

PERMANGANATE OXIDATION OF CORN STARCH¹

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ABSTRACT

The production of functional groups in corn starch by permanganate oxidation has been investigated under both acidic and alkaline conditions. The effect of increasing permanganate oxidation levels on the degree of formation of carbonyl and carboxyl groups was determined with starch at pH 1 and 25°–27°C. and at pH 9–11 and 2°–4°C.

Pasting characteristics of aqueous dispersions of the neutralized oxystarches were observed on the recording Corn Industries Research Foundation viscometer. High initial viscosities were obtained, which declined irreversibly on further heating. The final low viscosities indicated existence of unstable groupings in the oxystarches, which influence polymer degradation under the conditions of pasting. Ultracentrifugal sedimentation of various oxystarches dispersed at 98°C. showed a broad distribution of molecular weights with a considerable proportion in a low-molecular-weight range.

Starch was oxidized by potassium permanganate as early as 1868 (12). Between the years 1890 and 1933 a number of patents were issued that disclosed the preparation of soluble starch by permanganate oxidation under various conditions of reaction (1,3,13,14,19). Such oxidized starches apparently were degraded sufficiently to produce aqueous dispersions of stable fluidity for use as textile-sizing agents.

Permanganate is generally recognized as a nonspecific oxidant. However, under carefully controlled conditions, it has been utilized for converting a large proportion of the primary alcohol groups in methyl glucoside, monoacetone glucose (2), and soluble starch (10) to carboxyl groups for the preparation of *D*-glucuronic acid. It was also observed earlier by Pictet and Cramer (11) with beta-glucosan and by Karrer and Hurwitz (4) with diacetone glucose, that the secondary alcohol groups were not readily oxidized by a neutral solution of potassium permanganate.

Despite the past interest in the permanganate oxidation of starch, little is known about the amount and nature of the functional groups produced by such oxidation under various conditions of reaction. Therefore, the course of the oxidation of starch by permanganate was investigated, and some of the physical properties were determined of the oxystarches produced under pH- and temperature-controlled reaction conditions.

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Materials and Methods

Commercial pearl corn starch was oxidized with reagent-grade potassium permanganate under acid and alkaline conditions.

Acid Oxidation of Corn Starch. A representative permanganate oxidation of starch at pH 1 was conducted as follows: Corn starch, 162 g. d.b. (1.0 mol.), was suspended in 500 ml. of distilled water and the pH of the slurry was adjusted to 1 with 6*N* sulfuric acid. The slurry was stirred mechanically while a solution of 13.68 g. of potassium permanganate (0.216 g. atom of available oxygen) in 200 ml. of water was added dropwise during 15 min. The temperature was maintained at 25°–27°C. and the pH held at 1 by the addition of 6*N* sulfuric acid. Manganese dioxide appeared a few minutes after addition of permanganate began. After 2 hours' reaction, the manganese dioxide was reduced by adding a small amount of sodium metabisulfite solution. The snow-white oxystarch was filtered and washed free of sulfate and manganous ions. It was then allowed to equilibrate at laboratory humidity and temperature.

Alkaline Oxidation of Corn Starch. A representative alkaline oxidation was conducted as follows: To 162 g. of corn starch, d.b. (1.0 mole), in 300 ml. of distilled water maintained at 2°–4°C. in an ice-salt bath 6*N* sodium hydroxide was added to a pH of 10. A solution of 9.12 g. of potassium permanganate (0.087 g. atom of available oxygen) in 300 ml. of water was added dropwise in 50 min. Manganese dioxide was formed shortly after permanganate addition began. The pH was kept at 10 during the 3-hr. reaction by adding 6*N* sodium hydroxide. Then the pH was adjusted to 3 with 6*N* sulfuric acid and sodium metabisulfite solution added, along with additional sulfuric acid to maintain a pH of 3, to convert manganese dioxide to manganous sulfate. The white oxystarch was washed free of sulfate ions and dried as described.

The filtrates from the acid and alkaline reactions contained strongly reducing substances. The alkaline-oxidation filtrates gave a strong naphthoresorcinol test for uronic acids (18). Attempts to detect glucuronic acid in these filtrates after acid hydrolysis, by paper chromatography, were not successful.

Rate of Oxidation of Starch. In rate study experiments the permanganate solution was added all at once to the starch slurry. The pH and temperatures were controlled as described. Samples were withdrawn periodically with a pipet, the pH was adjusted to 3, and the manganese dioxide and excess permanganate were immediately reduced with sodium metabisulfite solution. The resultant oxystarches were washed

free of sulfate ions and equilibrated at laboratory humidity and room temperature.

