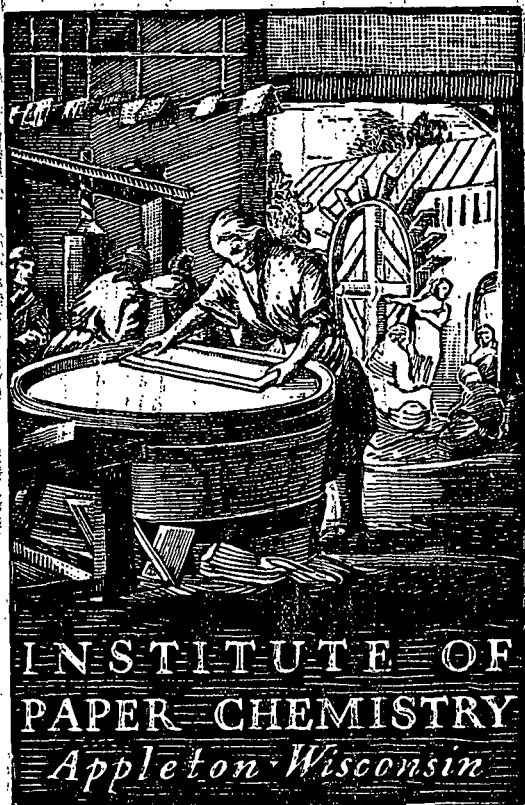




Institute of Paper Science and Technology
Central Files

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

II. EXTENDED STUDIES

Project 2580

Report Eleven

A Phase Report

to

**AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE**

March 25, 1968

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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

II. EXTENDED STUDIES

SUMMARY

This report summarizes the results of the work specified for Phase II in the plan of work included in the research contract for Project 2580. It deals mainly with the practical aspects of using ex situ starch xanthide in papermaking in contrast with the more theoretical orientation of Phase I.

The starch xanthide reaction leading to the cross-linking of starch xanthate has been examined in terms of the reactivity of sodium hypochlorite. On the basis of mechanisms proposed for disulfide bond formation from analogous compounds, it is deduced that starch xanthide is formed by consecutive second-order nucleophilic substitutions. Side reactions detrimental to cross-linking are minimized when the xanthate groups are the strongest nucleophile in the system. Acidification of sodium hypochlorite to pH 5.0-5.5 adequately suppress ionization of hypochlorous acid so that the positive halogen moiety is a suitable electrophilic site for the first nucleophilic displacement.

The stoichiometry of the cross-linking reaction is discussed and related to end-point reactions with potassium iodide. Addition of the cross-linking reagent until a small excess forms iodine (from potassium iodide thereby producing the blue color of the starch iodine complex) is related only to the first reaction step and is not related to the cross-linking step. This provides an explanation for the amount of reagent needed to reach the end point being affected by the addition rate. However, one is led to question whether the

xanthide bond is the explanation for the changed characteristics of starch xanthate treated with sodium hypochlorite.

On a practical basis, the product called starch xanthide is adequately prepared by using the blue end-point reaction for terminating reagent addition. This was established by comparing the performance of handsheets made with starch xanthides produced by using 50, 100, and 150% of the acidified sodium hypochlorite demanded by the end-point reaction.

In the studies for Phase I of this project, mutual repulsion of like electrokinetic charges on the xanthide and the fiber provided an explanation of the lack of xanthide sorption in the absence of alum. The extent and rate of absorption increase up to a maximum as the alum concentration increases.

On the basis of the laboratory studies described in this report, alum may not be used to neutralize the starch xanthate prior to cross-linking. Starch xanthide coagulates under these conditions before the end point is indicated. The strength enhancement in the handsheets is reduced in spite of improved retention efficiency. Transparent spots are also produced which further reduce the quality of the paper.

The fiber consistency has little effect upon the performance of ex situ starch xanthide in paper provided the alum concentration in the aqueous phase is maintained at a level consistent with the fiber characteristics. This level is from 2×10^{-4} to 2×10^{-3} molar for lightly beaten fibers. The xanthide should be added to the fiber suspension after the alum in order to obtain the maximum benefit from the xanthide.

Mixing conditions which improve blending of the starch xanthate and the cross-linking reagent allow the reagent to be added at a faster rate and improves xanthide retention and performance of paper made with xanthide-treated fibers. The amount of reagent required to produce the end-point reaction is greatly reduced.

The wet tensile strength of xanthide-containing handsheets improves as drying conditions become more drastic. Thus, air drying, drying on a steam drum, and drum drying followed by oven drying produce increasingly higher wet tensile strengths from handsheets prepared from a single fiber suspension treated with starch xanthide.

Xanthation by-products may be removed from acidified starch xanthate by bubbling nitrogen through the solution. By so doing, the cross-linking reagent consumption is reduced at low and at high mixing rates but the performance in paper is scarcely improved at low mixing rates. At high mixing rates during the cross-linking reaction, removal of the xanthation by-products lowers retention and, consequently, lowers the performance of the handsheets subjected to wet and dry tensile failure.

In comparison with fines-free pulp, whole pulp shows higher wet and dry tensile strength and better xanthide retention. This shows that the fiber fines in the handsheet preparations are not detrimental to the xanthide performance.

The linear relationship between an increasing xanthide content and the decreasing specific scattering coefficient indicates that the improved handsheet performance due to starch xanthide is brought about by increased bonded area rather than stronger fiber-to-fiber bonds or improved sheet formation.

Bleached and unbleached softwood kraft pulps, bleached hardwood kraft pulp, and unbleached softwood groundwood all show strength enhancement with xanthide treatment consistent with the characteristics of the fibers. An interaction between starch xanthide and the fines of softwood kraft pulps produces paper with an unexpected water repellency. Unbleached softwood kraft has its fluorescence size time increased from 9 to 35 seconds by the xanthide treatment. Whole bleached softwood kraft pulp has a size time of 4 seconds compared with instantaneous penetration of water with fines-free xanthide-treated paper and with the whole pulp itself. It is to be emphasized that the water repellency developed in the absence of rosin size.

The effect of the scale of preparing xanthide-containing paper is assessed by comparing: handsheets, paper formed on the Institute Continuous Web Former and at the cooperating agency on their production-scaled pilot machine. The response of the trial papers expressed as percent of the control papers most similar are for the papers made on the handsheet mold and the pilot machine. It appears that blending starch xanthide with the whole fiber for 15 minutes simulates continuous addition with recirculating white water on the pilot machine. The data for the continuous web former runs are lower than the other two sets of data. White water was not recirculated and the contact time was 5 minutes rather than 15 minutes before dilution to 0.05% running consistency. The web former runs do show that the delay in using ex situ starch xanthide in the laboratory does not change the performance of the paper in a detrimental way. It was shown in the report on Phase I that laboratory preparations retain their properties from 5 to 60 minutes after preparation.

INTRODUCTION

Research contract Number 12-14-100-8308(71), approved September 29, 1965, has been the basis of Project 2580 carried out by The Institute of Paper Chemistry in cooperation with the Agricultural Research Service of the United States Department of Agriculture. The purpose of the project is to expand the use of cereal products in papermaking by determining the factors governing sorption of starch xanthate and starch xanthide by wood fibers in dilute aqueous suspensions.

During the course of this investigation, the contract was amended on October 4, 1967 to conform with both the consequences of the work already completed and the interests of concurrent work being done by the cooperating agency. The basic change was to emphasize the study of forming starch xanthide separately from the fiber (ex situ) over the study of starch xanthide formed in the presence of the fiber (in situ). In this way the work done under this project was focussed upon those aspects most likely to be involved in the introduction of starch xanthide into commercial processes.

The contract contains a Plan of Work indicating the areas to be investigated. There are two phases designated as: I, Exploratory Studies, and II, Extended Studies. This report deals with Phase II and is principally concerned with the application of the information obtained from studying the sorption process. However, two sections placed in Phase II during the initial planning of the project were covered in the report on Phase I since they are either intimately involved in the sorption process or were involved in establishing the techniques for studying sorption. These areas deal with the effect of electrokinetic charge, and the effect of contact time. In order to simplify reviewing this report on Phase II for compliance with the contract, attention will be drawn to the appropriate sections of the preceding report.

The work covered in the report on Phase I has shown the sorption process to follow a physical sorption mechanism that is inhibited by mutual electrokinetic charge repulsion of xanthide and fiber. Alum can be used to overcome these effects. However, it is the aqueous concentration that is the controlling factor rather than the ratio of alum to fiber. For bleached softwood kraft fibers an alum concentration between 2×10^{-4} and 2×10^{-3} molar is usually sufficient to allow the maximum sorption rate. However, the minimum alum concentration needed to achieve this maximum sorption rate varies with the degree of fiber refining. As the refining level increases the minimum alum requirement increases. The higher alum demand is in addition to the effects of increased fiber surface area.

MATERIALS USED

STARCH XANTHATE

Starch xanthate was prepared by the Northern Utilization Research and Development Division of the A.R.S. by a continuous method (1). The product was diluted to about 10% starch, analyzed, and shipped in an insulated package by Air Express. The analytical results (concentration, D.S.) were phoned to the Institute and then sent with processing details by mail for a more permanent record. The xanthate was prepared with a D.S. near 0.12 (moles substituent per anhydroglucose unit).

WOOD FIBER

A quantity of Rayonier WBS-W bleached western softwood kraft pulp (Lot 3398) was set aside for this project. As needed, portions of the dry lap pulp were soaked overnight in deionized water and beaten to 700-ml. Schopper-Riegler freeness in a laboratory Valley beater in deionized water. The beaten fiber was flushed through a Bauer-McNett classifier with city tap water. Those fibers retained by the 12-, 20-, 65-, and 150-mesh screens were combined and then dewatered on a cloth-covered filter box. The classified fiber was washed several times with deionized water and pressed on a table-top Buchner funnel covered with dental dam. For greater ease in handling, the filter pad was broken up mechanically in a pulp breaker.

The fines-free, dewatered pulp (ca. 75% water) was stored in polyethylene bags in a cold room (34-38°F.) for at least three weeks so that its properties would be stabilized at the time of use. When needed for the laboratory work,

portions of the fiber were redispersed in a British disintegrator for 300 counts (2-1/2 minutes). Three other kinds of fiber were used in a specific comparison. These fibers are identified and the proportion is described in the appropriate section of this report.

ALUM

Baker's reagent grade $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, was dissolved in deionized water (10 g./100 ml. solution) and aged several weeks at room temperature before use.

20% ACETIC ACID

Reagent-grade glacial acetic acid was diluted with deionized water to 5 times the original volume; that is, for example, 100-ml. glacial acetic acid diluted to 500 ml. This solution was used to neutralize both the xanthate and sodium hypochlorite solutions and is referred to only as acetic acid.

SODIUM HYPOCHLORITE

A commercial laundry bleach, Hi-lex, was diluted 1 volume to 5 to give a nominal concentration of 1% sodium hypochlorite. The actual concentration of one sample of Hi-lex was 5.57% NaOCl.

DEIONIZED WATER

Deionized water was used in all phases of this work except where it is specifically stated that another water source was used. The water was obtained from a three-bed resin system (two single, one mixed) serviced by Culligan. The resistance ranged from 1 to 5 megohms, but usually was 1.5 to 2.0 megohms.

