

# Starch Polyampholytes with Amine and Xanthate Substituents: Characterization and Application

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## Synopsis

Starch polyampholytes (xanthated starch amines) that contained either diethylaminoethyl or 2-hydroxypropyltrimethylammonium ether and xanthate substituents were prepared, characterized, and evaluated as wet- and dry-strength agents in paper handsheets. In aqueous solutions, these xanthated starch amines (XSA), which had degrees of substitutions (D.S.) of 0.023–0.33 amine and 0.005–0.165 xanthate, underwent intra- and interionic bonding at their isoelectric points to form soft flocculent precipitates. Properties of XSA resembled those of “complex coacervates.” Paper that was prepared from an unbleached kraft furnish treated with XSA (amine/xanthate molar ratios, from 1.5 to 4.0) had significantly stronger wet and dry strengths than paper treated with cationic starch amines typically used in commercial papermaking.

## INTRODUCTION

Since about 1960, interest has steadily grown in the unique properties and practical applications of polyionic “complexes,” which can be formed readily in aqueous media by reaction of their oppositely charged polyions.<sup>1–13</sup> A polyelectrolyte complex (PEC) is typically insoluble but swollen in aqueous electrolyte solutions, chemically stable, and essentially stoichiometric in polyionic reaction (i.e., cation/anion molar ratio approaches 1.0). In contrast, a complex coacervate usually involves a polyampholyte with nonstoichiometrically reacted polyions and has physical properties easily affected by such variables as pH, temperature, and electrolytes. However, certain polyionic complexes cannot be easily categorized as either a typical coacervate, e.g., gelatin–gum arabic, or a PEC, e.g., complex formed from sodium poly(styrene sulfonate) and poly(vinylbenzyltrimethylammonium) chloride. Apparently, such complexes include either cellulose or starch xanthate with polyethylenimine and starch xanthate with a polyamide–polyamine–epichlorohydrin resin.<sup>3–5</sup> When conditions are appropriate, the xanthate–amine complexes may be induced to increase solution viscosity, gel, and precipitate and, in some instances, react stoichiometrically. We have reported the application of the starch xanthate–polyamine complexes as paper-strengthening agents.<sup>6,7</sup>

Several patents have been issued, between 1969 and 1974, describing various starch polyampholytes that have utility in paper and textile products.<sup>8–13</sup> Apparently, paper wet strength has not been previously developed from starch polyampholytes through ionic bonding. In efforts to develop a polyanion–polycation complex involving low-cost starch xanthates that would require only a one-step application procedure of the complex components, we prepared, characterized, and evaluated “xanthated starch amine (XSA)” polyampholytes. The cationic substituents of XSA were diethylaminoethyl [ $-\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$ ]

and 2-hydroxypropyltrimethylammonium [ $-\text{CH}_2\text{CHOHCH}_2\text{N}^+(\text{CH}_3)_3$ ] attached through ether linkages. The effectiveness of these XSA polyampholytes as wet-end additives for improving paper wet strength as well as dry strength of unbleached kraft paper handsheets is reported.

## RESULTS AND DISCUSSION

### XSA Polyampholyte Characteristics

**Isoelectric Point Precipitation.** An XSA polyampholyte was prepared that had an amine (quaternary ammonium) degree of substitution (D.S.) of 0.072 and a xanthate D.S. of 0.060. When pH of a 0.05% aqueous solution of this XSA (original pH 10.8) was adjusted to 5.7, a flocculent precipitate was formed. This pH was the isoelectric point (IP) of XSA as indicated by a streaming current detector. The precipitate slowly dissolved when pH was adjusted either higher (e.g., 10) or lower (e.g., 4) than 5.7 but could then be completely reprecipitated at the IP. Whereas the XSA precipitated nearly quantitatively from a 0.05% solution, it did not precipitate completely from a 1% solution. At 5.0% concentration, thickening but no precipitation occurred. With XSA concentrations between 0.005% and 1%, the IP values did not change.

By gradually decomposing the xanthate substituent of XSA (D.S. 0.072 quaternary amine, 0.060 xanthate), which was accomplished by lowering the XSA solution pH momentarily to 2–4, the IP values increased correspondingly. Salt, which accumulated from use of HCl and NaOH in repetitive reprecipitations of XSA, decreased the IP values. When 5% XSA solutions were diluted to 0.05% with 0.1*N* solutions of NaOH, NaCl, or KBr, cloudiness but no precipitation occurred at the IP. This ionic suppression of XSA precipitation by salts appeared to be minimum at the lowest XSA concentration investigated (0.01%).

