Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Hypochlorite-Oxidized High-Amylose Starches

Viscosity Behavior

R. L. MELLIES, C. L. MEHLTRETTER, and F. R. SENTI
Northern Regional Research Laboratory, Peoria, Ill.

CORNSTARCH that contains approximately 50% amylose compared to the usual 27% is currently of great interest to the starch industry. This significantly increased proportion of amylose portends improved film-forming properties of aqueous dispersions of the starch or of appropriate derivatives which may be reflected in better adhesives and coatings for paper products and sizes for textiles.

A drawback to utilization of the desirable film-forming properties of high-amylose cornstarch in such sizing operations is its lack of dispersibility which is needed for effective application. This disadvantage can be overcome by appropriate chemical modification. Hypochlorite oxidation of high-amylose cornstarch imparts water solubility and reduces the tendency of the starch to retrograde; the technique was developed industrially to solubilize ordinary cornstarch (*5*).

MATERIALS AND METHODS

High-amylose corn, furnished from the 1956 crop, was processed by conventional wet-milling methods in the pilot plant. Processing included a sulfur dioxide steep of the corn and a retabling of the starch to lower the nitrogen content to 0.12%, dry weight basis. The finished starch was stored at 4° C. to minimize aging effects which cause difficulties in solubilization. Analysis by iodine sorption (*1*, *6*) showed an amylose content of 50%.

A set of seven oxidized starches was prepared from high-amylose starch by altering the proportions of oxidant to starch. Methods used to prepare the oxidant and to oxidize with sodium hypochlorite are described elsewhere (*5*). Analysis for carboxyl was by paste titration (*4*) and for carbonyl content by the hydroxylamine method (*3*). Results are expressed as moles of carboxyl or moles of carbonyl per 100 anhydroglucose units (AGU) or as moles functional groups (MFG) per 100 AGU. The set of four oxystarches used for comparison (Table I) was prepared earlier from ordinary starch.

Yields in each set were better for the high-amylose starch, perhaps caused by the higher content of amylose, the more insoluble constituent of starch, or by a lower carboxyl content with some of the high-amylose starch series. If the oxidation level is high (VI-VII) the losses become considerable.

The Corn Industries viscometer was used to show viscosity changes in the products on heating in distilled water for 45 minutes. The slurry was added at room temperature to the previously warmed (92° C.) bath.

Viscosity of the pastes was determined at 25° C. with a Brookfield Synchro-Lectric viscometer at a constant spindle speed of 20 r.p.m. Setting volume, expressed as percentage of toal volume, was obtained 24 hours after preparation by centrifuging a 40-ml. aliquot of the 1% paste at 715 times gravity for 10 minutes. Clarity (percentage transmission) of another portion was measured at 650 mμ in a Coleman spectrophotometer Model 6A, using tubes with a mean internal diameter of 1.55 cm. Each tube with its contents was inverted before reading to resuspend any settled matter. A distilled water blank set at 100% transmission was used.

VISCOSITY BEHAVIOR

Granule Swelling. Five per cent slurries of the oxystarches and of the parent starches were heated and continuously stirred in 100-ml. beakers for 25 minutes in a steam bath. After cooling the paste, the original volume was restored with distilled water, and the beakers allowed to stand for about 48 hours. The letter *H* in Figure 1 indicates the high-amylose starches (*H-S* is the parent starch); *O*, the ordinary starch series. When the high-amylose starch slurry was brought from pH 6.8 (*H-S*) to pH 8.9 (*H-S* Alk.) before heating, the lower layer decreased in volume, because of better dispersion at the higher pH. The pH of 8.9 was near that found for slurries of the high-

Table I. Oxystarches Were Prepared from High-Amylose and Ordinary Starches at a pH Level Above 8.5 during an 8-Hour Oxidation Period

Sample[a]	Mole NaOCl per Mole Starch	Yield, %	MFG/100 AGU Carbonyl	MFG/100 AGU Carboxyl	MFG/100 AGU Total
H-I	0.024	98	0.14	0.43	0.6
O-I		97	0.14	0.25	0.4
H-II	0.044	98	0.83	0.68	1.5
O-II		97	0.12	0.72	0.8
H-III	0.089	98	0.64	1.44	2.1
O-III		94	0.98	2.05	3.0
H-IV	0.131	95	1.33	2.30	3.6
O-IV		91	0.87	3.46	4.3
H-V	0.174	94	1.89	4.14	6.0
H-VI	0.218	92	1.32	5.49	6.8
H-VII	0.262	87	3.47	6.33	9.8

[a] *H* = high-amylose; *O* = ordinary starch.