ANALYTICAL PROCEDURES

STARCH XANTHIDE

The basic procedure for analyzing the starch xanthide content of paper was developed at the Northern Utilization Research and Development Division of the A.R.S. (2). Some modifications were made to shorten analysis time and to use similar techniques already routine in our laboratories. The sequence of steps in the analysis, presented on pages 7 and 8 of Report Four, were used to obtain the data used in an interlaboratory comparison of results. It was concluded that the method was sufficiently in control to produce meaningful data over the expected range of xanthide levels.

The analytical procedure involves swelling the starch xanthide in hot alkali followed by acid hydrolysis to produce free sugars which are then determined by one of the standard methods for reducing power.

The basic procedure for xanthide analysis calls for treating the alkali-swollen sample for 2.5 hours in hot acid. The results of a study using different acid hydrolysis times showed there is no advantage in using more than one hour for this step. All subsequent analyses were done using one hour in a boiling water bath.

About 20% of the xanthide is not accounted for when the method was evaluated with ex situ starch xanthide. However, the results of the xanthide analysis of the paper samples given in this report do not contain a correction based on this observation. It was felt that there was not sufficient information about the effects of drying, of film thickness, or of particle size upon the penetration of the alkali and acid into the xanthide to assume that the conversion

factor would be the same for xanthide in paper. If it is assumed that the conversion factor is constant, then the data may be adjusted by multiplying by 1.28.

PHYSICAL TESTS ON HANDSHEETS

Certain physical tests were done on the handsheets. These tests are described in the TAPPI Standards and Suggested Methods manual. The only exception is that for Fluorescence Size Time (3).

STUDY OF THE USE OF SODIUM HYPOCHLORITE
AS A CROSS-LINKING AGENT

The relatively low cost of sodium hypochlorite makes it a desirable cross-linking agent for starch xanthide processes directed toward commercial applications in the paper industry. However, there are peculiarities about this oxidant which make its use uncertain unless its characteristics are understood. For example, sodium hypochlorite is used to determine total sulfur in cellulose xanthate (4). Therefore, conditions suitable for oxidizing sulfur compounds to sulfate ions would not be useful for obtaining the cross-linked product.

Over a pH range of 5.5 to 11.0 in the starch xanthate solution, the net effect of adding alkaline 1% sodium hypochlorite (pH 11.1-11.5) is to reduce the pH of the reaction mixture up to the point of complete reaction of the sulfur components. With each increment of hypochlorite, the pH is immediately elevated and then drops over several seconds. However, if the xanthate is added to the hypochlorite the pH decreases without temporal fluctuation. Figure 1 illustrates the pH changes occurring as pH 11 starch xanthate is added to acidified sodium hypochlorite. Stabilization due to the buffering capacity of acetic acid (pK_a 4.76) is also illustrated in Fig. 1 which compares acetic acid with hypochloric acid for establishing the pH level specified in the standard procedure for in situ starch xanthide (5).

The difference in the initial pH response when xanthate solution is added to hypochlorite (pH depressing) and when hypochlorite is added to the xanthate (pH elevating) indicated that the pH of the system probably was a strong factor in the cross-linking reaction mechanism. The reasons for specifying pH 5.5 in the standard procedure as well as the involvement of iodide ions under

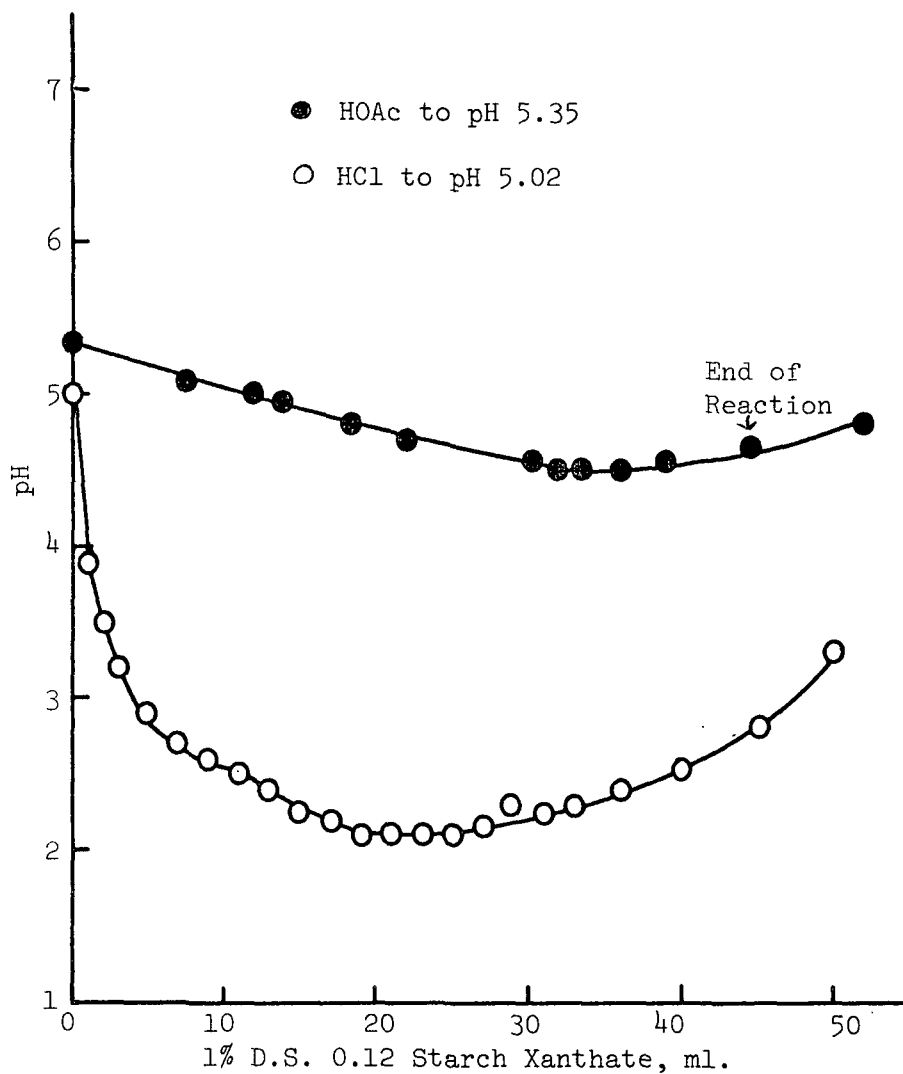
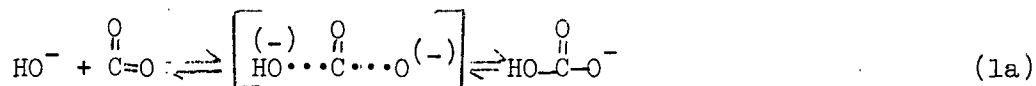


Figure 1. Titration of Acidified Sodium Hypochlorite with pH 11 Starch Xanthate Solution 50 ml. = 1.57 m.e.q. NaOCl

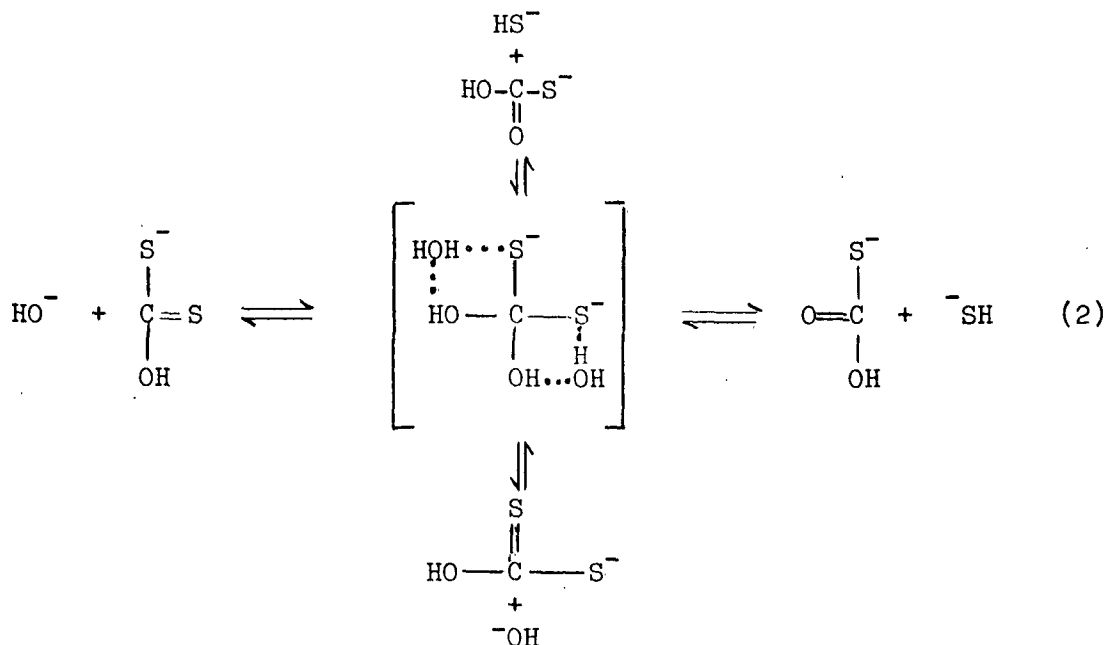
some conditions were probably dependent in some way upon the variation of the nature of the reactive species with the pH of the system.

The composition of the starch xanthation reaction mixture is complex. However, where one considers the starch as a contaminant in the sulfur-oxygen exchange reaction between carbon disulfide and carbon dioxide (6), the xanthation components become reasonable consequences of this idea. The unifying concept lies in the ortho carbonate transition state used by Ingram and Toms to describe the results of their studies (6). The aqueous solvent plays a major role in this mechanism as a stabilizer for the transition state.

The initial step in the sulfur-oxygen exchange is visualized as a nucleophilic attack at the carbon of carbon disulfide or carbon dioxide.



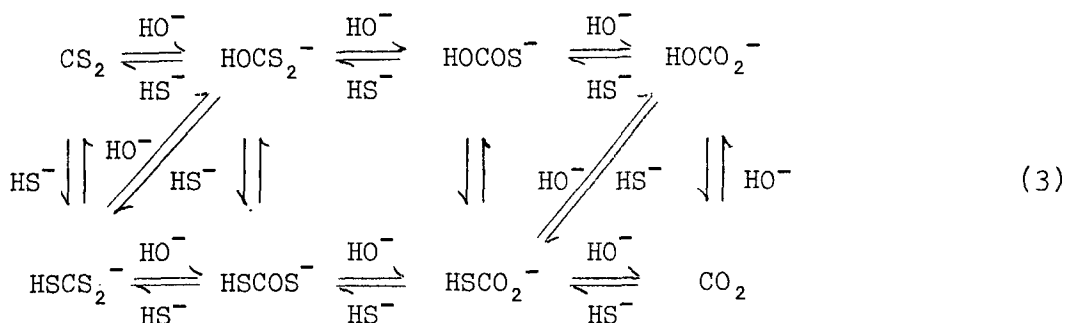
The ionization of the products is dependent upon the concentration of the nucleophile inasmuch as the proton on the products could be exchanged in a second step. In the xanthation medium, the hydroxyl ion concentration would favor these products being present as the carbonate forms rather than as bicarbonate. However, in the reaction sequences which follow [Equation (2)] the bicarbonate form will be shown with the understanding that the product could subsequently become fully ionized under xanthation conditions.