Carbonyl Content of Oxystarches. The Somogyi method (17) was used to determine carbonyl content (combined aldehyde and ketone groups) of the oxystarches. The applicability of alkaline-oxidation methods of analysis for carbonyl groups in carbohydrates is questionable when high percentages are present (6). However, the Somogyi method seemed adequate for determining the low percentages of carbonyl groups in the permanganate-oxidized starches. Analysis of samples of periodate-oxidized starches of known low levels of oxidation indicated a satisfactory correlation of dextrose equivalent (D.E.) with dialdehyde content. A factor of 1.55 times D.E. was useful to convert D.E. to the approximate value of moles of carbonyl per 100 moles of starch.

Carboxyl Content of Oxystarches. Carboxyl content of the oxystarches was determined by the paste titration method of Mattisson and Legendre (9) and is recorded as moles of carboxyl per 100 moles of starch.

Alkali Lability. The method of Schoch and Jensen (16) was used to determine alkali lability. The oxystarches were pasted and neutralized to thymol blue end point before treatment with 0.4*N* sodium hydroxide.

Hot-Paste Viscosity. In this study, the hot-paste viscosity of a 7% dispersion of the products in distilled water was measured in a Corn Industries Viscosimeter² (5) at a bath temperature of 92°C. during 30 min. with a scraper speed of 25 r.p.m. and a propeller speed of 62 r.p.m. The viscosity in g.-cm. was recorded automatically on a chart as the temperature rise of the paste was observed by a thermometer that dipped into the paste. The pH of the suspensions before pasting (25°C.) was adjusted to 6.0 with 0.5*N* sodium hydroxide. After pasting, the pH was between 3.5 and 4.5. Portions of the paste were used for the following:

Brookfield Viscosity. Viscosity of the pastes was determined at 25°C. and 30 r.p.m. with a Brookfield Synchro-Lectric Viscosimeter Model LVF.

Clarity. Percentage transmission was measured at 650 m μ in a Coleman Spectrophotometer Model 6A and compared with a distilled-water blank at 100% transmission.

Settling Volume. A 40-ml. portion was centrifuged in an Interna-

²Mention of firm names or trade products does not imply that they are endorsed by the Department of Agriculture over other firms or similar products not mentioned.

tional Centrifuge Size 1, Type SB, at $715 \times g$ for 5 min., and the settling volume was expressed as a percentage of the total volume.

Sedimentation Measurements. Sedimentation measurements were made with solutions prepared by pasting 0.125 g. of oxystarch in 15 ml. of water for 10 min. at 98°C . in a 25-ml. volumetric flask. Dispersions were cooled to room temperature in an ice-water bath, and distilled water was added to the mark. For the more highly oxidized products a shorter time of dispersion (under 5 min.) was used.

Sedimentation constants were determined at 0.5% concentration of oxystarch in water from patterns taken in a Spinco analytical centrifuge where a mean centrifugal force of 165,000 g was applied. Some of the oxystarch sedimented to the bottom of the cell. The remainder of the sample was observed as a peak on the schlieren patterns, and its concentration was calculated from the area under the peak of a separate run with a synthetic boundary cell (15). As a control, the sedimentation coefficient of corn starch, which had been slurried in water at pH 1 and 25°C . for 2 hr., was determined.

Results and Discussions

Rate of Oxidation. The rates of increase of carbonyl and carboxyl groups in corn starch oxidized over a period of 3 hr. at pH 1 ($25^\circ\text{--}27^\circ\text{C}$.) and pH 10 ($2^\circ\text{--}4^\circ\text{C}$.) using 0.216 and 0.260 g. atom oxygen per mole of starch, respectively, were determined. Figure 1 shows that the rate of permanganate oxidation of corn starch is rapid under acid and alkaline conditions and that the major reactions occur within the first 10 min. It is also seen that acid oxidation at 25°C . produces more carbonyl groups than carboxyl groups in oxystarch. In contrast, alka-