The above XSA characteristics were basically representative for all thirty XSA polyampholytes that were prepared for this study. These polyampholytes included XSA that had amine D.S. from 0.023 to 0.330 and xanthate D.S. from 0.005 to 0.165.

**Ionic Substituents.** The relationships of cation substituent type and amine/xanthate ratio (A/X ratio) to IP of XSA were determined (Fig. 1). At a given A/X ratio, a change in amine D.S. from 0.023 to 0.330 did not significantly raise the IP. Also, at a given A/X ratio, XSA with the quaternary group (D.S. 0.072) had higher IP values than XSA with the tertiary amine group, which would be an advantage in forming insoluble complexes under alkaline conditions. The A/X ratios, particularly between about 1 and 3, sharply affected the IP values.

**Solution Temperature.** Temperatures of XSA (e.g., D.S. 0.023 amine, 0.013 xanthate) solutions between 15° and 50°C did not appreciably affect their IP values (Table I). The change in IP from 9.1 to 9.6 that resulted from increasing the temperature from 15° to 50°C was attributed to decomposition of about 30% xanthate as evidenced by ultraviolet (UV) spectroscopy. Conversely, cooling the sample from 50° to 25°C had no effect on IP of XSA.

**Salt.** Table I illustrates the effect of adding NaCl to XSA (D.S. 0.023 amine, 0.013 xanthate) solutions. The lowest and highest salt concentrations, 1.6 and 33.0 moles/mole of XSA [starch anhydroglucose unit (AGU) basis], lowered the IP value from 9.1 to 7.5 and 4.5, respectively.

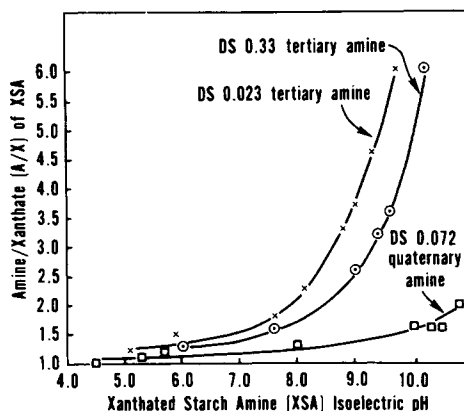


Fig. 1. Effect of xanthate and amine substituents on isoelectric point of xanthated starch amine (XSA). Solutions at 0.05% concentration and 25°C.

TABLE I  
Change in Isoelectric Point of Xanthated Starch Amine (XSA)<sup>a</sup> with Temperature and NaCl Concentration

Temperature, °C	Moles of NaCl/mole XSA (0.05% XSA solutions, starch basis) <sup>b</sup>	Isoelectric point pH
15	0	9.2
25	0	9.1
50	0	9.6 <sup>c</sup>
25	1.6	7.5
25	3.3	6.7
25	8.2	6.0
25	16.5	5.5
25	33.0	4.5

<sup>a</sup> XSA (D.S. 0.023 tertiary amine, 0.013 xanthate) solutions contained 0.4 mole NaOH/mole starch AGU. NaOH was used in the xanthation procedure.

<sup>b</sup> NaCl molarities were 0.005, 0.001, 0.025, 0.05, and 0.10 for values 1.6–33.0.

<sup>c</sup> Change in isoelectric pH from 9.1 to 9.6 was due to slight xanthate decomposition occurring at 50°C.

The XSA polyampholytes did not precipitate completely at their IP values as a result of excessive salt content of their solutions. This effect of salt on precipitation was greatly accentuated at relatively high XSA concentrations. For example, when 5% XSA solutions contained 16.5 moles NaCl (per mole XSA), the XSA polyampholytes would not precipitate at any pH.

### Chemical Properties

**Cation–Anion Interaction.** Analytical data of two XSA polyampholytes, D.S. 0.072 quaternary amine, 0.045 xanthate, and D.S. 0.110 tertiary amine, 0.042 xanthate, indicated that only ionic interaction occurred in formation of XSA precipitated complexes (Table II). At their IP values, these polyampholytes were precipitated nearly quantitatively from 0.05% solutions. Supernatants of the precipitated complexes contained approximately 4 to 6% of the original starch and only traces of xanthate.