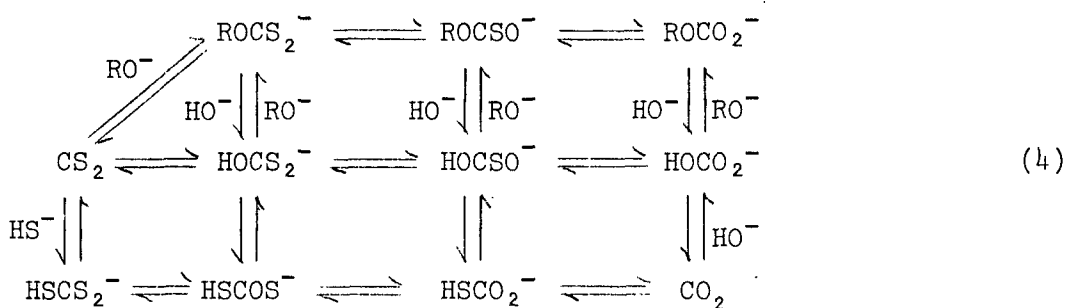
The second step involves the ortho carbonate structure in the transition state as illustrated in Equation (2). Two water molecules are shown associated with the ortho carbonate structure to illustrate the equivalency of ionization throughout the structure. The orientation of making and breaking of the carbon bonds of the ortho carbonate intermediate has been indicated in Equation (2) in order that the consequences of decomposition of less symmetrical intermediates would be evident.

Since sulfur on carbon could be expected to be a little less likely to maintain a negative charge than oxygen on carbon, $\text{HO}-\overset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{O}^-$ is probably the favored ionized structure.

Equation (3) illustrates the steps in the sulfur-oxygen exchange expected on the basis of Equation (2):



When an ionized alcohol, such as starch in concentrated sodium hydroxide, is introduced, it participates in the sulfur exchange reaction in the same way as hydroxyl ions. This is illustrated in Equation (4).



While monothiocarbonate forms of xanthates have been shown (7) to exist it would be difficult to establish the presence of the sulfur-free monocarbonate ester. However, the presence of such an ester is very strongly indicated by this mechanism.

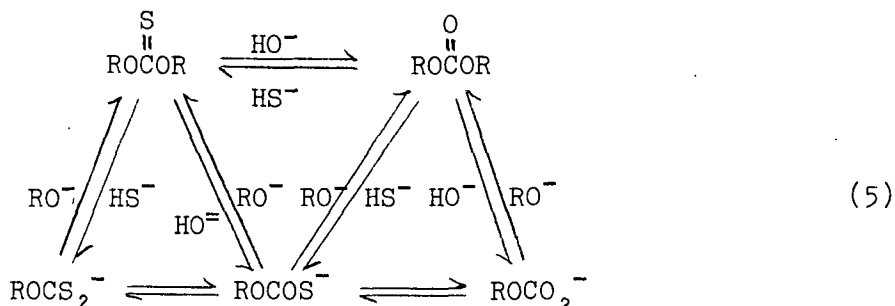
Since each step toward the left in Equation (4) is due to addition of hydrosulfide ions, it is evident that this by-product from the decomposition of carbon disulfide [Equation (2)] has a stabilizing effect upon the concentration of the xanthate derivative (starch dithiocarbonate).

By using the reaction scheme presented in Equation (4), the effects of removing ionized alcohol (dilution, partial neutralization) and hydrosulfide ions

(air oxidation or addition of NaOCl) are more easily deduced. Both disturbances favor dexanthation of the starch and the formation of new hydrosulfide ions. For this reason, the equilibrium concentration of starch xanthate must be stabilized by neutralizing the hydroxyl ions rapidly in order to obtain the maximum benefit of the xanthation reaction. Slowly adding alkaline sodium hypochlorite solutions to alkaline starch xanthate may form some xanthide linkages but the net effect is dexanthation and the consumption of large amounts of sodium hypochlorite. As mentioned earlier, alkaline hypochlorite added to pH 5.5 starch xanthate elevates the pH, frequently above pH 7, thereby encouraging dexanthation.

On the basis of Equation (4), starch carbonate and starch monothiocarbonate should be present in rapidly neutralized starch xanthate solutions. These products are not likely to be able to participate in the cross-linking reactions. The monothiocarbonate is more likely to be ionized so that the negative charge resides mainly on the oxygen rather than on the sulfur (that is, $\text{RO}-\overset{\text{S}}{\underset{\text{H}}{\text{C}}}-\text{O}^-$). Since, as will be explained subsequently, it is felt that the cross-linking reaction depends upon the sulfide form of sulfur ($-\text{S}^-$), this derivative could be involved only to a limited extent in xanthide cross-linking.

If the concepts presented in Equation (4) are extended, other derivatives may be proposed:



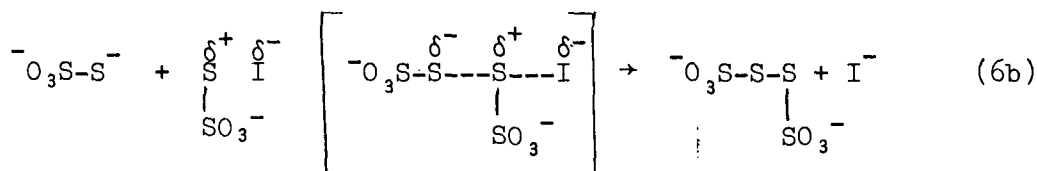
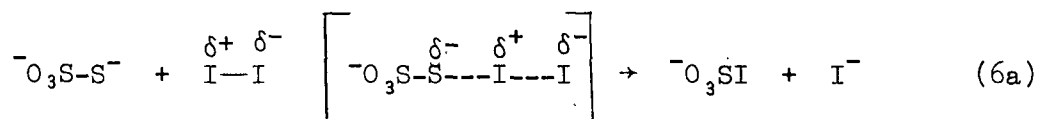
With time, the dialkyl carbonate forms could contribute to intermolecular bonding. Intermolecular bonds are less likely to occur, but once such a bond does form due to thermal motion having brought two polymer chains close enough for this to happen, the probability of a second bond forming increases. Further intermolecular bonding becomes more likely with each additional bond. This mechanism could explain the gelation of cellulose xanthate solutions in closed containers which occurs after aging the product for some time. The proposed formation of the dialkyl derivative is also interesting from the standpoint that its mechanism is the only one restoring both HS^- and HO^- to the system. All the other steps in the reaction scheme either exchange or consume these two reactants.

It is unlikely that distarch monothiocarbonate or distarch carbonate bonds can participate in the cross-linking reaction. However, the reactivity of free xanthate groups on the two starch molecules joined by a carbonate bridge should not be greatly affected. It is possible that cross-linking by the xanthide reaction produces different results with already partially cross-linked xanthates. The concentration at which coagulation occurs during ex situ cross-linking in the laboratory does vary from batch to batch of xanthate (8). The only difference in xanthate properties that has been associated with this has been a higher viscosity for the xanthate which coagulated at the lower concentration.

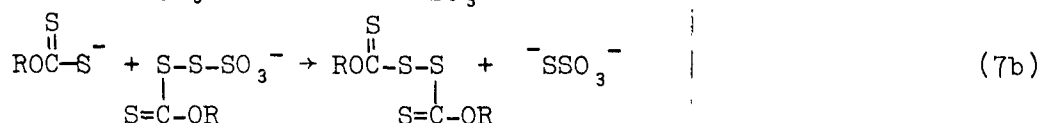
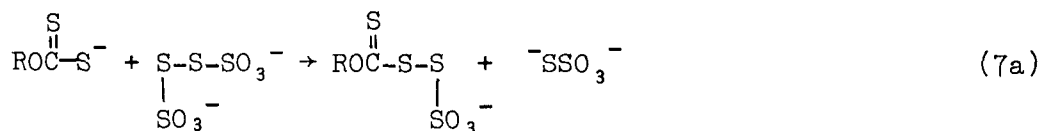
A study of electrometric titration curves of the alkaline starch xanthate solution leads to the conclusion that at pH 5 to 5.5 the xanthate groups are ionized (estimated pK_a 3.5) and that the sulfur by-products are essentially nonionized H_2S but with some hydrosulfide ion present (pK_a 7.02) (9).

An understanding of the xanthide reaction may be derived from the reviews by Pryor (10a) and Foss (10b) on sulfur chemistry and the original work by Cambron

(11) particularly from those sections dealing with the disulfide bond and its displacement reactions. By comparison of the reactive elements involved, it is proposed (10b) that the phototype of the xanthide reaction can be considered the cross-linking of sodium thiosulfate by iodine to form sodium tetrathionate. This reaction mechanism has been illustrated as involving consecutive S_N2 displacements.



The disulfide bond can undergo further displacement reactions by reagents more thiophilic than the leaving group (10a). Xanthate groups are more thiophilic than thiosulfate ions. Consequently, xanthate will displace thiosulfate ion to regenerate sodium thiosulfate from sodium tetrathionate to leave a xanthide linkage (12).

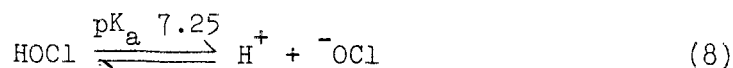


The starch xanthide reaction appears to progress more slowly with sodium tetrathionate than with iodine or sodium hypochlorite. An excess of sodium tetrathionate may be added to starch xanthate and blended in before the effects of cross-linking are seen. In fact, a minute or so passes before the viscosity

increases to the point the mixture cannot be stirred. The whole reaction mixture gels rather than forming a coagulum such as occurs when sodium hypochlorite reacts with xanthate solutions more concentrated than about 0.2 to 0.4%. By comparison, the reaction with the hypochlorite reagent seems to occur instantaneously.

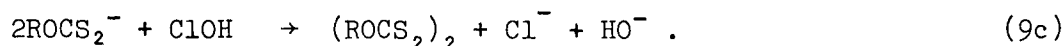
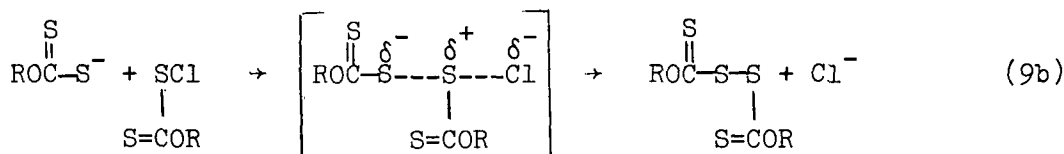
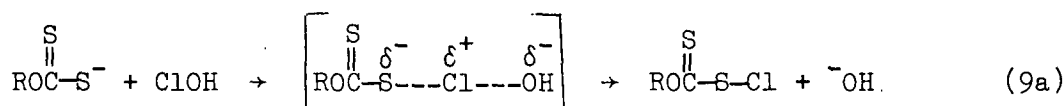
In order to replace iodine for cross-linking starch xanthate with the economically more desirable sodium hypochlorite, reaction conditions must be adjusted to compensate for the stronger oxidizing potential of hypochlorite ions. It was mentioned earlier that sodium hypochlorite is a reagent used to determine total sulfur, as sulfate ions, in cellulose xanthate mixtures in contrast with the use of iodine for xanthate sulfur determinations. Conditions must be selected which encourage the active agent in sodium hypochlorite to behave like the active portion of the iodine molecule.

