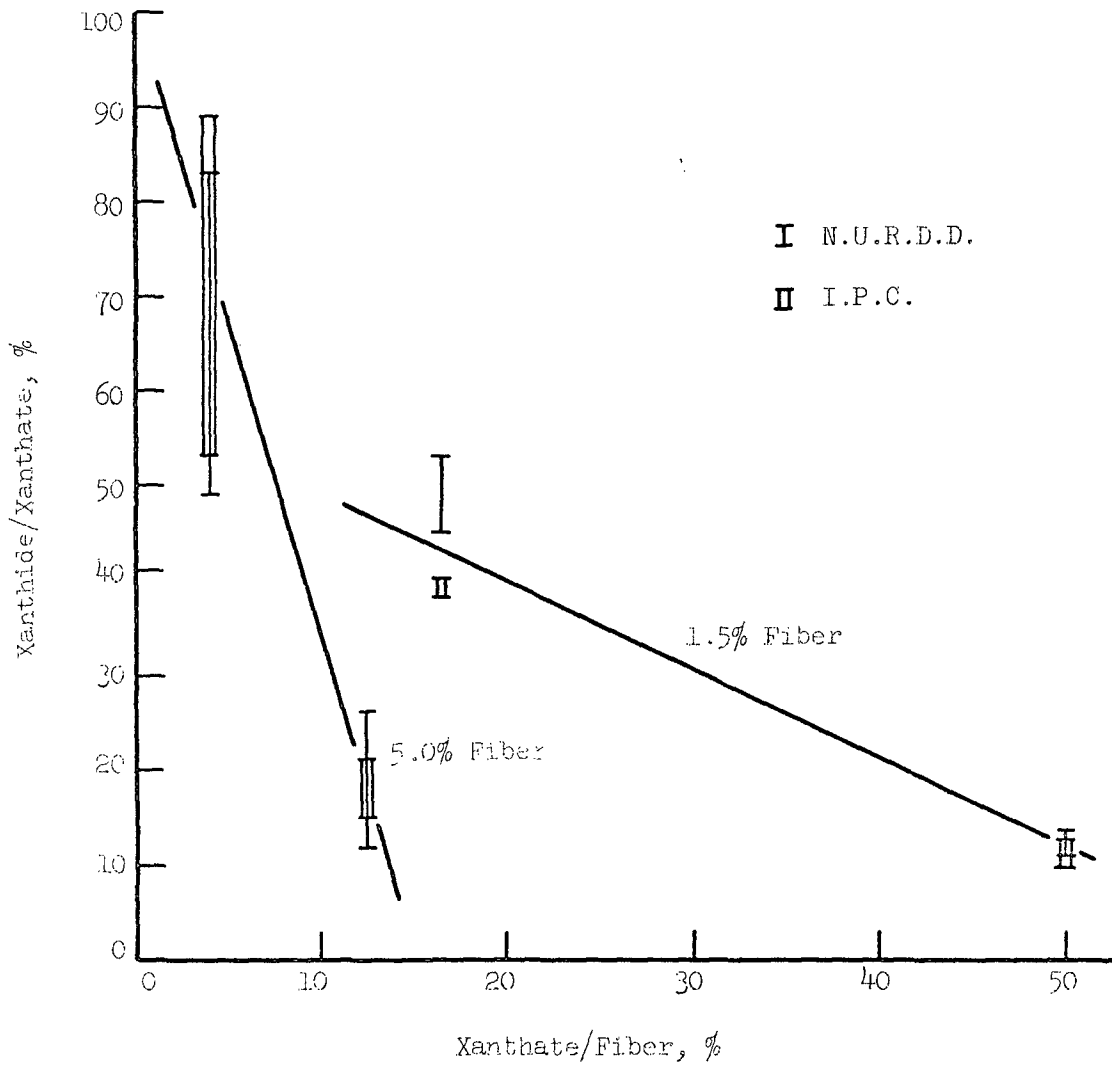


Figure 8. 95% Confidence Range of Retention Efficiency vs. Xanthate-to-Fiber Ratio