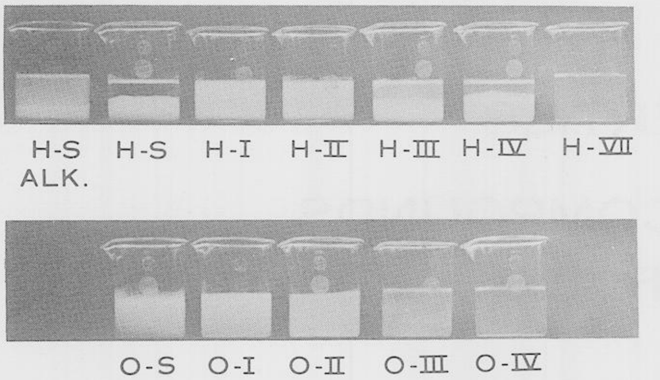

Figure 1. Contrast between ease of swelling of the granule in the two series of oxidized starches and of the parent starch is readily apparent

amylose oxystarches. Slurries of oxystarches from ordinary starch also had pH values in this range, but dropped to a lower level on heating.

Although *H*–I and *H*–II appeared homogeneous, the lower layers comprised 28 and 26% of the total volume, respectively, and indicated limited swelling of the granules at these low oxidation levels. Swelling increased with increase in modification until with *H*–V and *H*–VI (not shown) dispersion predominated and the volume of the lower layer decreased progressively below that of *H*–IV. Dispersion of *H*–VII was complete. Oxystarches from ordinary starch showed no settling and almost no opacity at a much lower level of oxidation (*O*–III) than in the other series.

Corn Industries Viscometer Studies. No measurable viscosity developed in any of the 5% slurries of the high-amylose oxystarches upon heating for 45 minutes, although swelling occured. The pastes were homogeneous, but separated on standing, except *H*–VII. With oxystarches from ordinary cornstarch (5) maximum viscosities averaging 190 gram-cm. were obtained from 5% slurries after 2 to 5 minutes of heating. Viscosities then fell rapidly, except *O*–I.

High-amylose oxystarches were also tested at higher concentrations and at higher pH levels than 8 to 9 (Figure 2 and Table II). No viscosity developed in high-amylose starch itself at 8% concentration, even at pH 11.5, although a yellow color appeared. Concentrations higher than 5% of high-amylose oxystarches at pH 8 to 9 gave measurable viscosities (Figure 2), which approached those found earlier (5) for 5% slurries of ordinary oxystarch, but then fell off rather rapidly. At 8% concentration and pH levels of 8 to 9, oxystarches *H*–I to *H*–VII, inclusive (except *H*–IV), gave no measurable hot viscosity. No viscosity developed with *H*–III and *H*–IV at 8% concentration when the pH was adjusted to 11.5 before heating.

Table II. With High-Amylose Oxystarches, Concentrations of 8 to 14% Were Needed to Give Measurable Viscosities

		Gelatinization				
Sample	Concn., %	Time range,[a] min.	Temp. at start, ° C.	Maximum Viscosity, Gram-Cm.	pH[b] Slurry	pH[b] Paste
H–III	11	5.3–6	81.4	203	8.3	6.1
H–IV	8	6–8.5	82.5	8	8.3	5.8
H–IV	11	4.75–10.5	75	188	8.3	5.8
H–V	11	2.4–5.5	73.5	71	8.7	5.9
H–VI	14	2.8–4.3	66	161	8.2	5.8

[a] From time gelatinization began until maximum viscosity was reached.

[b] At 25° C.

An 8% slurry of *H*–IV had a maximum viscosity of 8 gram-cm., which increased to 188 gram-cm. at 11% concentration. Because *H*–VI required a 14% slurry to give a maximum viscosity of 203 gram-cm., probably at least an 18% slurry of *H*–VII would be needed to obtain a comparable viscosity.

High alkalinity at 8% concentration produced a yellow color and affected the settling volume and the clarity. The pastes also separated on standing.

Brookfield Viscosity. When cold pastes from the viscometer trials were examined (Table III) at 5% concentration, slight increases in viscosity (setback) of the oxystarches were observed on standing. High-amylose starch doubled in viscosity after a week. When the starch was heated at pH 11.5 and 8% concentration, cold paste viscosity increased from 246 to 726 centipoises. Some rather striking increases are also shown for several of the oxystarches at concentrations above 5%.