When XSA complexes were redissolved in 0.1N NaOH, immediately after they

TABLE II  
Characterization and Analyses of Precipitates from Freshly Prepared Xanthated Starch Amine (XSA)

Degree of substitution (D.S.)		Precipitates			
Xanthate	Amine	Isoelectric point pH	Yield, %	D.S. <sup>a</sup>	
				Xanthate	Amine
0.045	0.072 (quaternary)	10.3	94 <sup>b</sup>	0.043	0.07
0.042	0.110 (tertiary)	9.6	92	0.040	0.11

<sup>a</sup> Precipitates were dissolved in 0.1N NaOH to determine D.S. by UV spectroscopy.

<sup>b</sup> Yields are starch basis.

were precipitated at the IP, their xanthate contents were essentially unchanged. These data are substantially representative of all the XSA complexes investigated.

**Stability.** Xanthate groups are characteristically labile under a variety of conditions and release CS<sub>2</sub> during decomposition.<sup>14</sup> The rate of CS<sub>2</sub> decomposition is affected by factors such as solvent, pH, temperature, ionic environment, and chemical nature of the xanthated molecule. Our XSA polyampholytes were routinely stored as 5% aqueous solutions at pH 12 and 1°C. Table III illustrates the XSA stabilities under these and other conditions.

The rate of xanthate decomposition that is shown for the routine storage condition was significantly lowered by storing XSA as a powder (90% solids) at 1°C. Apparently, polyionic crosslinking of XSA does not provide a means for significantly improving stability of the xanthate group at conditions investigated.

Infrared and UV spectroscopy of XSA samples aged 6 months at 1°C gave no evidence that chemical reactions had occurred other than loss of xanthate as CS<sub>2</sub>.

TABLE III  
Stability of Xanthated Starch Amine (XSA)

Sample	Amine D.S. <sup>a</sup>	Age, days <sup>b</sup>	Xanthate degree of substitution (D.S.)			
			5% Solution		90% Solid <sup>c</sup>	
			25°C	1°C	25°C	1°C
1	0.023	0.5	0.013	0.013	— <sup>d</sup>	—
		5	0.005	0.009	0.008	0.010
2	0.110	0.5	0.035	0.035	0.033	0.034
		5	0.018	0.024	—	—
		0.5	0.077	0.077	0.072	0.072
3 <sup>e</sup>	0.110	49	—	0.015	—	0.057
		84	—	—	—	0.044
4	0.072	0.5	0.045	0.045	0.045	0.045
		45	—	—	0.011	0.030

<sup>a</sup> Sample numbers 1–3 = tertiary amine group; sample 4 = quaternary amine group.

<sup>b</sup> Xanthate D.S. of 0.5-day-old XSA samples are original D.S.

<sup>c</sup> Precipitates obtained by adjusting pH of 0.05% XSA solutions to the XSA isoelectric points.

<sup>d</sup> Xanthate D.S. not analyzed.

<sup>e</sup> The solid was XSA freeze-dried at 5% concentration (pH 12.5).

### Paper Application

**Internal Bonding Strength.** A preliminary evaluation of XSA polyampholytes as wet-end additives in unbleached kraft paper handsheets showed that they not only improved dry strength of paper considerably over that obtained using the nonxanthated starch amine (SA) but also imparted wet strength, a property not developed by starch amine groups alone (Table IV). Addition of 3% XSA (D.S. 0.11 tertiary amine, 0.077 xanthate) oven-dry (o.d.) pulp-weight basis to furnish kept at pH 7 improved dry tensile and burst strengths about 55% and 75%, respectively, over the untreated control. Wet strength increased six-fold. These strength improvements compare to 37% dry tensile (54% burst) and no wet-strength increases obtained using either the experimental or commercial cationic starch amines.

Addition of 3% XSA that contained the quaternary amine (D.S. 0.072 amine, 0.065 xanthate) improved dry-tensile strength by 60%, burst by 84%, and wet-tensile strength about 8.5-fold. Surprisingly, XSA imparted a permanent-type wet-strength bond to paper (distilled or tap water soaking). This wet strength, however, was reduced with exceptional ease under warm alkaline conditions.