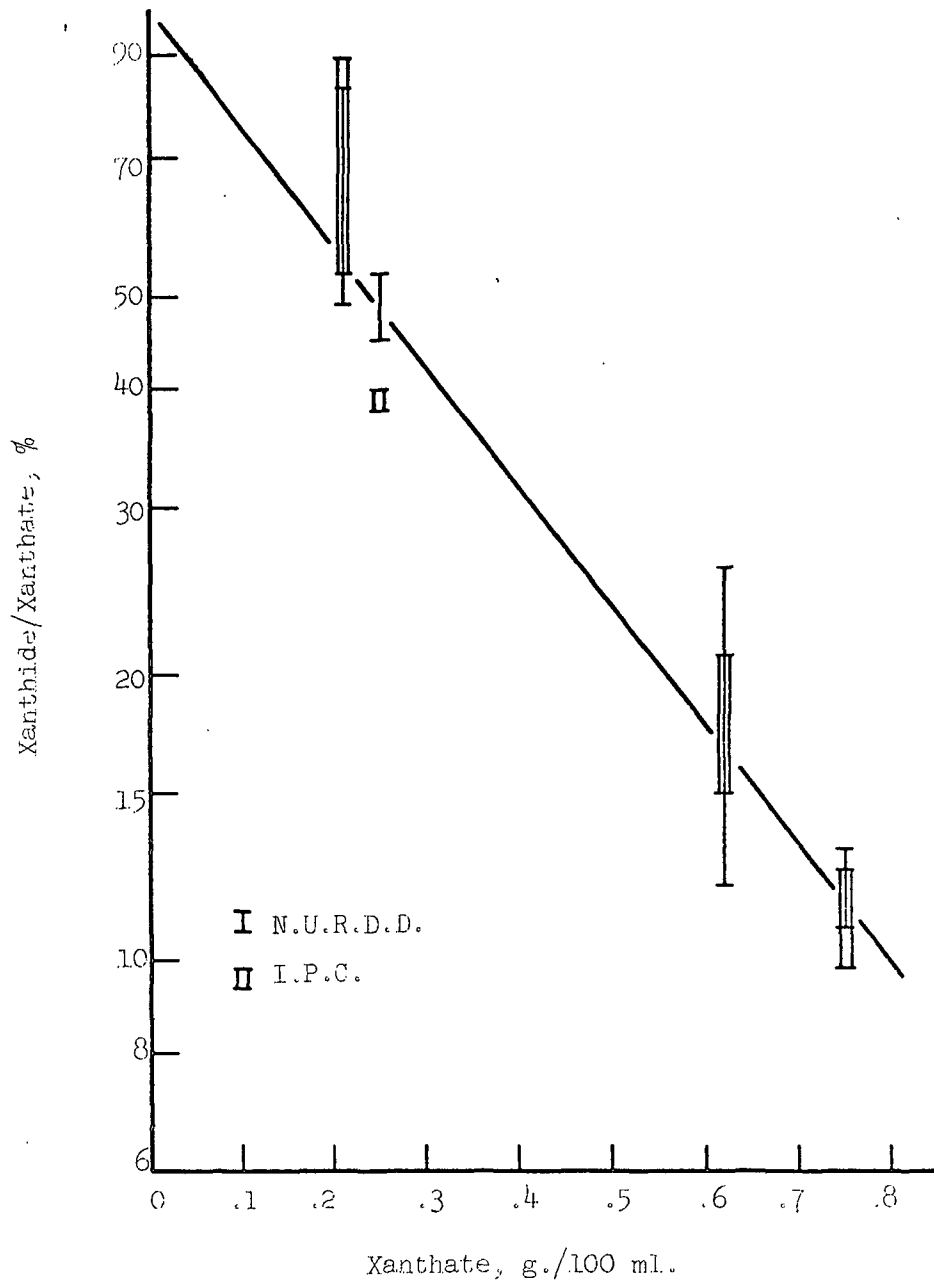


Figure 9. 95% Confidence Range of Retention Efficiency vs. Xanthate Concentration

Replotting Fig. 8 on semilogarithmic paper again produces two relations showing retention efficiency to be a function of fiber consistency and the starch-to-fiber ratio (Fig. 10).

The evidence supports the conclusions that the xanthate concentration in the aqueous phase of the stock system controls retention efficiency more than fiber consistency or the amount of xanthate present in respect to the

A more fundamental relationship would be for the retention efficiency to be a linear function of the logarithms of the xanthate concentration. The data have been plotted in this fashion in Fig. 11. A straight line fits this representation of the data as well as it does the plot in Fig. 9. One advantage is the prediction of 100% retention at a finite xanthate concentration.

The negative slope of the lines in Fig. 9 and 11 is not in keeping with the idea that intermolecular cross-linking favors polymer sorption over intramolecular cross-linking. If this were the controlling factor, the slope would be positive.

It is interesting to note that the data point derived from the I.P.C. determination of starch xanthide in Set II does not fit on the curves shown in Figs. 7 through 11. This contrasts with the observation made earlier that the burst and tensile strength of the handsheets favor the validity of the data for Set II over those from N.U.R.D.D.

#### RELATIONSHIP OF IONIC STRENGTH

The conclusion that the concentration of starch xanthate controls retention efficiency must be tempered by recognizing that the ionic strength