Settling Volume. Settling volumes, as determined on 1% pastes from the viscometer trials and for three trials at pH 11.5 are given in Table IV. As expected, high alkalinity markedly reduced the volume of swollen granules, especially for the oxystarches. At pH levels of 8 to 9 the settling volume of *H*–I increased over that of starch, then decreased (*H*–II) presumably due to greater dispersion. At still higher oxidation levels (*H*–III and *H*–IV) swelling became the dominant factor, and the settling volume reached a maximum of 14 to 15%. Then it showed a progressive decrease with an increase in oxidation level due to increased susceptibility of the granule to rupture. With *H*–VII, dispersion became virtually complete. A similar relationship of settling volume and modification has been reported for pastes from the oxidation of ordinary corn-

Table III. Viscosities of Cold Pastes Increased on Storage for Extended Periods

		Brookfield Viscosity, Cps.	
Sample	Concn., %	Initial	After 1 week
H–S	5	17	34
H–S	8[a]	246	726
H–III	8	635	740[b]
H–III	11	6780	7520[b, c]
H–IV	11	1650	2840[b]
H–V	8	53	84
H–V	11	339	1502
H–VI	14	2000	8000
H–VII	8	13	13

[a] Slurry at pH 11.5.

[b] After 19 days.

[c] 10,000 cps. after 28 days.

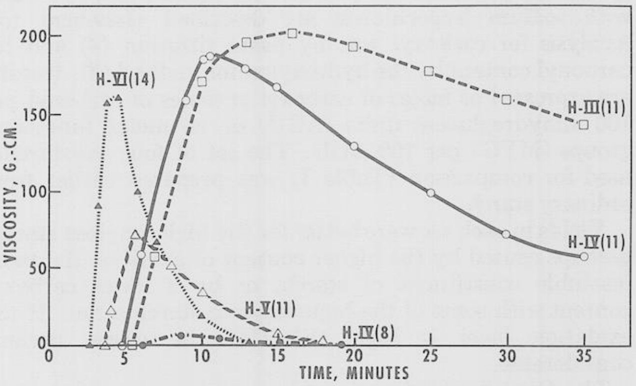

Figure 2. Corn Industries viscometer curves for high-amylose oxystarches resemble those for ordinary oxystarches.

Paste concentration in parentheses

Table IV[a]. Clarity of 1% Pastes Increases with Extent of Oxidation, While Settling Volume Increases and then Declines

Sample	*H*-S	*H*-I	*H*-II	*H*-III	*H*-IV	*H*-V	*H*-VI	*H*-VII
Settling vol., %	8.8 (6.8)	9.3 ...	6.8 ...	14.5 (7.5)	14.0 (6.8)	5.0 ...	2.5 ...	0.2 ...
Clarity, %	7 (9)	8 ...	9 ...	24 (25)	60 (52)	88 ...	98 ...	97 ...

[a] Values in parentheses for pastes prepared at pH 11.5 in Corn Industries viscometer.

starch by electrolysis in alkaline sodium chloride solution (2).

Clarity. High alkalinity appears to have less effect on clarity (percentage transmission) than on settling volume of 1% pastes. For example, *H*-IV in Table IV changed in clarity from 60 to 52%, but the settling volume decreased by over 50%. Clarity increased slowly at first at normal pH levels with increase in oxidation, then rose suddenly as greater rupture and dispersion of the granule occurred, and finally leveled off at nearly complete transmission. Clarities of pastes of *H*-V at 11, 8, 5, and 1% concentration were, respectively, 9, 16.5, 44, and 88%, nearly doubling for each increment of decrease in concentration.

Paste clarity decreased on storage, in line with the setback observed when measuring Brookfield viscosities, although the change was not as marked. A 1% paste of *H*-III decreased in clarity from 28 to 24% in 72 hours. The effect was greater with more concentrated pastes.

Microscopic Observations. Photomicrographs of some slurries and pastes of high-amylose starch and oxystarches are shown in Figure 3. The pastes were obtained by heating 5% slurries for 25 minutes in a steam bath.

Unheated high-amylose starch and oxystarch granules are similar in appearance. Under crossed Nicols the granules of both types show the typical Maltese cross, and the hilum can be detected in some. Upon heating the starch in water the granules swell, although many are resistent and birefringence is largely lost. Oxidized starches also swell on heating and lose birefringence, *H*-II resembling the parent starch in not exhibiting much fragmentation.