**pH.** Maximum wet and dry strengths of paper were obtained when pH of the pulp furnish was 7.0, regardless of IP values of XSA. Furnish pH values from 5 to 9 were investigated. Original IP values of XSA ranged from about 5 to 10.

**Xanthate D.S.** At a constant amine D.S., a change in xanthate D.S. that corresponded to a change in A/X ratio from about 1.5–2 did not significantly affect the strength performance of XSA in paper. For example, an XSA with a tertiary amine D.S. 0.11 had an initial xanthate D.S. 0.077 and, after storage, a D.S. 0.057 (freeze dried, stored 49 days at 1°C). This loss of xanthate D.S. did not appreciably affect the performance of the XSA in paper (Table IV). However, when the xanthate substituent of this stored sample was reduced to a trace by acid treatment (pH 2), performance of the sample in paper was reduced to that of the starch amines.

**Drying Temperature.** Paper treated with 3% XSA (D.S. 0.11 tertiary amine, 0.057 xanthate) that was air dried at 23°C (50% relative humidity) had an additional wet-strength increase of 32% (breaking length of 1330 meters increased

TABLE IV  
Xanthated Starch Amine (XSA) in Unbleached Kraft Handsheets

Additive (3%, oven dry pulp basis)		pH		Burst factor, (g/cm <sup>2</sup> )/(g/m <sup>2</sup> )	Tensile breaking length, meters	
D.S. Amine	D.S. Xanthate	Isoelectric point	Handsheets furnish		Dry	Wet
No additive			7.0	43.8	6,800	200
Commercial starch amine			5.5, 7.0	69.1, 67.2	9,600, 9,320	225
0.11 <sup>a</sup>	0		5.5, 7.0	68.0, 67.7	9,450, 9,120	225
0.11	0.077	6.1	6.1, 7.0	74.0, 76.6	10,100, 10,560	1,050, 1,230
0.072 <sup>a</sup>	0		7.0	69.6	9,632	225
0.072	0.065	5.3	7.0	80.4	10,880	1,725
0.11 <sup>b</sup>	0.057	7.1	7.0	76.0	10,760	1,330
0.11 <sup>c</sup>	Trace		7.0	70.0	9,500	300

<sup>a</sup> All D.S. 0.11 = tertiary amine; D.S. 0.072 = quaternary amine.

<sup>b</sup> Freeze-dried XSA stored 49 days at 1°C.

<sup>c</sup> Acid-treated (pH 2) freeze-dried XSA.

to 1750 meters) when oven dried at 105°C for 30 min. The dry-strength increase from about 66% to 71% over the untreated control was not appreciably greater than the effect of oven drying SA-treated paper.

**Repulpability.** Paper wet strength imparted by XSA was easily removed under mild alkaline conditions, greatly facilitating paper recycling. For example, wet strengths imparted by XSA were completely destroyed by soaking the papers in 0.025*N* NaOH at 83°C for 30 min.

**XSA Paper-Strengthening Mechanisms.** It is proposed that some of the wet strength of XSA-treated paper results from crosslinking between cationic nitrogen groups and anionic xanthate groups  $[-C(S)S^- - \pm N \leq]$  of the XSA polyampholyte complex intimately sorbed into and around interfiber bonding areas. However, when xanthates *per se* (e.g., sodium ethyl xanthate and sodium starch xanthate) were heated at 100°C (or above), carbonyl sulfide (COS) as well as carbon disulfide (CS<sub>2</sub>) was isolated. The evolution of COS from xanthates under paper-drying conditions suggests that secondary rearrangement reactions could contribute to wet strength of XSA-treated paper.

A preliminary study of additive retention in the handsheets indicated that superior dry-strength improvement imparted by XSA over SA was a result of higher retention of the XSA as well as its superior enhancement of interfiber bonding.

## EXPERIMENTAL

### General

A streaming current detector (Model 65), manufactured by Waters Associates, Inc., was used to determine the IP values of XSA. Either NaOH or HCl was used to adjust pH of XSA solutions (generally, 0.05% concentration) to obtain the IP values. A Beckman spectrophotometer (Model DB) and recorder were used to determine xanthate ( $\lambda_{\max}^{\text{H}_2\text{O}}$  305 nm,  $\epsilon$  17,000) D.S. of XSA. Nitrogen, sulfur, chloride, and starch were determined by the methods of Kjeldahl, White (sulfur and chloride),<sup>15</sup> and Munson-Walker,<sup>16</sup> respectively.