It is our conviction that ionization of the hypochlorite ion must be suppressed so that the xanthate groups are the strongest nucleophile in the system. This may be done by acidifying sodium hypochlorite solutions.



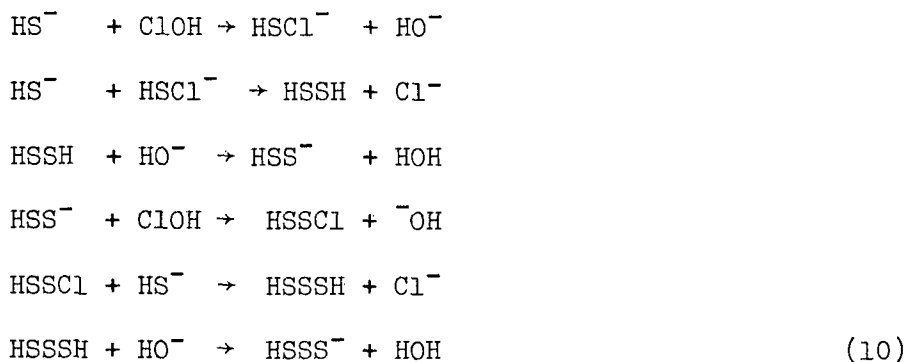
A pH of 5.0 to 5.5 is adequate for this purpose. Consequently, this concept probably is the most basic reason that pH range came to be specified in the standard procedure for in situ starch xanthide.

The cross-linking sequence becomes:

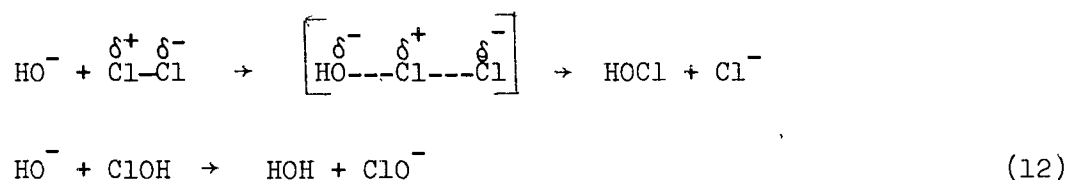


This mechanism indicates that the pH of the system should rise as the cross-linking reaction proceeds. This does occur when pH 5.5 hypochlorous acid and pH 5.5 starch xanthate solution are combined. A small but stable pH elevation (e.g., 5.5 to 5.9) does occur with acetic acid present.

Xanthation by-products in the acidified (pH 5.0-5.5) xanthate solution are mainly present as hydrosulfide ions or potential hydrosulfide ions. The latter either from the ionization of dissolved hydrogen sulfite or from mono- or dithiocarbonic acid and their ionic forms [see Equation (4)]. Reactions of the by-product forms of sulfur with small amounts of hypochlorous acid are expected to lead mainly to polysulfide ions and free sulfur.



This could account for the yellow cast of paper having a high loading of starch xanthide. With an excess of hypochlorous acid, oxidation to sulfite and sulfate ions also would be expected. The mechanism involving hypochlorous acid is consistent with that for iodine since both use the positive halogen function of the cross-linking agent. It is also consistent with the initial step in the formation of the hypochlorite ion.



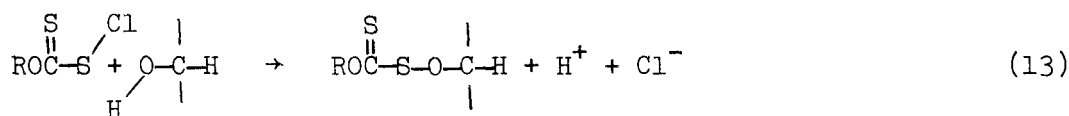
The fact that the pK_a of hypochlorous acid at 7.25 is higher than that of H_2S (7.08) and of water (7.00) suggests that the HO^- and HS^- ions are slightly stronger nucleophiles than ClO^- . The HS^- and HO^- ions would be considered of about equal strength but with HO^- slightly favored over HS^- .

The bond polarization involved in the concept of positive halogen participation in the first bimolecular reaction in xanthide bond formation, is consistent with the characteristics of other known xanthide formers. Thus, polarization of the peroxide bond (in acid but not in base), the chlorine in Chloramine T ($\text{CH}_3\text{O}-\text{SO}_3-\text{N}(\text{Cl})\text{Na}$) and the appropriate bonds in cyanogen bromide, nitrous acid, nitrosyl chloride, and benzene sulfonyl chloride, is consistent with the reactivities of known xanthide-forming reagents (12).

There are some disquieting aspects of a xanthide mechanism involving consecutive second-order reactions. The xanthide bond-forming step is dependent upon the mobility of the second xanthate group. Thus, in order for intermolecular bonds to be formed, two starch polymer chains must be oriented in specific

relationships between chlorinated xanthate and unreacted xanthate groups. Intra- and interbranch xanthide bonds are thereby favored over intermolecular xanthide bonds. Chain conformation of the polyelectrolyte, starch xanthate, in solution also is quite important and may be the reason low ionic strength (or absence of alum) appears more favorable for laboratory preparation of ex situ starch xanthide.

Another bothersome feature of the two-step mechanism is that the blue color (produced by starch complexing with iodine formed from potassium iodide in the presence of a small excess of active chlorine) is not necessarily related to xanthide bond formation unless the second cross-linking step occurs about as fast as the first. That is, the method used to control the amount of reagent added is not directly related to the reaction it is meant to control. Further, one is led to question whether xanthide bonds are formed at all, and, if not, what does account for the sorptive properties of starch "xanthide" on wood fibers and the properties of paper made from wood fibers treated with starch "xanthide." Does the sulphenyl chloride form of the xanthate react with starch directly (13)?



Does the blue end point indicate that all of the available xanthate groups have been converted to the sulphenyl chloride rather than to xanthide?

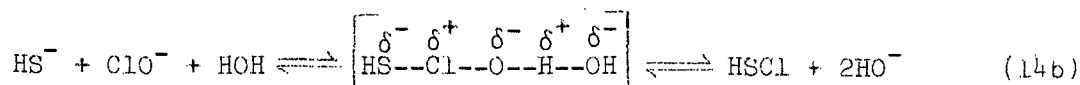
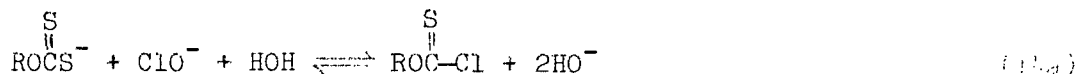
Disregarding these questions, a useful product called starch xanthide can be made reproducibly, but not stoichiometrically, if the pH of sodium hypochlorite solution is suppressed to the point that nonionized hypochlorous acid is the dominant form of the active chlorine. The hypochlorous acid consumption is usually considerably in excess of the amount indicated by Equation (9c).

The excess consumption varies under different conditions (Table II) but frequently is about 2 to 3 times that expected for forming only starch xanthide cross-links.

The consequences of adding hypochlorite ions to starch xanthate under alkaline conditions are highly ramified. It is the nature of sodium hypochlorite solutions that two nucleophiles (ClO^- and HO^-) are introduced at the same time and both are more reactive than the ionized sulfur of the xanthate groups (pK_a about 3.5). Both the sulfur and the carbon atoms in the xanthate groups become reacted upon rather than the xanthate sulfur being the reactant. The effects of hydroxyl ion attack are represented in Equations (3) and (4) and already have been discussed.

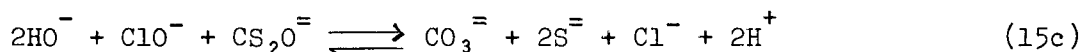
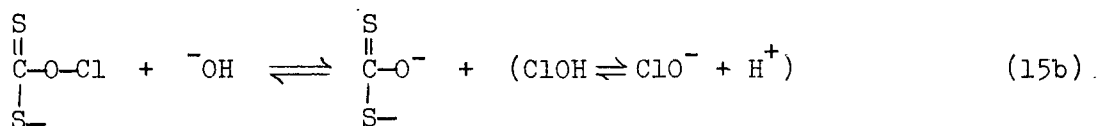
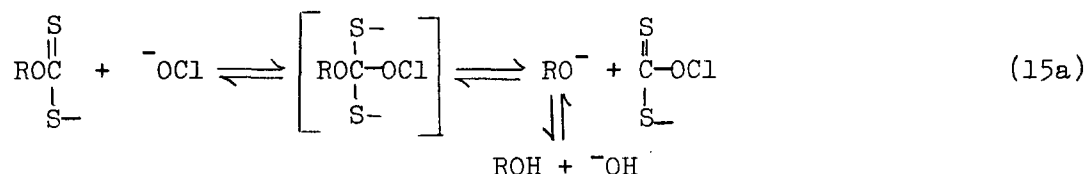
It must be kept in mind that, unless mixing is unusually efficient, local concentrations of high alkalinity will persist for periods of time significant in relation to the rates of inorganic ion reactions in water. Therefore, acidifying the xanthate solution before adding the sodium hypochlorite only partially negates the consequences of adding the alkaline reagent.

When hypochlorite addition begins, the concentration of xanthate sulfenium ions and hydrosulfide ions is large in relation to the concentration of hypochlorite. For this reason nucleophilic attack by the sulfur forms probably dominates the system at first.



Each mole of hypochlorite introduced produces two moles of hydroxyl ion by the first reaction steps [Equation (14a)]. This doubling of the concentration of the basic ions, in addition to the sodium hydroxide accompanying the sodium hypochlorite, provides an explanation for the pH rise when this reagent is first added to starch xanthate solutions. Hydrolysis of the sulfenyl chlorides reverses the upward trend of the pH and acidic products are formed as regenerated hypochlorite ions react as nucleophiles.

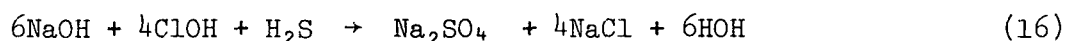
Hypochlorite ions can be expected to behave like hydroxyl ions to bring about dexanthation.



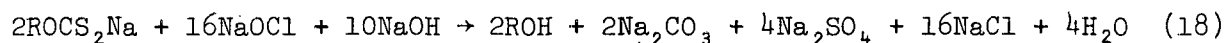
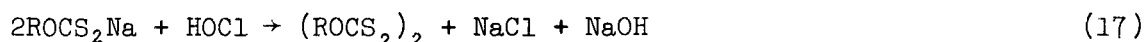
The oxidation level of active chlorine is not changed in these sequences but the dithiocarbonate substituent has been removed and converted to one carbonate ion and two sulfide ions. Two hydrogen ions are produced at the expense of the solvent and account for part of the pH depression following the initial elevation.

It must be noted that whatever amount of starch xanthide may form subsequently from the product of Equation (14a) is subjected to uncoupling by the mechanisms shown in Equation (15a) by both ClO^- and HO^- ions. Not only does a high pH reduce the number of sites available for cross-linking but also cross-links which do form are likely to be broken.

Further acidification of the reaction mixture is due to the hypochlorite oxidation of sulfide ions in steps leading to sulfate ions. This reaction, Equation (16), would go to completion in an excess of hypochlorite ion in an alkaline medium (14). However, the pH depression is accomplished almost as well at lower oxidation levels, such as to sulfite ions.