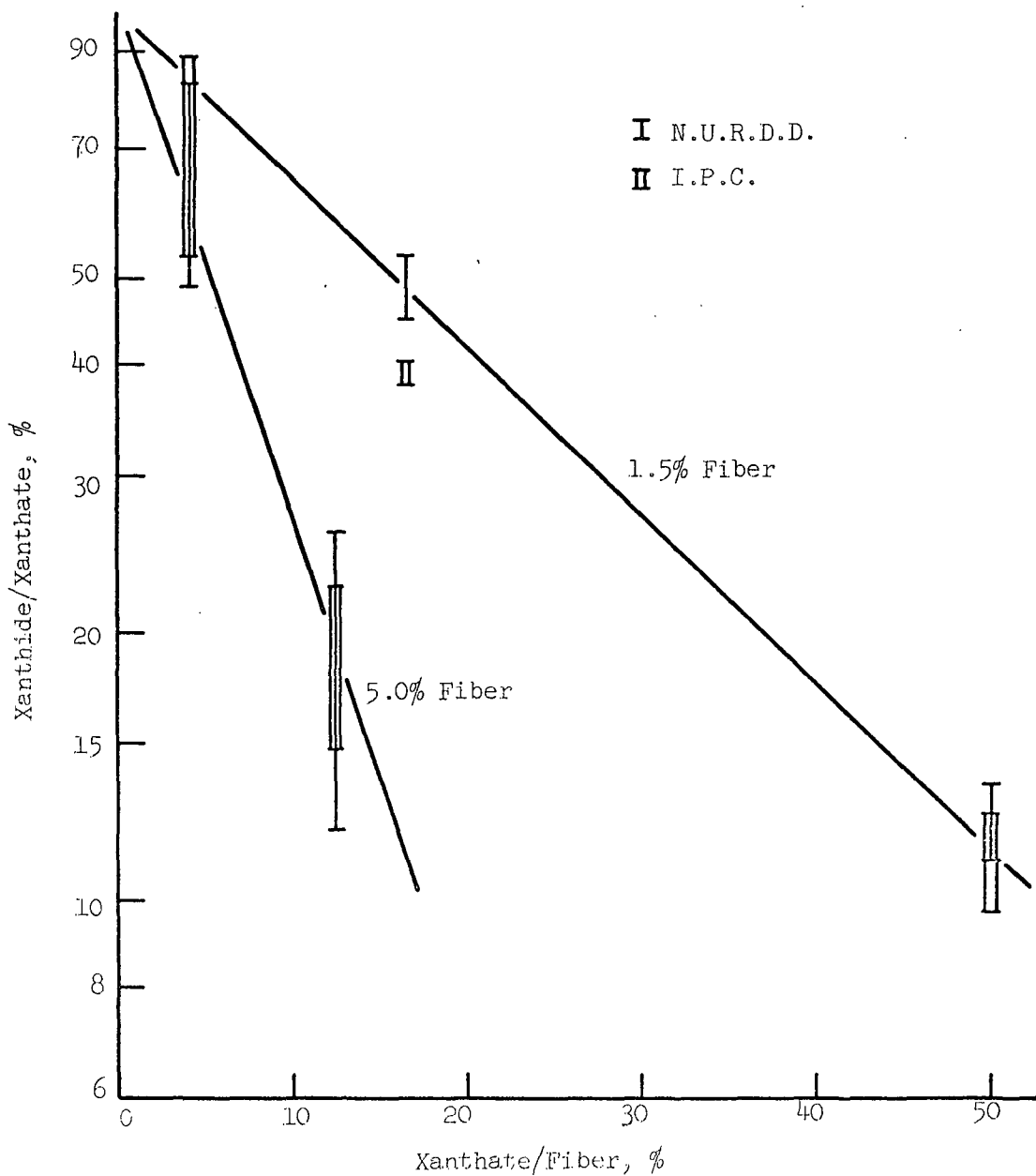


Figure 10. 95% Confidence Range of Retention Efficiency vs. Xanthate-to-Fiber Ratio

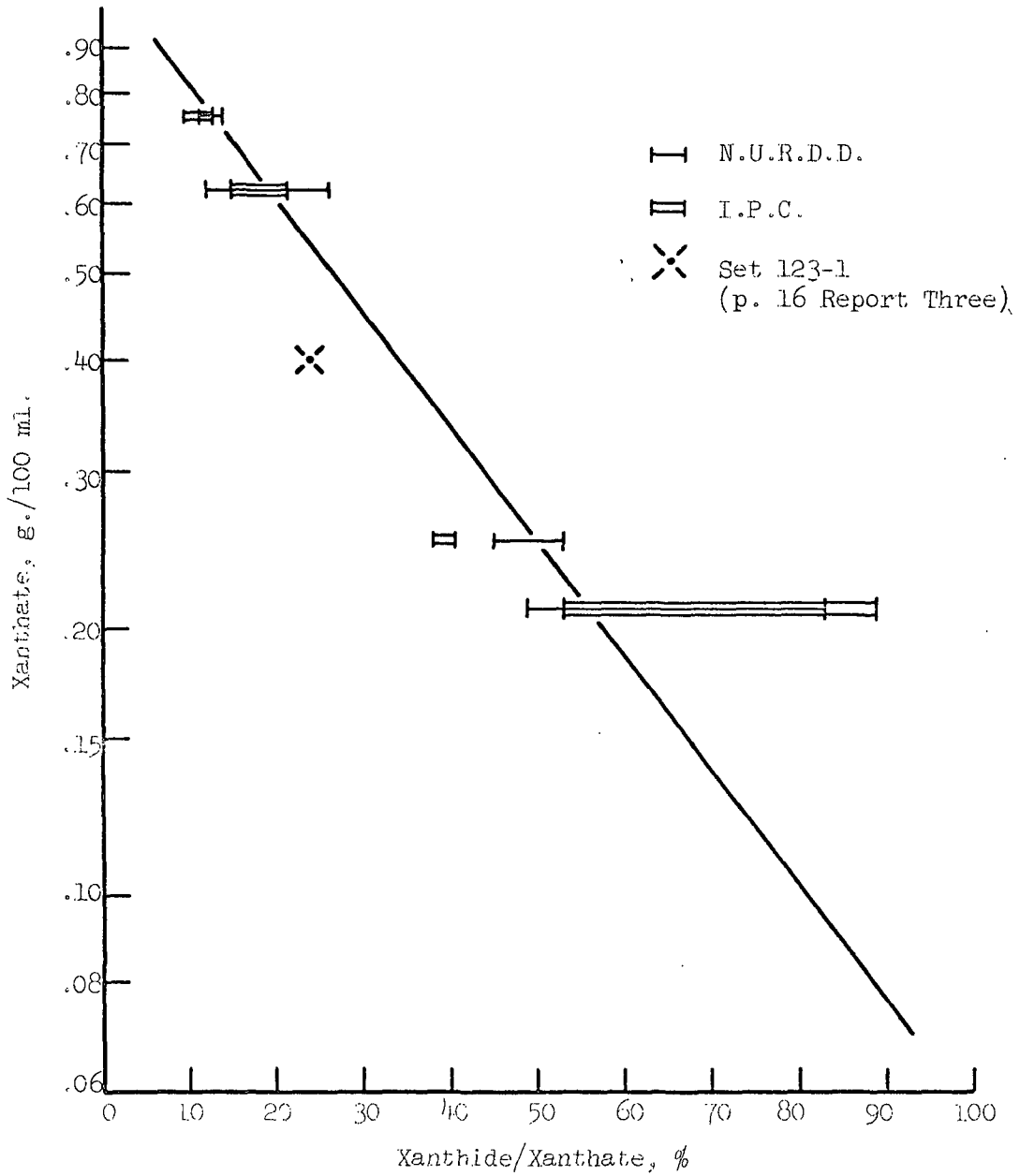


Figure 11. Xanthate Concentration vs. 95% Confidence Range of Retention Efficiency

