

# INFLUENCE OF PREPARATIVE VARIABLES ON INTRINSIC VISCOSITIES AND SEDIMENTATION VALUES OF PERIODATE-OXIDIZED STARCHES<sup>1</sup>

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## ABSTRACT

A study was made on the effects of reaction conditions and isolation techniques on solution properties of periodate-oxidized corn starch having from 5 to 96% of the anhydroglucose units oxidized to the dialdehyde structure. Samples were prepared for viscosity and ultracentrifugal studies by dispersion in 0.5N potassium hydroxide containing 25% (w/v) urea after the aldehyde groups were reduced with potassium borohydride to the corresponding primary alcohols. The polyol thus formed is stable toward alkali.

On the basis of measurements of solubility, sedimentation velocity, and intrinsic viscosity, the effects of preparative variables on particle size may be summarized thus: Cross-linking occurred during oxidation of granular starch and was most extensive at intermediate levels of oxidation. More cross-linking occurred at a reaction temperature of 35°C. than at 1°C. Less cross-linking occurred during oxidation of pasted starch than of granular starch. Drying at 105°C. instead of at room temperature caused little degradation. Granular, 96%-oxidized starch became cross-linked when treated at pH's less than 4, but degraded at higher pH's. This degradation was shown to reduce the efficacy of oxidized starch as a wet-strength additive in paper.

A previous report from this laboratory (1) described a procedure for dispersing dialdehyde starch (DAS) in alkaline urea after reduction to the polyol with borohydride to impart alkali stability. Application of this procedure revealed wide variations in the solubility of polyols from DAS samples and, hence, variations in molecular size of parent DAS samples. For example, polyols from starches with 5% of their anhydroglucose units oxidized to the dialdehyde structure have exhibited solubility ranging from 16 to 87% under the dispersing conditions.

During periodate oxidation of starch and subsequent isolation of the resulting DAS, a variety of environmental conditions can exist that would permit several known reactions to occur, either separately or in various combinations. During oxidation, which is performed under mildly acidic conditions, both cross-linking due to intermolecular reactions and chain scission due to hydrolysis are possible (2). During washing of DAS to remove spent reagent, a wide range of pH's can be

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encountered. If alkaline tap water were used, for example, degradation of DAS would be expected (3). To determine the causes of variation in molecular size, a study was made of the effects of reaction conditions and isolation techniques on solution properties of reduced DAS.

### Materials and Methods

*Periodate-Oxidized Starches.* Samples of different levels of oxidation were prepared from commercial pearl corn starch in both pasted and granular form by oxidation with paraperiodic acid. Oxidations were conducted at 1°C., pH 3.5, to provide conditions reported to minimize side reactions (4) and at 35°C., pH 1.5, to provide conditions recommended for commercial production (5). Paste-oxidized samples were purified by dialysis against distilled water and isolated by lyophilization. Granule-oxidized samples were filtered, washed with either distilled water, pH 6.5, or tap water, pH 7.5, and dried at either room temperature or 105°C.

*Analytical Methods.* Degree of oxidation was determined by the borohydride procedure (6). Viscosity and sedimentation samples were dispersed in 0.5*N* potassium hydroxide containing 25% (w/v) urea after they had been reduced to the polyol with potassium borohydride to impart alkali stability (1). Undispersed material was removed by centrifugation at  $2,500 \times g$  for 30 min., and the amount was determined gravimetrically (1). Some products appeared to be cross-linked, as indicated by partial insolubility under these conditions. Intrinsic viscosity was determined at 25°C. with Cannon-Fenske No. 100 viscometers (7). Kinetic energy corrections were not applied.

Sedimentation patterns were obtained with a Spinco Model E ultracentrifuge<sup>2</sup> equipped with a 30-mm. double-sector plastic centerpiece. The sample at 0.5% concentration was in one sector, and the solvent was in the other. The base line on each photograph facilitated pattern area measurements, which were used in calculating concentration of the sample in the cell during centrifugation (8). The centrifuge was operated at either 12,590 or 47,660 r.p.m. Sedimentation coefficients were measured by a method of Svedberg (9) and are expressed in Svedberg units (S).

### Results and Discussion

Pasted starch was oxidized with periodate at 1°C. to 5, 47, and 87% oxidation, and the products were reduced and dispersed as indicated above. Data in Table I show a progressive decrease in particle size

<sup>2</sup>Mention of firm names or trade products is for identification only and does not imply endorsement by the U.S. Department of Agriculture.

TABLE I  
 PROPERTIES OF POLYOLS FROM PASTE-OXIDIZED STARCHES PREPARED AT 1°C.

LEVEL OF OXIDATION <sup>a</sup>	INSOLUBLES <sup>b</sup>	INTRINSIC VISCOSITY	SEDIMENTATION COEFFICIENT	FRACTION IN CENTRIFUGE PEAK <sup>c</sup>
%	%	dL/g.	S	%
0 <sup>d</sup>	< 1	1.44	2.9	20
5	12	1.35	41	43
47	< 1	0.68	22	67
87	< 1	0.51	18	100

<sup>a</sup> Percentage of anhydroglucose units oxidized to dialdehyde structure.