Comparison of the overall stoichiometry of the sulfur nucleophilic reaction with that of the oxygen nucleophilic reactions is instructive.



Whereas the cross-linking reaction consumes but one mole of active chlorine, 16 moles are consumed in the oxidation of the same number of sulfur atoms to sulfate ions. The reaction in Equation (18) is self-limiting. It is base-consuming rather than acid-producing.

Since the cross-linking reaction [Equation (17)] is pH elevating, it has a tendency to encourage dexanthation if it is not carried out almost instantaneously. Thus, it is not likely that cross-linking can ever be carried out with exactly the stoichiometric amount of hypochlorous acid.

It is suggested that potassium iodide reduces the tendency toward the reactions embodied in Equation (18) by altering the relative strength of the competing nucleophiles.



The sensitivity of the cross-linking reaction to elevations of the hydroxyl ion concentration suggests that the system should be buffered between pH 5 and 7. Adding sodium acid phosphate to starch xanthate before adjusting to pH 5.5 with acetic acid establishes a dual buffer system having its maximum buffering capacity at pH 4.7 and 7.2. This system was found to stabilize the pH of the cross-linking reaction mixture, and to reduce the effects of potassium iodide concentration and reagent addition rate upon the amount of alkaline sodium hypochlorite required to produce the blue end-point reaction (15). If the sodium hypochlorite is first neutralized to pH 5.0-5.5 there is apparently less need for a pH "ceiling" being built into the reaction system.

DEVELOPMENT OF METHODS FOR REPRODUCIBLY
FORMULATING EX SITU STARCH XANTHIDE

ELECTROKINETIC CHARGE AND TIME OF CONTACT

Part of the work prescribed for this section has been covered in the report on Phase I of this project. The electrokinetic charge was shown to be the controlling factor in xanthide sorption since no absorption occurs without additives, such as alum, which will negate this effect. The study on sorption rates also brought out that most of the xanthide sorption occurs in the first 15 or 16 minutes of contact (16).

EXPERIMENTAL PROCEDURES

The conditions selected for the basic procedures used in this report reflect the findings of the earlier work plus certain judgments concerning the practical significance of these findings. For example, the stock temperature on a paper machine is about 35°C. rather than 15°C. where xanthide sorption is favored. The range of alum concentrations favoring xanthide sorption, 2×10^{-4} to 2×10^{-3} M, covers alum concentrations frequently encountered in handsheet making and commercial operation. For example, 2% alum [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] on the fiber weight is 6.0×10^{-4} M alum when the fiber consistency is 2%.

The standard conditions selected were: 25°C., 2% alum on 2% fines-free Rayonier bleached softwood kraft fiber (700-ml. S.-R. before classification) and 10% D.S 0.12 xanthide on the weight of the fiber. Variations from these conditions will be specified as the discussion proceeds.

Basic Procedure for ex situ Starch Xanthide

D.S. 0.12 starch xanthide (3.75 g. as starch) was diluted with 2300 ml. deionized water and blended 5 minutes in a 20.0°C. water bath with a 2-inch magnetic

stirrer in a 4-quart, wide-mouth jar. The pH was adjusted to 5.1 ± 0.1 . Following an additional 5-minute blending interval, 4 ml. of 5% potassium iodide was added and an acidified 1% solution of sodium hypochlorite was run in from a buret until a blue color persisted. The xanthide preparation was diluted to 3000 ml. (0.125%) and aged 15 minutes before using.

The acidified sodium hypochlorite was prepared by diluting 50 ml. of Hi-lex with 150 ml. deionized water, adjusting to pH 5.1 ± 0.1 with 20% acetic acid and diluting to 250 ml. At the pH specified, the active reagent is hypochlorous acid at a concentration of about 0.14 molar in the dilute solution. This reagent was used within 10 minutes of preparation and then discarded.

Basic Handsheet Procedure

Dewatered, fines-free Rayonier bleached softwood kraft pulp (30.0 g. oven-dry, 700-ml. S.-R. freeness before classification) was dispersed 2-1/2 minutes in a British disintegrator and made up to 1500 ml. (2% consistency). The stock temperature was adjusted to $25.0 \pm 0.1^{\circ}\text{C}$. by external steam heating. Alum was added (6 ml., 10%) to give 2% on the fiber or 6×10^{-4} molar concentration. The dilute xanthide preparation (2400 ml., 0.125%, 3.0 g.) was added to the stock and blended 15 minutes by means of a laboratory model Lightnin' mixer. At this point the consistency was 0.77% and the alum concentration 2.3×10^{-4} M. The fiber and xanthide mixture was diluted to 6000 ml. (0.5% consistency) and made into 8, 8-in. by 8-in. Noble and Wood handsheets (500 ml. stock per sheet = 2.5 g. fiber) using deionized water. When rosin was used, the water in the deckle box of the sheet mold was adjusted to pH 4.5 to 5.0 with dilute sulfuric acid.

The handsheets were transferred to blotters by means of a couch roll, pressed between blotters at 50 p.s.i.g. for 5 minutes and dried 7 minutes on a single blotter blotter side down, with a steam drum set at 3-5 p.s.i.g.

The handsheets were equilibrated to 20% R.H. and then to 50% R.H. at 73°F. before testing.

Results

The data are shown in Table I. During the discussion following, specific aspects of the data will be brought out by referring to the handsheet set numbers shown in the first column of this table.

THE EFFECTS OF ALUM ADDITION OVER THE pH RANGE OF 5 TO 7

Cross-linking must be carried out in acid media if sodium hypochlorite is the source of oxidant; therefore, the sodium hydroxide in the starch xanthate reaction mixture must be neutralized. Since alum also must be added to the paper-making system as a flocculant and pH controlling agent, it would be a process simplification if alum could be used to neutralize the xanthate prior to cross-linking.

In this experiment, the dilute starch xanthate was neutralized to pH 5.0, 6.0, and 7.0 with 10% (weight per unit volume, w/v) alum. A fourth preparation used 20% acetic acid to pH 5 as specified in the standard procedure described above. One additional preparation was included after work on another section was completed. For this run, an Eppenbach homogenizer was used to agitate the xanthate solution (pH 5 with alum) during cross-linking. These xanthide preparations were added to the standard stock suspension described in the preceding section.

All of the preparations using alum coagulated before the blue end point was reached. This reduced the wet and dry tensile strength of the handsheets (Sets 71A vs. 72B, 72A, and 71B, Table I) but improved retention efficiency. More coagulated starch xanthide is retained as the cross-linking pH with alum increases from 5 to 7. There is no change in the tensile strength of the handsheets. This is consistent

TABLE I

BATCH TREATMENTS OF 700-ML. S.-R. FINES-FREE BLEACHED KRAFT FIBER USING 2% ALUM ON FIBER WEIGHT

Test No.	Remarks	Xanthide Preparation			0.14N HOCl ML.	Fiber Consistency		2% Rosin Present	Basis Wt., (25 x 40/500) lb./ream	Apparent Density, basis wt./ thickness	Instron Tensile Strength		Fluorescence Size Time, sec.	Xanthide Content	
		pH	Acid	Shear Rate		Before Xanthide, %	After Xanthide, %				50% R.H. lb./in. width	16-Hr. Soak lb./in. width		G./100 G. Fiber	Retention Efficiency %
	(Number of tests)										(5)	(5)	(5)	(2)	
71A		5.0	20% Acetic	Low	33.0	334	2.0	0.77	0	48.0	9.8	30.6	2.3	2.7	27
72B		5.0	10% Alum	Low	33.9	342	2.0	0.77	0	47.4	9.7	25.4	1.3	2.6	26
83A		5.0	10% Alum	High	14.3	144	2.0	0.77	0	46.0	9.6	25.5	1.2	1.1	11
72A		6.0	10% Alum	Low	32.6	329	2.0	0.77	0	47.1	9.8	25.7	1.3	3.2	32
71B		7.0	10% Alum	Low	35.5	359	2.0	0.77	0	48.1	9.8	25.3	1.0	4.1	41
74A	2% Rosin, then 4% alum,	5.0	20% Acetic	Low	31.4	317	2.0	0.77	+	47.5	10.3	34.0	4.5	4.3	43
74B	then 10% xanthide	5.0	20% Acetic	Low	36.6	370	1.0	0.56	+	48.0	10.4	33.2	4.5	5.0	50
74C		5.0	20% Acetic	Low	35.5	359	0.052	0.050	+	44.5	9.7	24.2	1.6	1.4	14
74D	Control (no xanthide)	--	--	--	--	--	0.05	--	+	45.5	9.7	18.5	0.8	0.0	--
78A	2% Rosin, then 10% xanthide, then 4% alum	5.0	20% Acetic	Low	35.1	355	2.0	0.77	+	46.8	9.8	21.4	0.95	1.0	10
80C	Control (no xanthide)	--	--	--	--	--	2.0	0.77	0	43.3	9.0	16.9	0.60	--	--
79A		5.0	20% Acetic	High	17.8	180	2.0	0.77	0	49.3	10.7	36.1	5.6	4.7	47
79B		5.0	20% Acetic	Low	29.0	293	2.0	0.77	0	46.2	9.8	32.3	3.5	2.5	25
80A		5.0	20% Acetic	Low	14.5	146	2.0	0.77	0	47.3	9.5	21.4	0.92	2.1	21
80B		5.0	20% Acetic	Low	43.5	440	2.0	0.77	0	46.0	9.6	21.7	0.86	2.6	26
81A	Aerated 20 min. with N ₂	5.0	20% Acetic	High	11.6	117	2.0	0.77	0	48.9	10.4	35.7	4.4	3.3	33
81B	Aerated 20 min. with N ₂	5.0	20% Acetic	Low	21.7	218	2.0	0.77	0	48.0	10.2	34.2	3.8	3.4	34
82A	Air dried	5.0	20% Acetic	Low	2.95	298	2.0	0.77	0	50.2	10.0	38.3	3.6	--	--
82B	Drum dried	--	--	--	--	--	--	--	--	48.4	9.7	36.4	4.0	3.8	38
82C	Drum dried then oven heated	--	--	--	--	--	--	--	--	49.9	9.8	35.2	4.9	--	--

High or low shear rates refer to using Eppenbach homogenizer or magnetic stirrer mixing during cross-linking.

with the findings presented on pages 8 and 12 of Report Six and pages 12 to 27 of Report Seven. Coagulated starch xanthide retained in the sheet by filtration does not enhance the strength of the handsheet.

Set 83A was prepared with a homogenizer agitating the reaction mixture during cross-linking. It would be anticipated that smaller xanthide coagulum particles would be present due to the mechanical action. This is apparently the case since retention decreased more than 50%. Smaller particles are less efficiently filtered out of the suspension in the sheet mold. The physical strength of the sheets prepared with alum-adjusted xanthide is greater than those in the set prepared without xanthide (Set 80C). It is proposed that only a portion of the xanthide is coagulated and that the remaining portion retains at least part of its desirable properties. The wet-tensile increments of the alum-adjusted xanthide sets indicate about 1.0 to 1.1 g./100 g. fiber is the retention level of effective xanthide (10 to 11% of total added) if it has the same wet-tensile efficiency as the standard xanthide. It is concluded that alum should not be used to neutralize the starch xanthate prior to cross-linking, at least in laboratory procedures. Furthermore, the quantity of alum needed to neutralize the xanthate solution is considerably in excess of that desired in the fiber suspension after the xanthide is added.

