THIN-BOILING STARCHES FROM THE REACTION OF CORN STARCH WITH CHLORINE IN METHANOL[1]

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ABSTRACT

Corn starch was slurried in approximately an equal weight of methanol and reacted with chlorine at concentrations up to 5%, based on methanol, for periods up to 2 hours and at temperatures ranging from 25° to 65°C. In the light of previous experience with dialdehyde starches, these reaction conditions would be expected to introduce methyl and carboxyl groups into the resulting products, but none could be detected by existing analytical procedures.

By varying temperature, reaction time, and amount of chlorine, thin-boiling starches were produced that had intrinsic viscosities ranging from 1.53 to 0.06 in 1*N* potassium hydroxide. These products and commercial thin-boiling starches having similar intrinsic viscosities were compared for several paste properties. The new starches had lower alkali numbers, similar pasting temperatures, higher paste viscosities and setback, and slightly lower paste clarities. Unsupported films of the new products were stronger.

The use of chlorine in methanol as a reagent for modification of periodate-oxidized corn starch of varying aldehyde content has been

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described previously (3). More than half of the aldehyde groups of the starting materials were replaced with methoxyl and carboxyl groups, and there was a concomitant reduction in molecular size. The resulting products had lower pasting temperatures, lower paste viscosity, less setback, and higher paste clarity than their respective starting materials.

During these studies on periodate-oxidized starch, the chlorine-methanol treatment was also applied to unmodified starch as a control reaction. Because the resulting product had pasting characteristics of a thin-boiling starch, the reagent appeared to offer a new method of preparing modified starches of this type.

In a continuation of these studies, unmodified corn starch has been reacted with chlorine in methanol under a variety of experimental conditions, and the resulting products have been compared with commercial thin-boiling starches of varying fluidities.

Materials and Methods

Materials. Unmodified corn starch and acid-modified thin-boiling corn starches of varying fluidity were obtained from commercial producers of starch products. Unmodified starch contained 11.5% moisture and was reacted without drying except where noted. When starch was predried, the moisture content was decreased to less than 1% by drying in a forced-air oven at 105°C. Chlorine was used as received in cylinders from the Matheson Company, Inc.[2] Methanol was reagent-grade absolute.

Reaction. One part by weight of starch was slurried in 1.1 parts by weight of methanol containing chlorine at concentrations up to 5% based on methanol, for periods up to 2 hours, and at temperatures ranging from 25° to 65°C. Experimental procedures were essentially as described earlier (3) for similar reactions with periodate-oxidized starch. All products filtered freely without clogging during isolation and purification.

In addition to the slurry reaction, which constituted the primary study in this investigation, an exploratory study was also made on the "percolation" reaction. Starch contained in a separatory funnel was reacted with 5% methanolic chlorine at room temperature by forcing the reagent slowly up through the bottom of the funnel until the reagent had completely permeated the starch. No exothermic heating nor swelling was observed. After a contact time of 2 hours, the product was separated by filtration, neutralized, washed, and dried as described

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

earlier (3). This technique required 0.56 g. of methanol per g. of starch.

A "dry" reaction was also explored. Under conditions analogous to those of a dextrinizing-type reaction, starch, both dried and undried, was treated in a rotating glass reactor (5) at 24 to 25 in. vacuum at a temperature of 150°C. for 1.5 hours with 0.0063 meq. chlorine per g. starch introduced as a 5% solution in methanol. The amount of chlorine was equivalent to the amount of hydrochloric acid which gave a pH of 3.0 to a slurry of 50 g. starch in 100 ml. of 0.5*N* aqueous potassium chloride. The products, which were neutralized by fuming with ammonia, had a paste pH of 5.0.

Evaluation. Alkali number was determined by the method of Schoch and Jensen (4).

Intrinsic viscosity was determined at 25°C. with Ostwald-Cannon-Fenske No. 100 viscometers (1). Kinetic energy corrections were not applied. Samples were dispersed at 0.5% concentration in 1.00 ± 0.01*N* potassium hydroxide by gentle shaking for 24 hours at 1.0°C. Undispersed material was removed by centrifugation at 2,500 × *g* for 30 minutes, and the amount was determined gravimetrically. Most products contained insignificant amounts of material that was insoluble in 1*N* potassium hydroxide. Exceptions are noted in the text.