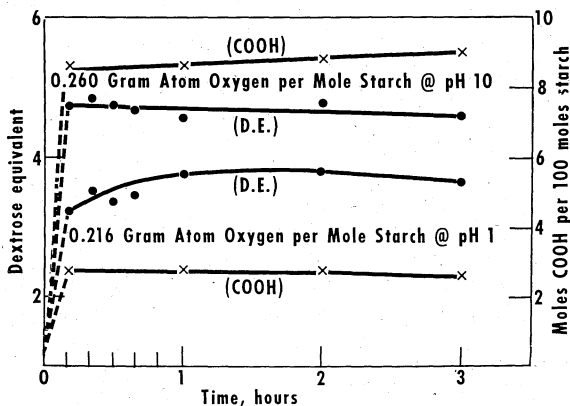


Fig. 1. Rate of change of carbonyl and carboxyl content of oxystarches with time of oxidation.

line permanganate oxidation at low temperature yields oxystarch with a higher ratio of carboxyl to carbonyl groups. Permanganate is present during the first 30–40 min. of the reactions, but apparently after the initial rapid reaction it is utilized in extensive oxidation of the soluble products formed.

Concentration of Oxidants. Under the conditions employed, an increase in the concentration of potassium permanganate produced increases in carbonyl and carboxyl content of the oxystarches (Tables I and II). The quantity of carboxyl groups formed under alkaline con-

TABLE I
EFFECT OF VARIATION IN AVAILABLE OXYGEN ON ACID PERMANGANATE
OXIDATION OF CORN STARCH
(pH 1; temp. 25°–27°C.; time, 2 hr.)

OXYSTARCH SAMPLE No.	GRAM-ATOM O/ MOLE STARCH	D.E.	MOLES COOH/ 100 MOLES STARCH	OXYSTARCH YIELD %
1	0.072	1.24	0.54	99
2	0.130	2.04	0.95	99
3	0.144	2.21	1.35	99
4	0.216	3.74	2.68	95
5	0.432	4.78	5.10	91
6	0.648	5.69	7.39	86

TABLE II
EFFECT OF VARIATION IN AVAILABLE OXYGEN ON ALKALINE PERMANGANATE
OXIDATION OF CORN STARCH
(Temp. 2°–4°C.; time, 3 hr.)

OXYSTARCH SAMPLE No.	pH	GRAM-ATOM O/ MOLE STARCH	D.E.	MOLES COOH/ 100 MOLES STARCH	OXYSTARCH YIELD %
7	9	0.087	2.14	3.37	99
8		0.130	2.84	4.58	99
9		0.260	4.40	8.48	95
10	10	0.087	2.24	3.68	99
11		0.130	2.89	5.02	99
12		0.260	4.89	9.06	91
13	11	0.087	2.33	4.05	98
14		0.130	3.15	5.55	97
15		0.260	4.70	9.85	89

ditions is about 3.5 times that produced by acid oxidation for a given oxidation level. The higher concentrations of permanganate used at pH 1 appreciably reduced the yield of oxystarch, probably because of the combined effect of hydrolysis and oxidation. Similarly, under alkaline conditions, higher permanganate concentrations lowered the yield of oxystarch significantly and more so with an increase in pH,

which undoubtedly is the result of depolymerization and subsequent solubilization through alkaline degradation.

The introduction of alkali-sensitive groupings into starch by permanganate oxidation is further corroborated by the high alkali numbers (Fig. 2) (20).

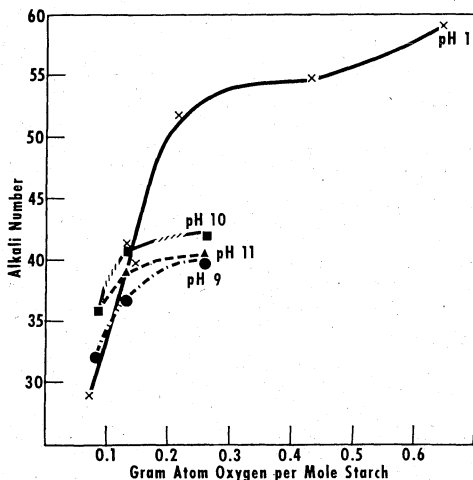


Fig. 2. Alkali lability numbers of permanganate-oxidized corn starches.

Alkali lability is an empirical method for estimating the relative hydrolytic degradation of starch, acid-modified starches, and oxidized starches (16). Alkali numbers of acid-modified starches increase with increasing degree of acid conversion and reach the value of 56.3 for a 90-fluidity thin-boiling starch. However, alkaline hypochlorite-oxidized starches have relatively low alkali numbers of 8.6 to 10.4, which is in sharp contrast to the high numbers of the permanganate-oxidized starches. This would indicate that the mechanism of permanganate oxidation might be different from that of alkaline-hypochlorite oxidation.