The alum-adjusted xanthides formed visible, translucent spots in the handsheets due to the large size of the coagulated xanthide particles. This is a quality defect in paper that cannot be tolerated.

THE EFFECTS OF PULP CONSISTENCY WHEN ADDING XANTHIDE, ROSIN, AND ALUM

The standard procedures were used in preparing the starch xanthide and the fiber suspensions. The variation introduced is the initial fiber concentration

which was adjusted from 2.0 to 1.0% to 0.052% by adding appropriate quantities of deionized water. Fortified rosin size was added to the stock (2% w/w on fiber) and blended for 5 minutes at 25°C. Alum was added (4% w/w on fiber, rather than 2%, to accommodate the neutralizing effects of the rosin) and blended 5 minutes. The xanthide preparation was added last and blended 15 minutes before diluting to sheetmaking consistency. The control set was run at 0.052% consistency (74D).

There is little difference between 2 and 1% initial fiber consistency (Sets 74A and 74B) in regard to wet and dry tensile, size time, and xanthide retention. These properties are harmed by making the addition at 0.052% consistency (Set 74C). Rosin sizing effects are completely eliminated. Part, if not all, of this is due to the fact that the alum concentration is low ($2 \times 10^{-5} \text{M}$) when the stock is diluted to 0.050%. It was shown in the preceding report (Phase Report I) that fiber consistency has little effect on xanthide sorption when it is carried out in at least $2 \times 10^{-4} \text{M}$ alum at 25° with a constant xanthide addition rate. Since the control run at 0.050% consistency had a reduced, but still significant, size time, it must be concluded that xanthide harms rosin sizing under marginal conditions.

The fiber consistency is not a major factor affecting xanthide efficiency if alum is added at a rate sufficient to maintain its concentration in the prescribed range of about 2×10^{-4} to $2 \times 10^{-3} \text{M}$.

The Effects of Order of Addition of Xanthide, Rosin, and Alum

Rosin is most effective in handsheets when it is thoroughly blended with the fibers before the alum is added. This was done for the paper produced for the preceding topic. The variation in addition order that is significant here, is whether starch xanthide should be added to the stock before or after alum.

For handsheet Set 78A at 2% fiber consistency, this question is examined by adding rosin, xanthide, and then the alum (the quantities used were those specified in the preceding section). Since xanthide sorption has been shown not to occur in the absence of alum (17), the 15-minute sorption interval started with the incorporation of that component. Blending the xanthide with the fiber and rosin was limited to a 5-minute interval.

Upon comparing the data for Set 78A (added before alum) with those for Set 74A (added after alum) it is concluded that, at least for handsheet evaluations, the starch xanthide should be added after alum is mixed with the stock. Xanthide retention, size time, and wet and dry tensile strength are all harmed by adding the alum last.

THE EFFECTS OF MIXING CONDITIONS ON THE EX SITU CROSS-LINKING REACTION

The standard procedures already specified were used with the following variation: an Eppenbach laboratory homogenizer was used to produce a high-shear rate during the titration of the xanthide with hypochlorous acid. The magnetic stirring used in the standard procedure is the low shear condition used for comparison (Set 79B).

Reagent consumption is decreased by using the high-shear rate from 290% of theory (Set 79B) to: 180% for the standard conditions (Set 79A), 144% for alum-adjusted xanthide (Set 83A), and 117% for xanthide prepared for nitrogen-aerated xanthide (Set 81A).

Under the standard experimental conditions (Sets 79A vs. 79B), the high-shear rate improves retention and wet and dry tensile strength. The strength

improvement is due to the higher retention since the wet tensile efficiencies are about the same (1.1 vs. 1.2).

The effect of the high-shear rate probably is not due to energy input alone. The time involved in titrating to the blue end point is drastically reduced due to improved mixing and more rapid blending in of the hypochlorous acid. Subsequently, it was found that titration using high shear could be accomplished in 10 to 12 seconds, compared with 60 to 90 seconds under less vigorous agitation.

In a separate experiment, starch xanthate was titrated with hypochlorous acid by the standard procedure. The following agitation variations were used: the standard magnetic stirring, magnetic stirring with a 10-inch spatula clamped in place to disrupt stream lines, and the Eppenbach homogenizer. Reagent consumption dropped from 28.5 ml. to 20.4 ml. to 15.0 ml. in the order given. It is likely that the effectiveness of blending the xanthate and the reagent is the controlling factor rather than the energy input.

THE EFFECT OF VARYING THE AMOUNT OF OXIDANT

Sets 80A and 80B were prepared using 50 and 150% of the volume of hypochlorous acid required to produce the end-point reaction in the xanthide prepared for Set 79B. The lower amount used (50%, Set 80A) is still in excess of that required for the end-point color reaction in Set 79A using high-shear mixing. When the 150% addition was made (Set 80B) the blue color appeared and then faded rapidly.

Xanthide retention efficiency is not affected when 150% of the practical hypochlorite requirement (440% theory) is used, but is decreased when only 50% of practical demand is used. Both wet and dry tensile strength are lowered

about equally for both variations of hypochlorous acid addition. It appears that the end-point reaction accurately reflects completion of "cross-linking" and that the oxidant should be added to about the extent indicated by the appearance of the blue color which occurs in the presence of potassium iodide.

THE EFFECTS OF HANDSHEET DRYING CONDITIONS

The conditions selected for evaluating the effects of drying conditions were: air drying at 50% R.H. and 73°F., drying on a steam drum (7 min., 3 p.s.i.g.), and drum drying plus oven drying (10 min. in forced draft oven at 120°C.).

In order to make valid comparisons between treatments, shrinkage and distortion of the handsheets must be minimized or made as uniform as possible. The approach chosen was to use the British sheet mold in place of the Noble and Wood mold used previously. Among the accessories for the British mold are drying rings for restraining the handsheets during air drying. These rings were used for the air drying treatment but with a disk of blotter paper replacing the usual chrome-plated metal disk. The use of blotter paper coincides with the practice of drying the handsheet on the couch blotter, blotter side down, on the steam drum. Thus, all three drying conditions were accomplished, on blotters, with as uniform restraint during drying as could be devised.

A set of 12, 1.2-g. handsheets was made following the procedures outlined earlier in Part II of this report. Three sets of four sheets each were randomly selected. These sets were then dried, one set for each condition specified above.

As the intensity of drying increases, wet tensile strength increases (Sets 82A, 82B, 82C) and dry tensile strength decreases. Thus, there is a heat-curing effect on starch xanthide functionality.

THE EFFECTS OF THE PRESENCE AND ABSENCE OF XANTHATION BY-
PRODUCTS AND THE EFFECTS OF MIXING CONDITIONS

Sets 81A and 81B in Table I were prepared from starch xanthate which had been aerated with purified nitrogen at pH 5.0 for 20 minutes at 20°C. This treatment removes volatile sulfur-containing by-products of the xanthation reaction. Acidification converts the thiocarbonate series of by-products to H_2S , CS_2 , CO_2 , and water. The H_2S , CO_2 , and residual CS_2 are then displaced from solution by the nitrogen. The two agitation rates used during the cross-linking reaction were produced by the Eppenbach homogenizer and by a magnetic stirrer as described earlier in the section dealing with mixing conditions.

The controls for this section are Sets 79A and 79B.

With Eppenbach mixing, the consumption of cross-linking reagent is decreased for both the standard and nitrogen-aerated xanthates. Removal of sulfur by-products also reduces the reagent consumption. However, with Eppenbach mixing, aeration reduces xanthide retention and wet tensile strength. Under the standard laboratory mixing conditions (magnetic stirrer), purification tends to improve xanthide retention and wet tensile strength.

Since the Eppenbach mixer produces the most desirable cross-linking conditions overall, there is no advantage in removing sulfur-containing by-products before cross-linking as far as the physical strength of the paper is concerned.

HANDSHEET PERFORMANCE UNDER "BEST" CONDITIONS

A series of handsheet sets was made using the Rayonier bleached softwood kraft pulp (whole and fines-free), a bleached hardwood kraft pulp (Weyerhaeuser), an unbleached softwood kraft (Bloedel Super Tare Kraft) and a softwood groundwood (John Breaky 120 Softwood Groundwood). All four pulps are commercial products obtained in dry form.

The chemical pulps were beaten to 700-ml. Schopper-Riegler freeness in a Valley beater while the groundwood was circulated (that is, with no load on the bed plate) in the beater one hour, soaked overnight in the beater, and then circulated one more hour in the beater before use (510-ml. S.-R.). The Rayonier pulp was divided in half after beating. One portion was dewatered immediately and the other run through a classifier to remove the fines before being dewatered. Both portions of this pulp had been in cold storage for several weeks before use. The other three pulps were used directly from the beater. All pulps were beaten in deionized water.

The sorption conditions were specified on the basis of all the preceding work. Where product properties were not involved, operational factors were the basis of specification.

The starch xanthide was prepared according to the basic procedure as described above except the Eppenbach homogenizer was used during cross-linking. Sorption was carried out at 25°C. in deionized water containing 1% fiber and 2% (3×10^{-4} M) alum on the fiber weight. Deionized water was used not because it is considered best but because day-to-day variations in the ionic strength of tap water introduce a variable to be controlled, although dissolved salts in tap water should favor xanthide retention.

Starch xanthide was added at the rate of 10.0 g. per 100 g. dry fiber. The stock suspension was blended with the xanthide for 15 minutes at 25°C. before being diluted to 0.5% consistency and made into 2.5-g. Noble and Wood handsheets. These sheets were wet pressed (5 min., 50 p.s.i.g.) and dried on a single blotter for 7 minutes (couch blotter down) on a steam drum having 3 p.s.i.g. steam pressure. The results of the testing program are shown in Table II. In the discussion following, attention will be focused on the data shown in this table by referring to the sets designated by the letters given in the first column.

THE EFFECT OF THE INCLUSION OF FINES

The effect of fines upon the properties of the bleached softwood kraft sheets, not treated with xanthide, may be seen by comparing Sets A and E. The fines in this pulp improve burst, wet and dry tensile strength, and folding endurance. Brightness and opacity are reduced and sizing is unaffected. When these pulps are treated with 10% xanthide, the presence of the fines improves xanthide retention (from 39 to 48%, Sets C and F). The brightness loss with xanthide is less with the fines even though there is more xanthide present. Opacity is reduced more by the xanthide with the fines present, as would be expected from the improved strength properties. The dry tensile increment is greater with the fines removed. However, wet tensile strength and folding endurance increase more with the fines present. Bursting strength is improved more by the xanthide with the fines removed.

The fine particles removed from the beaten stock by classification make a significant contribution to sheet strength. The combined action of the fines and xanthide lead to enhanced strength properties but optical properties are degraded slightly. The presence of fines in the stock suspension does not harm the beneficial effects of the xanthide upon this pulp.