of the system varies directly with the xanthate concentration. That is, the salts from neutralizing excess sodium hydroxide and xanthation by-products plus the salts derived from the sodium hypochlorite added to effect cross-linking can make a significant contribution to the ionic strength. In this experiment 2 milliliters of approximately 5.5% sodium hypochlorite were used per gram of starch in the starch xanthate. This is about equivalent to 0.0031 mole of sodium chloride since each mole of sodium hypochlorite is accompanied by one mole of sodium chloride and hypochlorite becomes chloride in the cross-linking reaction. Added to this is about 0.0031 mole of sodium hydroxide used in the xanthation reaction or a total of 0.0062 mole of monovalent salts (if acetic or hydrochloric acid is used to adjust the pH to 5.5) per gram of starch in the starch xanthate. This relationship is illustrated in Fig. 12.

It must be emphasized that the data obtained in this experiment do not distinguish between the effects of ionic strength and xanthate concentration. It is possible that ionic strength of the system at the time the cross-linking reaction occurs controls xanthide retention efficiency and the xanthate concentration is not important. Further work is needed to clarify this matter.

#### COMMENTS ON THE ROLE OF FIBER CONSISTENCY

In practical situations it is most convenient to use a constant fiber consistency and to vary the xanthate-to-fiber ratio in evaluating the effects of starch xanthide upon paper products. This means the starch xanthate concentration in the aqueous phase of the fiber suspension varies throughout the evaluation as shown in Fig. 13. The lowest fiber consistency possible for a given product would be predicted to be the optimum cross-linking condition for starch xanthide retention. On a paper machine, this would be after dilution of the stock to headbox consistencies.

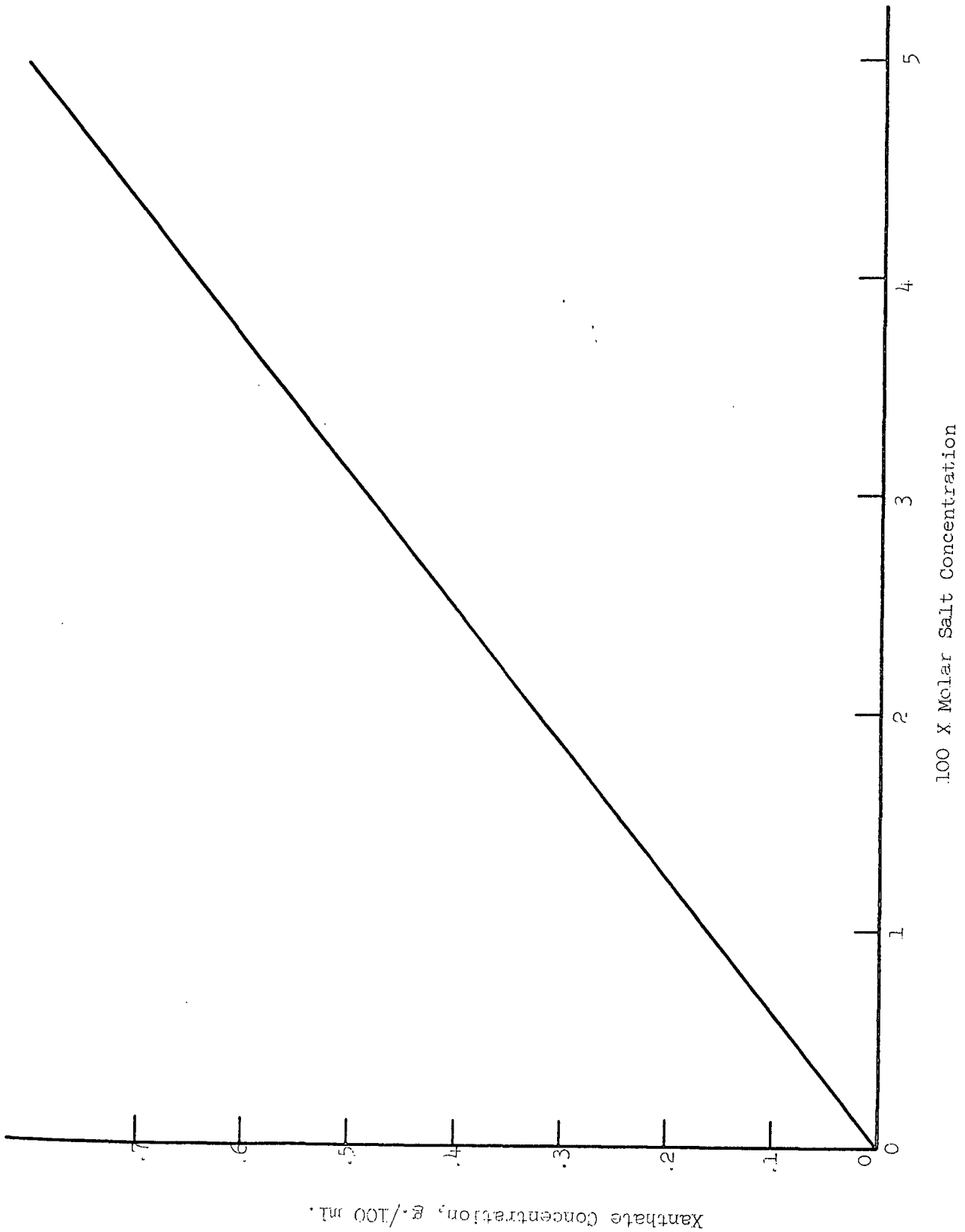
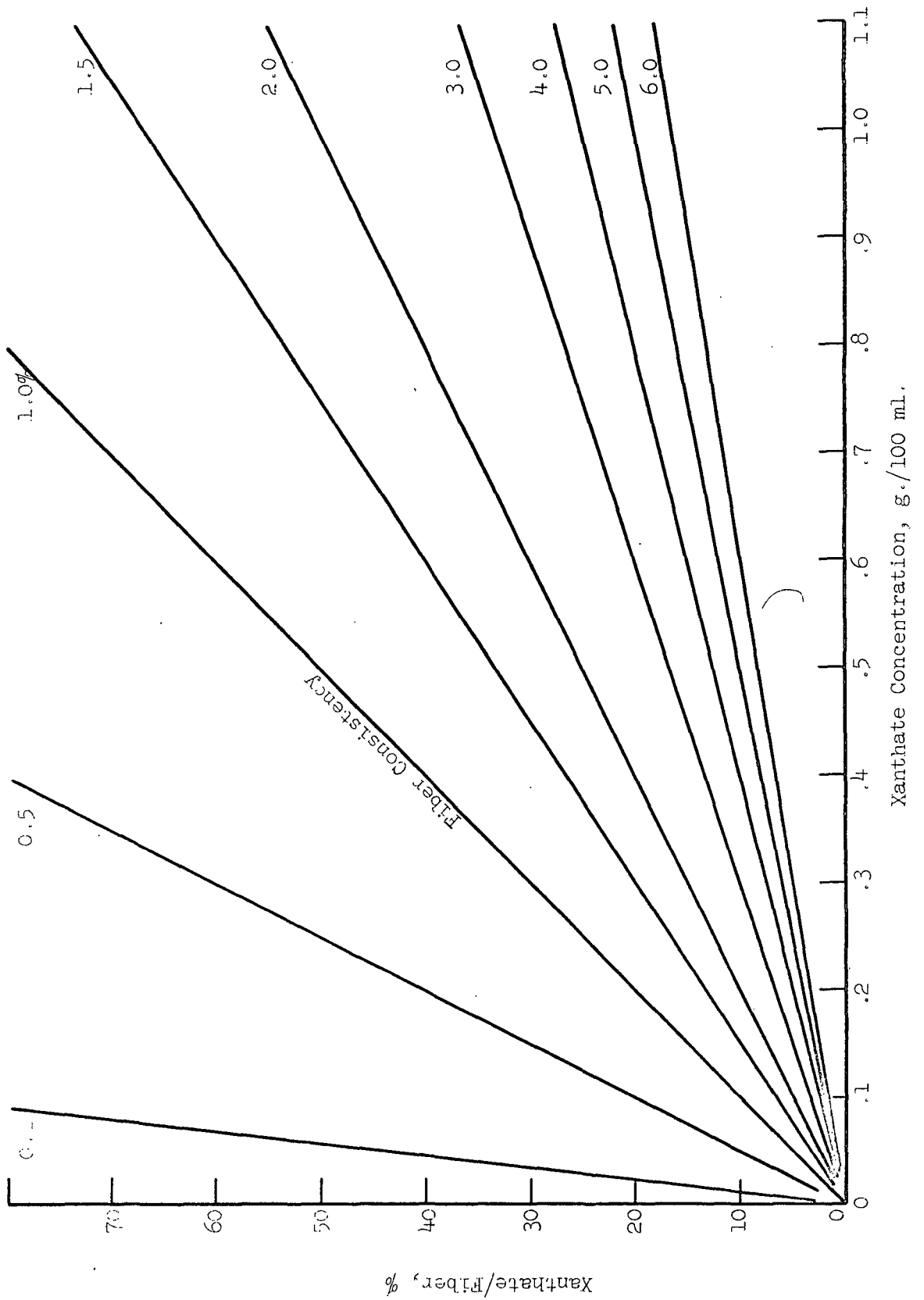