Figure 2 also shows effect of increased oxygen consumption at various pH levels and extent of degradation of oystarches as determined by alkali number. Oxidation at the same level or at increased levels of oxygen consumption over the pH range 9–11 did not greatly change alkaline degradation of the oystarches. However, a marked increase in alkaline degradation was observed when oxygen consumption was increased at the pH 1 level.

Size Distribution. Ultracentrifugal sedimentation studies on the

oxystarch dispersions were not extensive, so that only a broad pattern of molecular weight distribution could be established (Table III).

Insoluble components had molecular weights in the millions; soluble components, less than 300,000 when estimated from the S_{20} value of the peak of most numerous species. The weight-average molecular weight of the total soluble component is undoubtedly higher than reported because of the skewness toward higher S values of all samples measured.

TABLE III
SEDIMENTATION PROPERTIES OF PERMANGANATE-OXIDIZED CORN STARCH

OXYSTARCH SAMPLE NO.	SOLUBLE COMPONENT	
	Percent ^a	0.5% ^b S_{20}
10	83	2.22
11	69	1.66
12	80	1.73
1	69	4.13
2	55	2.64
4	68	1.70
16 ^c	38	5.91

^a Calculated from the area under the peak with a synthetic boundary cell.

^b A coefficient of 4.5 for amylose corresponds to a molecular weight of about 300,000. S values below 4.5 indicate molecular weights below 300,000.

^c Unoxidized acid-treated corn starch control.

Table III shows that corn starch oxidized at pH 10 and 2°–4°C. for 3 hr. with 0.087 g. atom oxygen per mole of starch (sample 10) produced a high percentage of hot-water-dispersible (soluble) component of relatively low molecular weight. Increasing the permanganate concentration to 0.260 g. atom oxygen per mole of starch (sample 12) did not greatly decrease the molecular-size distribution of the hot-water-dispersible component of the oxystarch. In contrast, however, increasing the available oxygen from 0.072 g. atom oxygen per mole of starch to 0.216 under the acid conditions of oxidation (samples 1–4) progressively increased fragmentation of the oxystarches, as shown by the significantly decreasing S_{20} values of the hot-water-dispersible (soluble) component. A control (sample 16), produced by slurring corn starch in water at pH 1 and 25°–27°C. for 2 hr., was not appreciably degraded.

Correlation between extent of oxidation with percent solubles and estimated molecular weights obtained from sedimentation coefficients was apparent. Detailed studies with light-scattering and intrinsic-viscosity measurements would be required to obtain a more accurate picture of the molecular weight distribution in aqueous dispersions of the oxystarches (7).

Hot-Paste Viscosity. As shown in Figs. 3-5, the maximum viscosity of the oxystarches was reached rapidly and declined quickly, indicating extensive degradation during pasting and substantiating further the presence of labile groupings in the oxystarch structure. In some instances the maximum viscosity exceeded that of unmodified starch and in all cases it was reached sooner. This effect might be caused by the starch granules not swelling at the same point but over a range of temperature (62° - 72° C. for unmodified corn starch) (8), whereas the

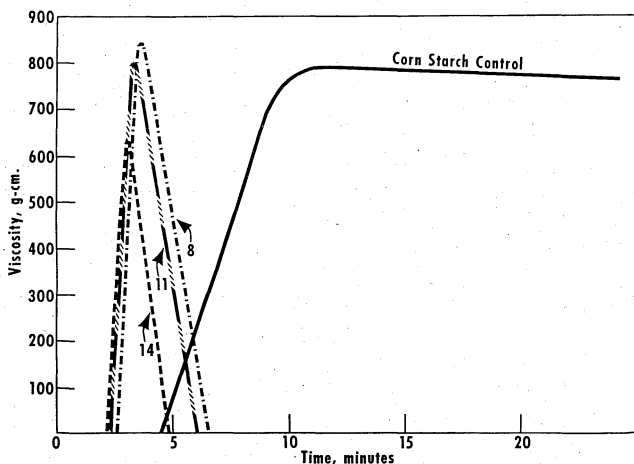


Fig. 3. Effect of pH of oxidation on pasting behavior of oxystarches at 7% solids (0.130 g. atom oxygen per mole of starch).