TABLE II
BATCH TREATMENT OF SEVERAL PULPS UNDER OPTIMIZED CONDITIONS

Set		Xanthide Added, 100 g. fiber	Xanthide Retained			Retention Efficiency, %	Specific Scattering Coeff. at 650 MM (s)	Standard Brightness	Opacity	Fluorescence Size Time, sec.	Instron 50% R.H. lb./in.	Tensile 16-Hr. Soak lb./in.	Burst. pt./ 100 lb.	M.I T. Fold	Basis Wt., (25 x 40/ 500),lb./ ream	Apparent Density
			Glucan, %	G./100 G. Sheet	G./100 G. Fiber											
A	Bleached softwood kraft (fine's-free)	0	5.18	--	--	--	298	87.4	74.9	0	17.2	0.65	81	719	46.9	9.4
B		5	7.27	2.09	2.1	42	266	81.8	73.0	0	28.4	2.43	129	2310	50.5	10.1
C		10	8.91	3.73	3.9	39	242	79.6	70.0	0	29.2	2.98	144	2730	48.2	10.0
D		15	9.22	4.04	4.2	28	222	79.9	68.5	0	33.0	4.68	153	3780	48.7	10.4
E	Bleached softwood kraft (whole pulp)	0	5.52	--	--	--	--	86.1	71.9	0	20.6	0.84	102	1260	44.7	9.9
F		10	9.36	4.54	4.8	48	--	78.6	66.5	4	31.8	4.38	156	4430	47.4	10.8
G	Bleached hardwood kraft	0	7.90	--	--	--	--	85.4	76.6	0	16.2	0.66	61	46	44.3	10.1
H		10	11.24	3.34	3.5	35	--	80.8	73.0	0	28.1	3.31	120	1470	47.5	10.6
I	Unbleached softwood kraft	0	6.69	--	--	--	--	26.8	90.8	6	22.2	1.16	96	1170	46.0	9.4
J		10	10.57	3.86	4.0	40	--	23.6	83.6	35	30.5	4.42	154	2650	44.2	9.9
K	Softwood groundwood	0	9.12	--	--	--	--	54.5	94.8	12	8.5	0.38	21	2	42.0	6.6
L		10	11.66	2.44	2.5	25	--	53.2	93.7	18	9.5	0.66	24	3	41.6	6.6

THE RELATIONSHIP BETWEEN BONDED AREA AND BONDING STRENGTH

In order to compare relative effects of starch xanthide upon bonded area and bond strength, handsheet Sets A, B, C, and D were prepared from the fines-free bleached softwood kraft pulp beaten to 700-ml. Schopper-Riegler freeness before classification. Starch xanthate was added at the levels of 0, 5, 10, and 15 g./100 g. fiber in the alphabetical order shown.

Figures 2, 3, and 4 show the linear relationship of the specific scattering coefficient (which is proportional to the unbonded surface area) to dry tensile strength, wet tensile strength, and xanthide content. These relationships led to the conclusion that starch xanthide improves paper strength by increasing the bonded area (18-20) rather than increasing the bond strength.

COMPARISON OF THE BEHAVIOR OF STARCH XANTHIDE ON SEVERAL DIFFERENT PULPS

The data for handsheets prepared from whole pulps are listed in Table II (Sets E-L). The most striking feature of these data is the 35-sec. fluorescence size time obtained with xanthide and the unbleached softwood kraft pulp. No rosin sizing was added to these handsheets. The sizing that did develop had to be due to interaction between the xanthide and the extractives in the pulp. Xanthide by itself has no water repellent properties, as is shown by the zero size time for fines-free bleached softwood kraft and whole bleached hardwood kraft (Sets C and H) pulps. This could indicate that the sizing effect is due to an interaction between xanthide and softwood fines since a measurable size time is produced by the bleached softwood kraft fines with xanthide present (Set F). If the interaction dealt only with unmodified softwood extractives, the groundwood sheets (Sets K and L) should show a greater improvement in size time with the xanthide than is found.

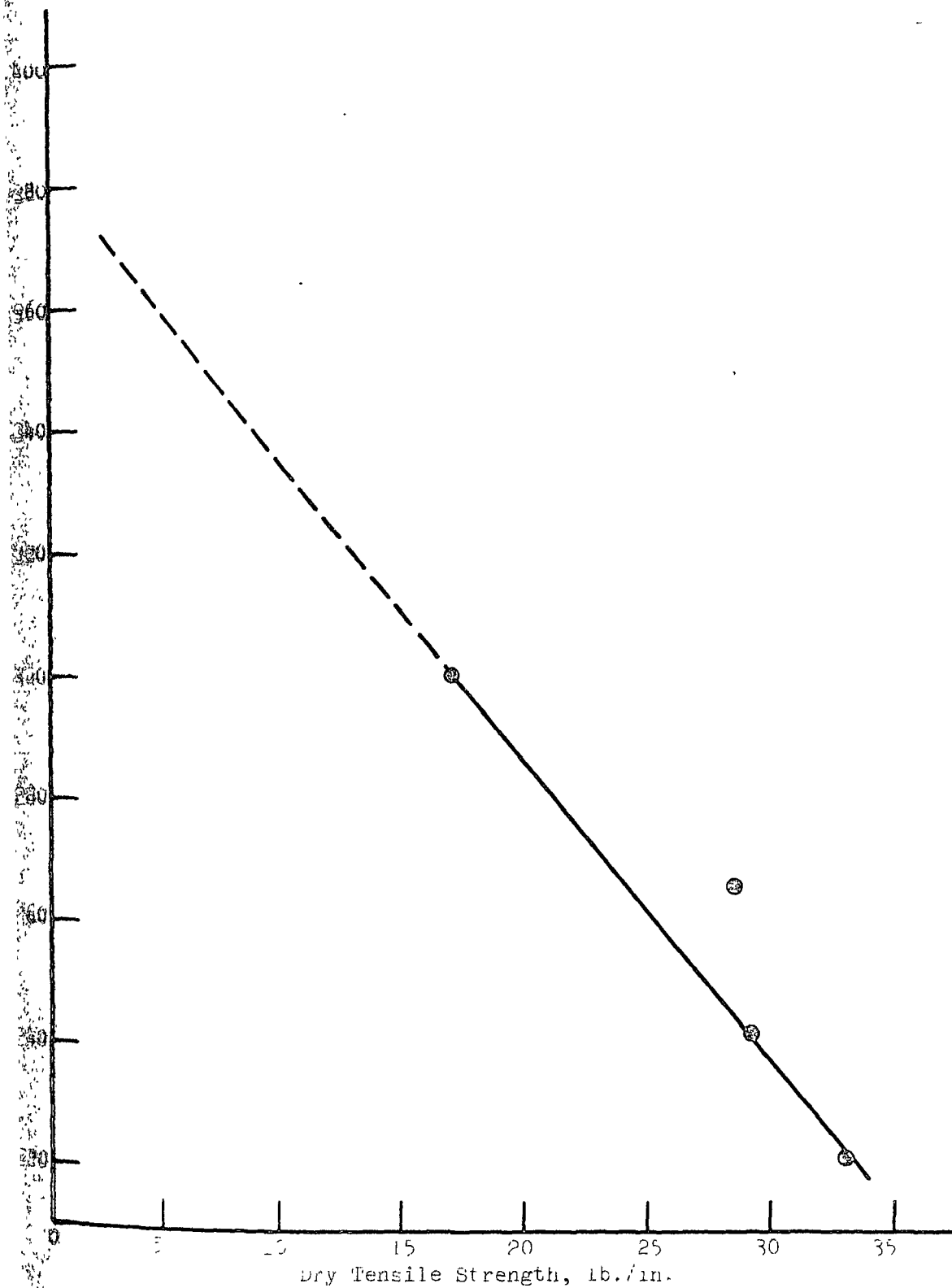


Figure 2. Optimum scattering Coefficient as a function of Dry Tensile strength.

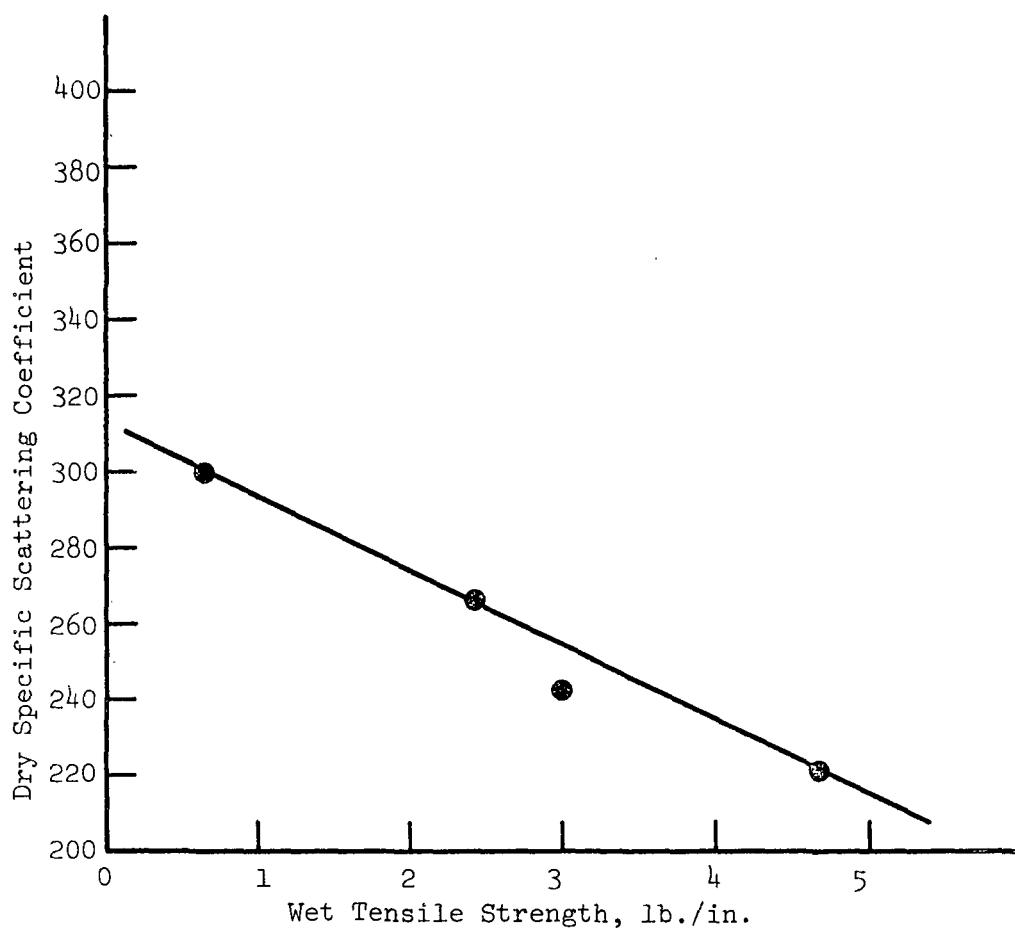


Figure 3. Dry Specific Scattering Coefficient as a Function of Wet Tensile Strength