Figure 12. Xanthate Concentration vs. Salt Concentration During Cross-Linking



EFFECT OF BASIS WEIGHT UPON XANTHIDE RETENTION

The high consistency for Sets III and V which was required by the design of the experiment, made it necessary to use much more fiber than was required to make a set of eight 2.5-gram handsheets. Consequently, very little effort was required to add several 5.0-gram handsheets to the sheet-making schedule.

Doubling the sheet weight improves retention efficiency (Table VI). This suggests that at least part of the starch xanthide is retained by filtration as well as by sorption mechanisms.

TABLE VI

XANTHIDE RETENTION IN HEAVIER HANDSHEETS

Set No.	I.P.C. Data					
	Xanthate Added g./100 g. fiber	Handsheet Weight, g.	Xanthide Content g./100 g. sheet	Std. Dev.	Xanthide g./100 g. fiber	Retention Efficiency
III	4.17	2.5	2.90	0.34	2.99	71.1
		5.0	3.67	0.35	3.81	91.6
V	12.50	2.5	2.20	0.20	2.25	18.0
		5.0	3.85	0.29	4.00	32.0



## REVIEW OF RESULTS COVERED IN REPORT THREE

### RETENTION AS A FUNCTION OF XANTHATE CONCENTRATION

If we assume the xanthide analyses covered in Report Three are reasonably accurate, we find that the retention efficiency is not dependent upon the xanthate concentration in the same way it is in the work covered in this report (Fig. 14, based on Table II, Report Three). However, it must be pointed out that we are comparing cross-linking in the presence of potassium iodide (Report Three) with cross-linking using about twice as much hypochlorite and in the absence of potassium iodide (this report). There have been several clues indicating that potassium iodide takes part in the cross-linking reaction (see below and page 20-1, Report Three). Consequently, we must separate the two cross-linking systems until we have more information.