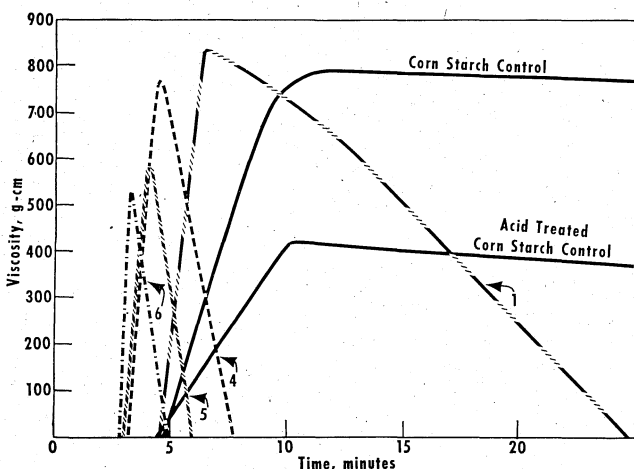


Fig. 4. Effect of concentration of oxidant at pH 1 on pasting behavior of oxystarches at 7% solids.

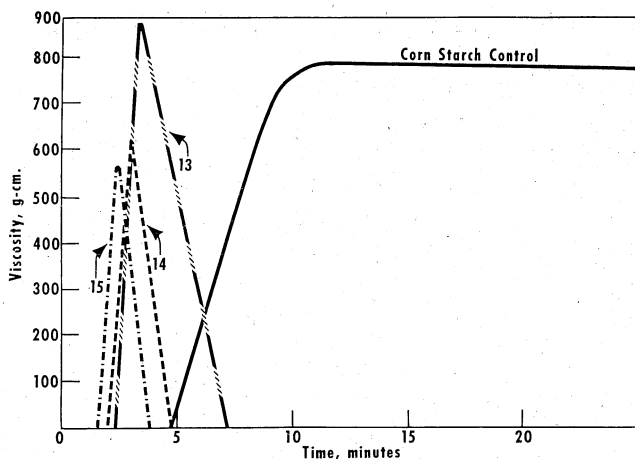


Fig. 5. Effect of concentration of oxidant at pH 11 on pasting behavior of oxystarches at 7% solids.

oxystarch granules had a tendency to swell over a narrower range. As shown in Table IV, when the extent of modification was increased, the gelatinization temperature and the maximum viscosity were lowered. Decreased viscosity is the result of molecular degradation of the oxystarch molecule caused by the presence of increased amounts of labile carbonyl groups. Corn starch treated with sulfuric acid at pH 1 (sample 16) gave a lower maximum viscosity than the oxystarches (about half that of unmodified starch) but was quite stable on prolonged heating.

Figures 3-5 also show that the hot-paste-viscosity pattern of the

TABLE IV
PASTING PROPERTIES OF PERMANGANATE-OXIDIZED CORN STARCHES

SAMPLE No.	GELATINIZATION		MAXIMUM VISCOSITY	PH PASTE	BROOKFIELD VISCOSITY		CLARITY (% TRANSMISSION)		SETTLING VOLUME	
	Time	Temp. at Start			Initial	After 1 Week	24 Hours	1 Week	24 Hours	1 Week
	min.	°C.	g.-cm.		cp.	cp.			%	%
Starch	4.8	78	780	5.9	9,700	Gel				
1	4.6	76	840	3.9	400	Gel				
4	3.0	71	765	3.7	9.0	7.4	13.4	13.2	0.8	0.8
5	2.8	68	580	3.2	5.6	6.8	8.4	8.7	0.5	0.5
6	2.8	66	525	3.3	4.6	6.8	23.5	22.5	0.0	0.0
8	2.7	67	840	4.3	4.3	4.6	7.0	7.0	6.9	6.3
11	2.8	68	810	3.8	5.2	7.4	6.5	6.7	7.5	6.2
13	2.4	65	870	3.8	4.6	5.6	5.9	6.0	7.5	5.0
14	2.1	62	625	3.8	3.8	4.8	6.0	6.0	7.5	6.3
15	1.6	56	560	4.1	3.4	3.8	10.2	9.0	5.6	5.6
16	4.3	76	425	5.8	7,340	Gel				

oxystarches at 7% concentration is not greatly affected by pH variations or increases in available oxygen of oxidations at pH 1 and 11, except for sample 1, which is the only oxystarch that gelled on cooling and standing for 1 week. Pastes of the oxystarches, on cooling, with the exception of sample 1, were thin and exhibited no set-back tendencies. Paste separations were noted only on samples prepared by alkaline oxidation. Clarity of the pastes changed little with increased modification under alkaline oxidation. However, with acid oxidation an increase in clarity was observed, except with sample 5. Settling volumes were much lower for pastes of samples prepared by acid oxidation.

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