<sup>b</sup> Percentage of material removed by centrifugation at  $2,500 \times g$  for 30 min.

<sup>c</sup> Percentage of solubles.

<sup>d</sup> Unmodified starch, dispersed in the same manner as the oxidized starches.

with increasing oxidation. The incomplete solubility of the 5% sample is evidence of cross-linking, since unmodified starch is completely soluble under these conditions. These data substantiate an earlier report that both chain scission and cross-linking occur during periodate oxidation of pasted starch (2).

Area analysis of ultracentrifugal patterns gave further evidence that particle size decreased with increasing level of oxidation. At 5, 47, and 87% oxidation, 43, 67, and 100% of the samples, respectively, appeared in the peak. Material not accounted for is assumed to be too small to be centrifuged out at  $2,500 \times g$  (insolubles) but large enough to migrate to the bottom of the centrifuge cell before the pattern was photographed.

Granular starch was oxidized at 1°C. and washed with distilled water, and portions were dried both at room temperature and at 105°C. Reduction with borohydride followed by dispersion in potassium hydroxide-urea yielded the data in Table II. The low solubility of the

TABLE II  
 SOLUBILITY OF POLYOLS FROM GRANULE-OXIDIZED STARCHES PREPARED AT 1°C., WASHED WITH DISTILLED WATER

LEVEL OF OXIDATION	DRYING AT ROOM TEMPERATURE	DRYING AT 105°C.
%	%	%
5	44	37
42	83	66
87	1 <sup>a</sup>	0 <sup>b</sup>

<sup>a</sup> Intrinsic viscosity 0.67.

<sup>b</sup> Intrinsic viscosity 0.62.

5 and 42% samples indicates that cross-linking occurred. At the 87% level, the granule-oxidized samples are similar to the corresponding paste-oxidized sample in Table I. Comparison of the two columns of data shows that little chain scission occurred when the samples were dried at 105°C. instead of at room temperature.

An unoxidized "control" sample was prepared by stirring an aqueous slurry of granular starch for 48 hr. at pH 3.8 with 1.5 moles of sodium iodate per mole of anhydroglucose units. When this sample was dispersed in the same manner as the oxidized starches, less than 1% of it was insoluble as defined in Table I, and the intrinsic viscosity was 1.43. The sedimentation coefficient was 3.0, and the peak contained 33% of the sample. Compared with the unmodified starch (Table I), this sample had a slightly lower intrinsic viscosity and contained more low-molecular-weight material in the amylose fraction. Thus, a small amount of chain scission occurred at pH 3.8 in the absence of oxidation.

Granular starch was also oxidized at 35°C. to four levels of oxidation, and each product was divided into two portions. One portion was washed with distilled water as were the products in Table II, and the other was washed with tap water at pH 7.5 (Table III). The solu-

TABLE III  
TAP-WATER WASHING COMPARED WITH DISTILLED-WATER WASHING OF GRANULE-  
OXIDIZED STARCHES PREPARED AT 35°C. AND DRIED AT ROOM TEMPERATURE<sup>a</sup>

LEVEL OF OXIDATION	DISTILLED WATER		TAP WATER	
	Insolubles		Intrinsic Viscosity	
%	%	%	dl./g.	
5	66	<1	0.42	
40	74	<1	0.56	
62	79	1	0.08	
84	55	<1	0.08	

<sup>a</sup>Data obtained after reduction with borohydride and dispersion in alkaline urea.

bility of distilled water-washed products in alkaline urea after reduction is similar to that of granule starches oxidized at 1°C. (Table II), except at the highest level of oxidation where the higher oxidizing temperature resulted in partial insolubility.

The tap water-washed samples after reduction were essentially completely soluble in alkaline urea. The increase in solubility and the low viscosities, especially at the two higher levels of oxidation (Table III), show degradation resulting from alkalinity of the tap water. Ultracentrifugal patterns indicated that these samples contained particles ranging from those which did not migrate away from the meniscus to those which sedimented to the bottom of the centrifuge cell. Heterogeneity was so great in the 40- and 62%-oxidized samples that no peak appeared in the pattern. The area in the other patterns accounted for only a portion of the total sample.

The effect of pH on periodate-oxidized starch was further studied

in a more definitive way. Granular starch, 96% oxidized at 1°C., pH 3.5, was washed with distilled water and dried at room temperature. Portions were suspended at room temperature for 24 hr. at pH's ranging from 1.0 to 6.9. Clark and Lubs buffer was used for pH 1.0; McIlvaine buffers, for pH's 2.0 to 6.9 (10). The samples were washed with distilled water until free of buffer and dried at room temperature. The samples that were completely dispersed by alkaline urea after borohydride reduction exhibited the viscosities given in Fig. 1. The sample