Keeping this in mind, Set 123-1 reported on page 16 of Report Three corresponds to the cross-linking conditions used for the experiments described in the current report. This data point is shown in Fig. 11 and is not far from the straight line.

### RETENTION AS A FUNCTION OF REAGENT pH

The effect of adjusting the pH of the hypochlorite solution used to cross-link starch xanthate was studied in the third report. Varying reagent pH from 8.5 to 4 had no effect upon the handsheet properties or upon the amount of reagent needed to produce the blue end-point color in the presence of potassium iodide. There was a trend toward higher xanthide content as the pH dropped. The xanthide content has been converted to retention efficiency and plotted against the pH of reagent solutions in Fig. 15 (based on Table V, p. 17, Report Three).

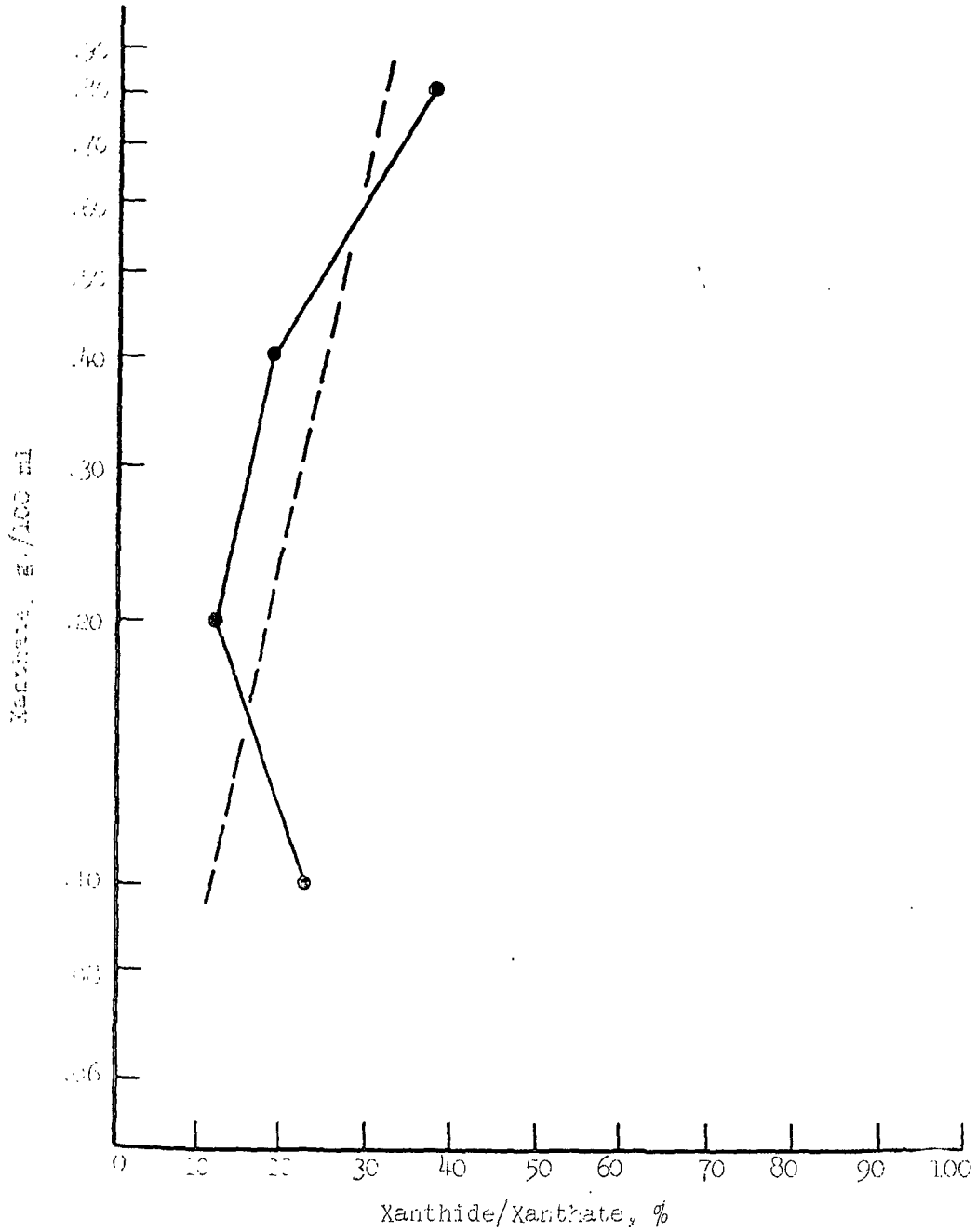


Figure 14. Xanthate Concentration vs. Xanthide Retention Efficiency  
Table II, Report Three