### Cationic Starch Amines (SA)

The procedure for preparation of the parent SA of XSA is exemplified by preparation no. 1 (Table V) as follows: To 32.0 g (o.d. basis) of unmodified pearl corn starch in a three-necked round-bottomed flask equipped with stirrer, condenser, and thermometer was admixed (1) 46 ml distilled H<sub>2</sub>O, (2) 12 g Na<sub>2</sub>SO<sub>4</sub>, (3) 5 ml 10% NaOH, and (4) 0.69 g 2-chlorotriethylamine hydrochloride dissolved in 10 ml H<sub>2</sub>O. The mixture was heated at 55°C for 6 hr, cooled to 25°C, and allowed to stand overnight before isolation of the product. By centrifugation-decantation procedures, the product was washed four times (each with 200 ml H<sub>2</sub>O), filtered, and washed successively with ethanol, hexane, and ether. The product contained 0.20% nitrogen, corresponding to an amine D.S. of 0.023.

Table V shows the amounts of materials that were added to 32.0 g (o.d. basis) of starch products used in preparation of other SA products (preparation numbers 2-5) and the corresponding product analyses. The exemplified procedure was followed throughout, except that SA of D.S. 0.110, 0.072, and 0.33, which

TABLE V  
Preparation of Experimental Starch Amines (SA)<sup>a</sup>

Preparation no.	Reaction mixture				Cationic reactant, <sup>b</sup> g	Product	
	Water, ml	Na <sub>2</sub> SO <sub>4</sub> , g	10% NaOH, ml	Nitrogen, %		D.S.	
1	46	12	5	0.69	0.20	0.023	
2	45	12	6	1.4	0.30	0.035	
3	37	12	14	4.1	0.89	0.110	
4	35	25	25	16.5	2.39	0.330	
5	37	12	14	4.1	0.60	0.072	

<sup>a</sup> Used 32.0 g (oven dry basis) unmodified pearl corn starch in all preparations.

<sup>b</sup> 2-Chlorotriethylamine hydrochloride (preparation numbers 1–4); 3-chloro-2-hydroxypropyltrimethylammonium chloride (preparation number 5).

were too swollen to be washed by centrifugation–decantation (or by filtration) procedures, were dialyzed and then precipitated in ethanol. The product of preparation no. 5 (Table V) is the SA derivative of starch and 3-chloro-2-hydroxypropyltrimethylammonium chloride (M-1 monomer, 52% by weight, Story Chemical Corporation).

### XSA

All XSA polyampholytes were prepared in the following manner. The SA (2.5 g o.d. basis) was (1) slurried in 28 ml H<sub>2</sub>O plus 5 ml 5% NaOH, (2) heated to 50°C for 10 min, (3) cooled to 35°C, and (4) xanthated by pipetting CS<sub>2</sub> (ranging in amounts from 0.01 ml to 0.3 ml for xanthate D.S. from 0.005 to 0.165) beneath the surface of the SA dispersion. After 1 hr, the XSA dispersion was diluted to 5% concentration and stored 16 hr at 34°C before analyses and evaluation of XSA as a paper-handsheet additive. The UV monitoring of portions of the XSA dispersion (diluted in 0.1N NaOH) showed that xanthation was 90% or more complete within 1 hr after CS<sub>2</sub> addition.

### Paper Handsheets

The preparation of paper handsheets containing (1) XSA, (2) the parent SA, and (3) commercial cationic starch is exemplified as follows: To a 1750-g pulp slurry (15.0 g, o.d. basis, of unbleached kraft pulp in tap water—560 ml Canadian Standard freeness), under good agitation, was added 45 ml of 1.0% starch product dispersion in about 1 min. After 2 additional minutes of mixing, the pH of the treated furnish was adjusted with 10% H<sub>2</sub>SO<sub>4</sub>. Then, the furnish was diluted with tap water to 0.24% consistency, and 1.2-g (60 g/m<sup>2</sup>) handsheets were prepared and tested according to TAPPI Standard Methods,<sup>17</sup> except that wet-tensile test strips were soaked 30 min (distilled H<sub>2</sub>O).

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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