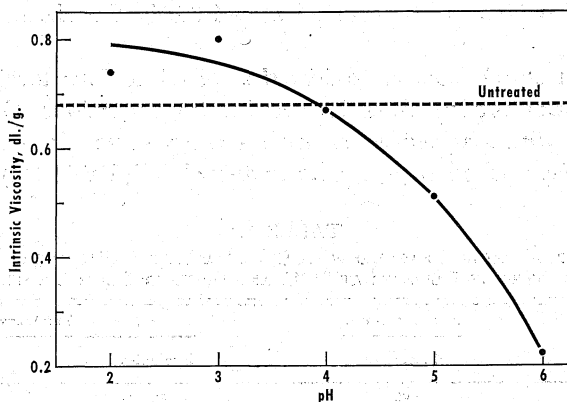


Fig. 1. Effect of pH treatment on intrinsic viscosity of 96% granule-oxidized starch prepared at 1°C., pH 3.5. Viscosity determined after reduction with borohydride and dispersion in alkaline urea.

that had been treated at pH 4.0 maintained essentially the same intrinsic viscosity as untreated oxystarch. At pH's less than 4, increased viscosity gave evidence of cross-linking until at pH 1 (not shown) 14% of the sample was insoluble; i.e., it centrifuged out at  $2,500 \times g$ . At pH's greater than 4, the predominant effect was chain scission, as shown by a progressive decrease in viscosity with increasing pH. At pH 6.9, the oxidized starch dissolved in the buffer and could not be recovered for viscosity studies. Sedimentation data on these samples was not informative, because only about half of each sample appeared in the peak and all of the sedimentation coefficients were in the neighborhood of 2S.

To determine whether these findings might have practical significance, samples treated at pH 2 and pH 6 were evaluated as paper additives to determine their efficacy in imparting wet strength. They were dispersed with betaine hydrazide hydrochloride and applied at a 2.5% level of addition to an unbleached softwood sulfate pulp with S.R. freeness of 700 ml. (11). Dispersion times in betaine hydrazide

TABLE IV  
EFFECT OF pH TREATMENT ON EFFICACY AS A WET-STRENGTH  
PAPER ADDITIVE IN CATIONIC DISPERSIONS

SAMPLE		Dispersion Time.	WET BREAKING LENGTH <sup>a, b</sup>
pH			
		<i>min.</i>	<i>m.</i>
2		25	2,300
2		35	2,560
2		45	2,510
6		25	1,860
6		35	1,650
6		45	1,730

<sup>a</sup> After immersion of paper in distilled water at room temperature for 30 min.

<sup>b</sup> Wet breaking length of control paper without additive was 230 m.

hydrochloride at 92°C. were 25, 35, and 45 min. The resulting paper sheets had the wet tensile strengths given in Table IV. These data show that the pH 2 samples were comparable with similar materials reported by Hamerstrand and co-workers (11). Treatment at pH 6, which was shown in Fig. 1 to cause chain scission, resulted in a significant decrease in wet strength. Thus, the data show that practical advantages can result from the use of conditions that minimize chain scission.

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#### Literature Cited

- SCHAEFER, W. C., MAURICE, JUDITH J., RUSSELL, C. R., and RIST, C. E. Intrinsic viscosity of dialdehyde starch in alkaline urea after reduction with borohydride. *Cereal Chem.* **39**: 304-310 (1962).
- LEVINE, S., GRIFFIN, H. L., and SENTI, F. R. Solution properties of dialdehyde starch. *J. Polymer Sci.* **35**: 31-42 (1959).
- WHISTLER, R. L., and BEMILLER, J. N. Alkaline degradation of polysaccharides. *In Advances in carbohydrate chemistry*, ed. by M. L. Wolfrom and R. S. Tipson; vol. 13, pp. 289-329. Academic Press: New York (1958).
- SLOAN, J. W., HOFREITER, B. T., MELLIES, R. L., and WOLFF, I. A. Properties of periodate oxidized starch. *Ind. Eng. Chem.* **48**: 1165-1172 (1956).
- PFEIFER, V. F., SOHNS, V. E., CONWAY, H. F., LANCASTER, E. B., DABIC, S., and GRIFFIN, E. L., JR. Two-stage process for dialdehyde starch using electrolytic regeneration of periodic acid. *Ind. Eng. Chem.* **52**: 201-206 (1960).
- RANKIN, J. C., and MEHLTRETTER, C. L. Determination of dialdehyde units in periodate-oxidized corn starches. *Anal. Chem.* **28**: 1012-1014 (1956).
- CANNON, M. R., and FENSKE, M. R. Viscosity measurement. *Ind. Eng. Chem., Anal. Ed.* **10**: 297-301 (1938).
- SCHACHMAN, H. K. Ultracentrifugation, diffusion, and viscometry. *In Methods in enzymology*, ed. by S. P. Colowick and N. O. Kaplan; vol. 4, p. 57. Academic Press: New York (1957).
- SVEDBERG, T., and PEDERSON, K. O. *The ultracentrifuge*. Clarendon Press: Oxford (1940).

10. LANGE, N. A. Handbook of chemistry (8th ed.), pp. 938-940. Handbook Publishers, Inc.: Sandusky, Ohio (1952).
11. HAMERSTRAND, G. E., HOFREITER, B. T., KAY, D. J., and RIST, C. E. Dialdehyde starch hydrazones — cationic agents for wet-strength paper. *Tappi* **46**: 400-404 (1963).