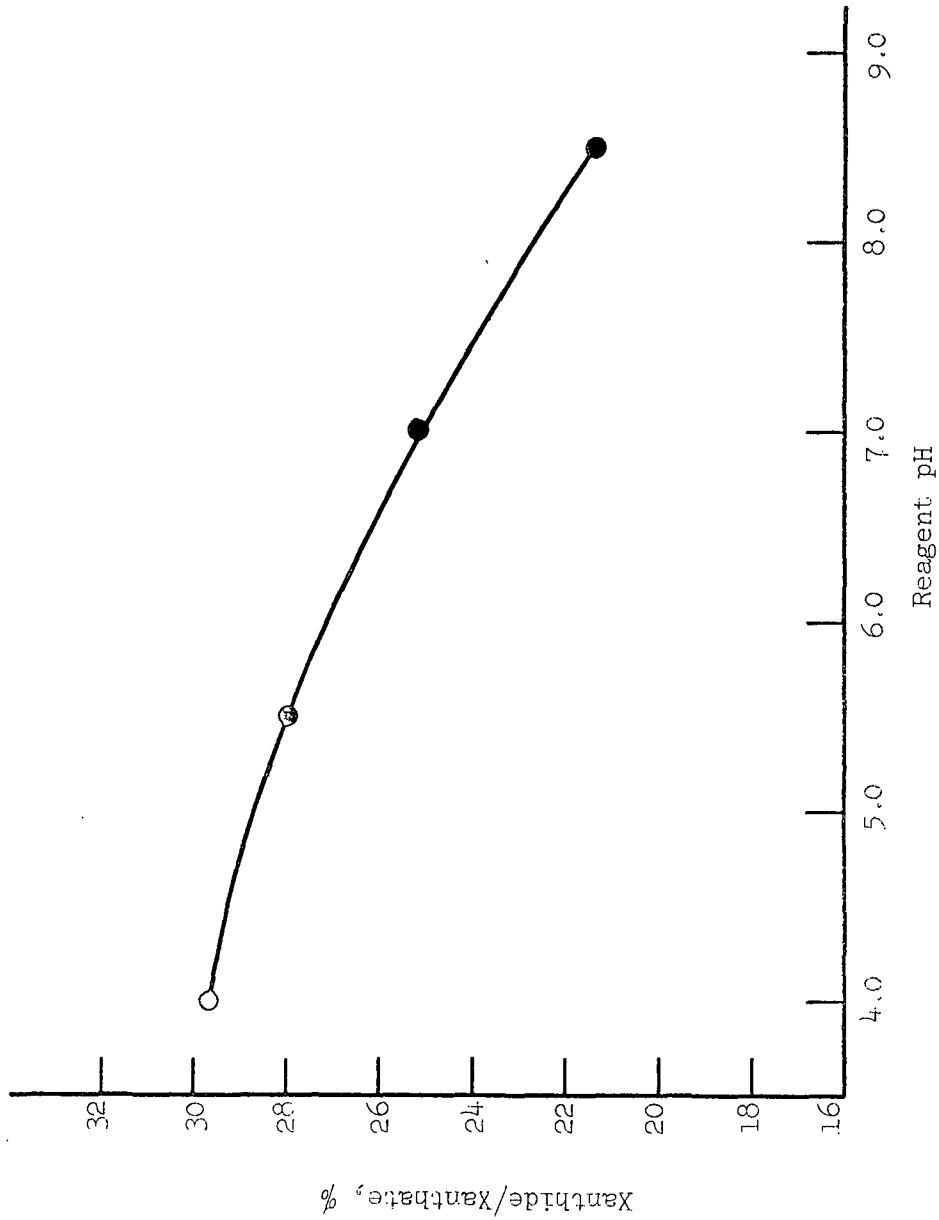


Figure 15. Retention Efficiency as of Function of Reagent pH (Table V, Report Three)