At higher oxidation levels (*H*-IV and *H*-VII) swelling becomes pronounced and fragmentation increases. At the highest level some granules still remain relatively intact, although greatly swollen, but the majority have deteriorated. The photomicrograph for *H*-VII was taken from a centrifuged sample of the 5% paste and represents a much higher concentration of granules than in the uncentrifuged paste. In the latter, the settling volume was negligible and the clarity over 90%, so that the number of granules or granule fragments in a given field is small. High-amylose oxystarch IV heated at pH 11.5 instead of the normal pH of 8.5 showed no marked differences in the appearance of granules.

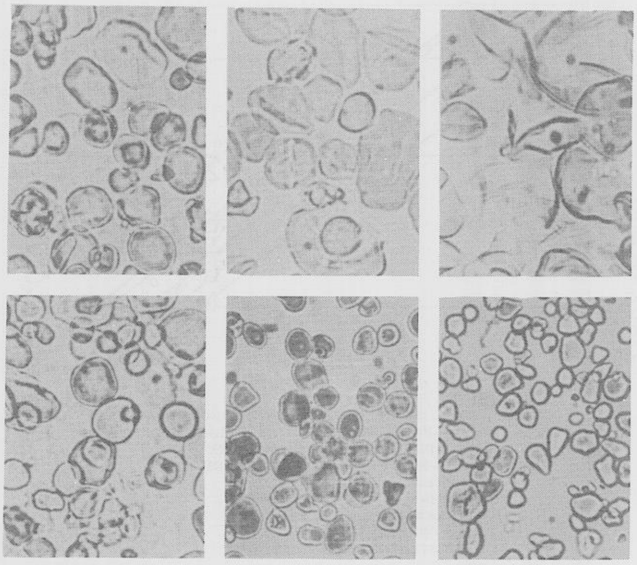

Figure 3. High-amylose starch and oxystarches (X 500)
Left to right, top row *H*-II, *H*-IV, *H*-VII, all heated
Bottom row *H*-S, heated; *H*-S, *H*-IV, unheated

DISCUSSION

Satisfactory dispersibility of high-amylose starch can be attained through oxidation with sodium hypochlorite; however, greater modification is required than with ordinary starch. Marked resistance of high-amylose starch granules to swelling on heating in water is observed, because the paste, even after 25 minutes at steam bath temperature, still contains unswollen granules. Oxidized starches, which resemble the parent starch in microscopic appearance before pasting, have greatly reduced numbers of unswollen granules in the pastes. At the highest oxidation level a relatively clear dispersion of low viscosity with few intact granules was obtained. At lower levels, 8 to 14% concentrations gave pastes with viscosities similar to those found on heating 5% slurries of oxystarches from ordinary starch. The low oxidized pastes tended to separate on standing and also to set back.

Increase in swelling and dispersibility with a rise in extent of modification is also shown by data for clarity and settling volume of the cold pastes. Clarity of the pastes increased rapidly with increased oxidation and reached a maximum of 98%. Settling volume also increased at first with increase in ability of the granule to swell, reached a maximum, and then decreased as the effect of granule rupture and degradation exceeded the swelling tendency. Properties of high-amylose oxystarches can also be modified by heating slurries at higher pH levels than the normal of 8 to 9. A marked reduction in settling volume at the higher oxidation levels was noted and indicates that a proper combination of oxidation level with the use of alkaline reagents to aid dispersibility may render a range of these oxystarches suitable for industrial use.

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LITERATURE CITED

(1) Bates, F. L., French, D., Rundle, R. E., *J. Am. Chem. Soc.* **65**, 142–8 (1943).
(2) Farley, F. F., Hixon, R. M., *Ind. Eng. Chem.* **34**, 677–681 (1942).
(3) Gladding, E. K., Purves, C. B., *Paper Trade J.* **116**, No. 14, 26–31 (1943).
(4) Mattisson, M. F., LeGendre, K. A., *Anal. Chem.* **24**, 1942–4 (1952).
(5) Mellies, R. L., Mehltretter, C. L., Wolff, I. A., *Ind. Eng. Chem.* **50**, 1311–14 (1958).
(6) Wilson, E. J., Jr., Schoch, T. J., Hudson, C. S., *J. Am. Chem. Soc.* **65**, 1380–3 (1943).

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