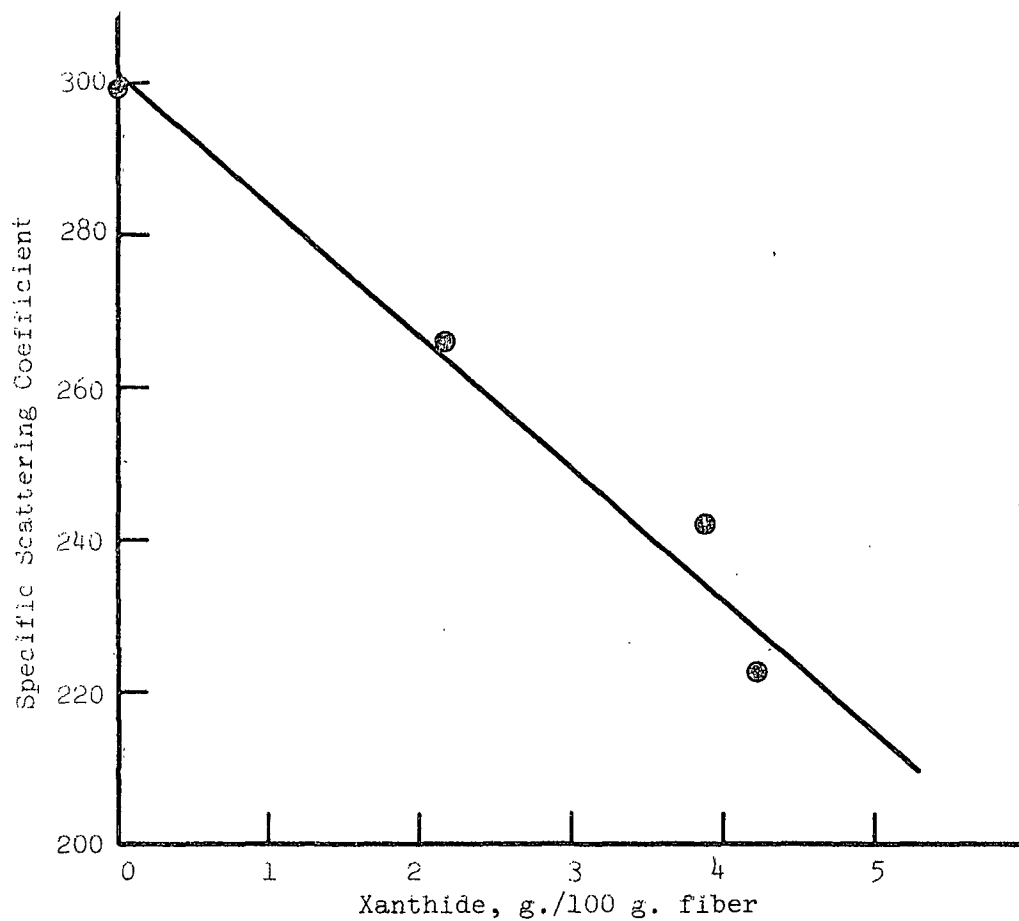


Figure 4. Specific Scattering Coefficient as a Function of Xanthide Content

The interaction between xanthide and whole softwood kraft pulps to produce sizing is unusual. It, therefore, is a strong indication that further investigation is needed if the greatest benefit is to be derived from starch xanthide in paper.

Xanthide treatment of the whole chemical pulps produces attractive strength improvements. The properties of wet and dry tensile strength, burst and folding endurance are improved in proportion to fiber length and flexibility characteristics. That is, bleached softwood kraft is better than unbleached softwood kraft, which in turn is better than bleached hardwood kraft.

Xanthide treatment of softwood groundwood does not produce much change. This is usually the case when groundwood is treated with internal adhesives. The effect is lost on the greater surface area of the small fiber fragments. It is suspected that the lower xanthide retention is due to part of the xanthide being carried through the wire on the fines not retained during sheet formation.

The loss in brightness and opacity per unit xanthide sorbed on the whole chemical pulps is proportional to the brightness of the pulp. This is but another way of saying the brighter the pulp, the more the internal adhesive affects the optical properties.

COMPARISON OF PAPERS MADE ON A HANDSHEET MOLD,
THE I.P.C. CONTINUOUS WEB FORMER, AND THE
N.U.R.D.D. PILOT MACHINE

The consequences of increasing the scale of production of starch xanthide-treated paper are examined in Table III. The preparation of the handsheets has been described earlier in this report. For these specimens, the data have been transferred from Table II, Sets E and F. The I.P.C. Continuous Web Former is a small experimental machine producing a 12-inch web at a speed of 9-11 feet per minute for these specific preparations. The web is transferred from the wire to a single drier drum to produce a machine-glazed product. Further details of the machine and its operation are presented on pages 5-8 of Quarterly Report Seven.

The N.U.R.D.D. Pilot Machine is a narrow version of conventional commercial fourdrinier machines. The paper from this machine was prepared by the cooperating agency using their supply of bleached western softwood kraft pulp.

The magnitude of the three operations varies from 30 grams of pulp for the handsheets, to 4 pounds for the Continuous Web Former, and to much larger quantities of pulp for the Pilot Machine.

The starch xanthide for the handsheets was prepared according to the laboratory procedure scaled up to produce 6 liters of 0.125% starch xanthide. For the Continuous Web Former, a small continuous cross-linking unit was devised (21) which would cross-link about 92 liters of 0.2% starch xanthate in a little less than 8 minutes. The starch xanthide was run directly into the machine chest (1.7% fiber consistency, 2% alum on the fiber weight, $5.1 \times 10^{-3} \text{M}$) in one instance (Set II) and in the other (Set III) was collected, aged 15 minutes, and then added to the stock chest. The purpose of these variations was to examine what happens

TABLE III

COMPARISON OF PAPERMAKING SCALE WHEN USING 10% EX SITU STARCH XANTHIDE AND 2% ALUM ON FIBER WEIGHT (2% CONSISTENCY)

Forming Equipment	Sample Number	Basis Wt., lb./ream (25x40-500)	Apparent Density, lb. basis wt./mil	Bursting Strength		50% R.H. Tensile Strength		Wet Tensile Strength		M.I.T. Fold, s	Opacity, %	Standard Brightness	Fluor- escence Size Time, sec.	Xanthide, g./100 g. fiber
				point	s	point/ 100 lb.	lb./in.	s	lb./in.	s				
No. tests				(5)			(5)		(5)		(10)	(5)	(5)	(2)
Handsheets:														
Control	2569:94-0	44.7	9.9	45.7 ± 2.6	102		20.6 ± 1.5	5829	0.8 ± 0.1	223	1260 ± 325	71.9 ± 1.5	86.1 ± 0.2	Inst. --
Trial	2569:94-10	47.4	10.8	74.1 ± 9.0	156		31.8 ± 2.7	8486	4.4 ± 0.2	1169	4430 ± 1254	66.5 ± 1.9	78.6 ± 0.3	4 ± 0.9 4.8
I.P.C. Web Former														
Control M.D.	2569:23-1	48.0	10.2	46.2 ± 6.4	96		33.1 ± 1.5	8764	1.2 ± 0.2	316	1209 ± 393	75.8 ± 1.3	84.5 ± 0.3	Inst. --
Trial ^a M.D.	2569:23-2	52.4	11.1	49.8 ± 4.9	95		38.1 ± 1.2	9231	5.3 ± 0.1	1285	3530 ± 475	70.7 ± 0.9	81.4 ± 0.3	Inst. 3.5
Trial ^b M.D.	2569:23-3	47.8	9.8	53.2 ± 6.9	111		38.7 ± 2.9	10285	4.5 ± 0.3	1299	4720 ± 473	71.6 ± 1.3	82.2 ± 0.04	Inst. 3.0
MURDD Pilot Machine														
Control M.D.	(80611)	66.0	12.7	52.8 ± 3.0	80		44.9 ± 3.8	8650	2.0 ± 0.1	376	2400 ± 275	80.2 ± 0.6	82.4 ± 0.2	Inst. --
C.D.							22.2 ± 1.2	4270	1.0 ± 0.01	195	809 ± 301			
Av.							33.6 ± 2.5	6460	1.5 ± 0.05	286	1605 ± 292			
Trial M.D.	(80618)	65.9	13.2	74.8 ± 4.1	114		57.1 ± 2.2	11000	10.4 ± 0.3	2000	4280 ± 523	75.7 ± 1.2	79.1 ± 0.2	2 1.8
C.D.							30.7 ± 1.4	5920	5.9 ± 0.2	1130	2620 ± 575			
Av.							43.9 ± 1.8	8460	8.2 ± 0.2	1565	3950 ± 549			

^a Xanthide added to stock directly from cross-linking unit.

^b Xanthide added to stock after holding 15 min.

s = standard deviation based on range.

to the starch xanthide between the time it is prepared and made use of in the laboratory procedures; that is, the changes occurring between 0 and 5 minutes after the blue end point appears. It was shown earlier that the interval between 5 and 60 minutes after preparation was not harmful (22).

The comparison is based upon the addition of 10 g. starch xanthide per 100 g. fiber to about 2% consistency bleached western softwood kraft pulp (about 700-ml. S.-R. freeness) suspension containing 2 grams of aluminum sulfate octadecahydrate per 100 grams of fiber.

The data in Table III for the two trials on the I.P.C. Continuous Web Former establish the fact that there is little difference between adding starch xanthide as it is formed to the fiber suspension and delaying the addition for 15 minutes. This establishes that differences between laboratory preparation of handsheets and paper produced by continuous operation on commercial-scale equipment are not due to the age of the xanthide.

When the data are compensated for differences in basis weight, the handsheet and Pilot Machine papers are remarkably similar in physical properties. This is more obvious in Table IV where the trial paper responses are expressed as percent of the control paper test values. It is encouraging that the handsheets procedures parallel the results of a continuous papermaking process which approaches a commercial scale of operation. It appears that the 15-minute contact period at high consistency after adding starch xanthate to the stock in the handsheet procedure duplicates the performance obtained with the recirculated white water used on the Pilot Machine. However, retention efficiency is better for the handsheet. The white water was not recirculated for the Web Former runs and the contact period was but 5 minutes before the stock was reduced to operating consistency.

TABLE IV
TRIAL PAPER DATA AS PERCENT OF CONTROL PAPER DATA

Process	Burst ^a	Dry ^b Tensile	Wet ^c Tensile	Fold	Opacity	Bright- ness
Handsheets	153	146	20	352	92.5	91.3
I.P.C. Web Former						
Unaged	99	106	15	292	93.3	96.3
Aged	116	117	15	390	94.5	97.3
N.U.R.D.D. Pilot Machine ^d	143	131	24	246	94.4	96.0

^a

Based on pt./100 lb.

^bBased on breaking length.

^cBased on breaking length vs. dry control.

^dBased on average of cross and machine-direction data.

The small fluorescence size time with bleached kraft fibers for the handsheet and Pilot Machine papers was shown to be a consequence of not removing the fines from the kraft fiber (23). It is not due to starch xanthide by itself. The lack of a measurable fluorescence size time with the Continuous Web Former paper probably is due to it having been necessary to use sodium oleate for a release agent on the single drier of that machine (24). A small amount of surface-active agent would be expected to cover up such a small degree of sizing.

The standard deviations of the test data have been calculated on the basis of the range of the individual tests. The magnitude of the standard deviation is not greatly affected by the size of the equipment used to make the paper. However, the variability of the xanthide handsheet folding test is about twice as large as found for similar folding endurances obtained with the Web Former and the Pilot Machine.

The laboratory procedures developed for using ex situ starch xanthide in handsheets appear to reflect adequately the properties that can be expected in relatively large-scale paper machine production. Preliminary product development can be carried out with handsheets by prospective users of starch xanthide in paper.

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George E. Lauterbach

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

Edward J. Jones

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

John W. Swanson

John W. Swanson, Chairman
Physical Chemistry Section