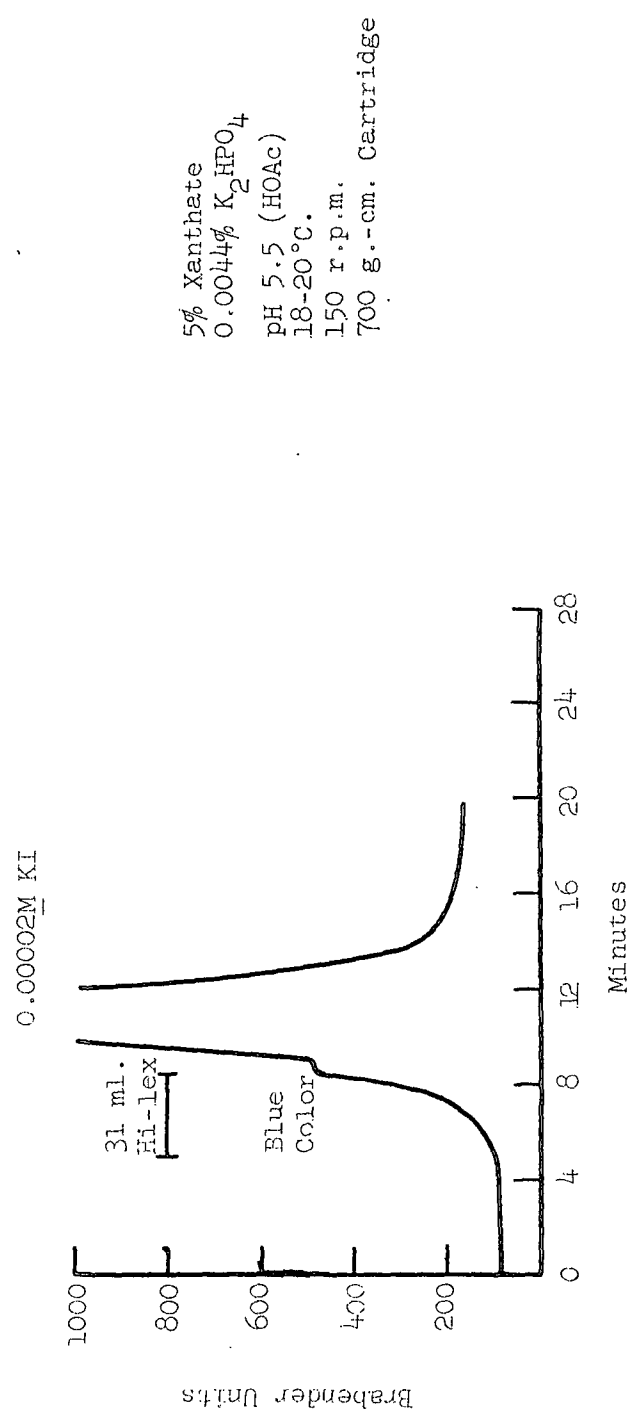
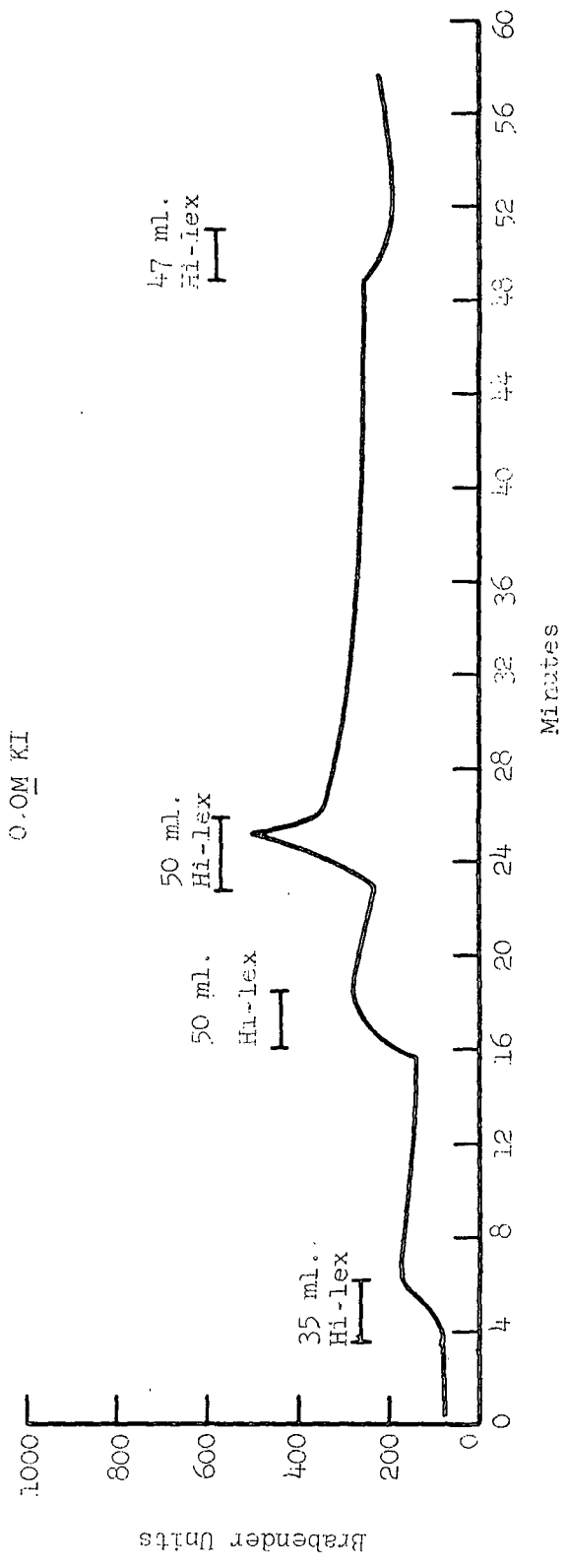
The trend toward higher retention efficiency at lower residual pH is consistent with the belief that hypochlorous acid is the active bleaching agent.

#### VISCOSITY CHANGES DURING CROSS-LINKING

Starch xanthate solutions were treated with sodium hypochlorite in a Brabender Corporation Amylograph Visco-graph operating at 150 r.p.m., 40 to 20°C., and using the 700 gram-centimeter sensitivity cartridge. The pH of the 5.0% xanthate solution (Run No. 442, C.14 D.E. was adjusted to 5.5 with acetic acid and dibasic potassium hydrogen phosphate 2.0 grams per 100 grams of xanthate solution) was added to prevent excursions above pH 7 while the sodium hypochlorite was being added. Undiluted Hi-lex (ca. 5% NaOCl) was the source of sodium hypochlorite.

The Brabender instrument provided us with a continuous record of viscosity changes produced by the cross-linking reaction at 20°C. in Run 15. Two experiments are illustrated: one without the potassium iodide, Run 15 with 10 ml. 1M potassium iodide.

Without potassium iodide, the viscosity increases as the concentration of hypochlorite and decreases as oxidation breaks down the starch. Finally, the viscosity increases and then decreases during the addition of hypochlorite as one would expect when the cross-linking is completed. Further additions of hypochlorite solution retards the viscosity of the system. About 120 milliliters of Hi-lex were required to complete the cross-linking of the xanthate by the viscosity criterion.



5% Xanthate  
0.0044%  $K_2HPO_4$   
pH 5.5 (HOAc)  
18-20°C.  
150 r.p.m.  
700 g.-cm. Cartridge

When 10 millimoles of potassium iodide were present, 31 milliliters of Hi-lex gave an intense blue color and the viscosity increased dramatically shortly after the color appeared. It was useless to add more hypochlorite to the xanthide coagulum.

These experiments demonstrate that potassium iodide is an active participant in the cross-linking reaction and greatly affects the amount of hypochlorite consumed. It is also shown that the rate of the cross-linking reaction can be evaluated in terms of viscosity as a function of time. An instrument capable of recording much lower viscosities is needed if the reaction is to be studied at the concentrations likely to be encountered in practical applications.

#### FUTURE WORK

Three lines of work are planned for the next report. They are:

1. Optimizing the conditions for determining starch xanthide and calibrating the method against known amounts of starch xanthide.
2. Evaluate the importance of ionic strength upon xanthide retention.
3. Attempt to determine the rate of xanthide absorption under one set of conditions.

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THE UNIVERSITY OF MICHIGAN

George E. Hambleton  
Research Scientist  
Chemical Engineering  
Department of Chemistry

Edward J. Mc...  
Research Scientist  
Chemical Engineering  
Department of Chemistry

John W. Swanson  
Research Scientist  
Chemical Engineering  
Department of Chemistry