Pasting behavior of the products was evaluated with a Brabender Amylograph-Viscograph, type DC2. Slurries were added at 25°C., heated at the rate of 1.5° per minute to 90°C., held at 90° until the total elapsed time from the addition of sample was 60 minutes, and then cooled at the rate of 1.5° per minute to 25°C. Results are reported in centipoises based on calibration of the instrument with oils of known viscosity obtained from the National Bureau of Standards.

Viscosity behavior of pastes was further characterized with a Brookfield Synchro-Lectric Model LVF viscometer. Almost all measurements were made at 30 r.p.m. with the largest spindle giving a scale reading. Pastes having viscosities greater than 20,000 cp. were determined with a Helipath attachment at 6 r.p.m.

Clarity determinations of cold pastes containing 1% solids were made with a Bausch & Lomb Spectronic 20 colorimeter equipped with Bausch & Lomb selected ½-in. test tubes. Any sedimented material was resuspended before readings were made. Results are expressed as percent transmission at 650 mμ compared with a distilled-water blank.

Unsupported films without plasticizer were prepared from hot 10% aqueous pastes 0.030 in. thick on sheets of clean glass coated with a thin layer of silicone grease. They were dried at 50% r.h. and tested on a Henry L. Scott Co. tensile tester.

Results and Discussion

Chemical Properties. The action of methanolic chlorine on periodate-oxidized starch results in the loss of more than half of the starting aldehyde groups and in the introduction of methoxyl and carboxyl groups (3). Similar conversion of reducing end groups in unmodified starch would be expected upon treatment with this reagent. Furthermore, oxidative and methanolytic cleavage of glycosidic bonds between anhydroglucose units would also be accompanied by introduction of carboxyl and methoxyl groups. However, the relatively small number of such conversions in unmodified starch poses difficult problems when attempts are made to determine these changes quantitatively. The problem is complicated because potential aldehyde groups can be masked by conversion to their methyl acetals and acid groups can be esterified with methanol. In the present studies no methoxyl groups could be demonstrated by Zeisel's procedure (2), no aldehyde groups were indicated by colorimetry (6), and no carboxyl groups were indicated by potentiometric titration of cold pastes with 0.1*N* sodium hydroxide.

Alkali number (4) and intrinsic viscosity were determined for several laboratory preparations and commercial acid-modified thin-boiling starches. The difference in properties developed by the two methods of modification is evident in Fig. 1. The curves indicate that the

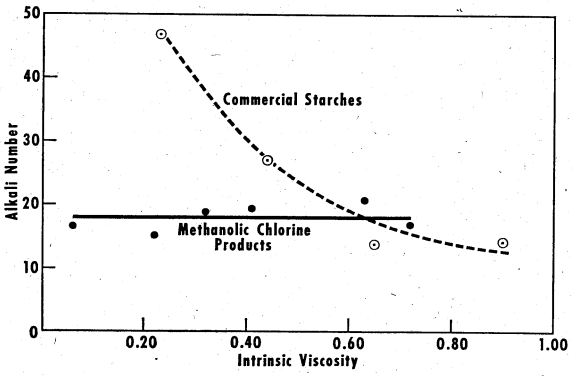

Fig. 1. The effect of type of modification on alkali number and intrinsic viscosity.

alkali number of laboratory preparations is independent of amount of chain scission, whereas commercial samples become more labile with decreasing intrinsic viscosity. The constant lability of the laboratory samples shows the influence of oxidation by chlorine and conversion of potential aldehyde groups to methyl acetals.

Influence of Reaction Conditions on Yield and Physical Properties. A wide range of physical properties was obtained within a 2-hour reaction period at temperatures ranging from 25° to 65°C. and with chlorine concentrations up to 5 g. per 100 ml. of methanol. Yields and selected properties of the experimental modified starches obtained after treatment for 0.5, 1, and 2 hours with 5% methanolic chlorine at 45° C. are given in Table I. Data for the untreated starch are included for comparison. All yields were essentially quantitative.

TABLE I

INFLUENCE OF REACTION TIME ON YIELD AND PHYSICAL PROPERTIES OF PRODUCTS OBTAINED FROM REACTION WITH 5% METHANOLIC CHLORINE AT 45°C.

Reaction Time	Yield, Original Starch Basis	Intrinsic Viscosity	Clarity of 1% Paste	Amylograph Data				
				Pasting			Viscosity	
				Concentration	Temperature at Start[a]	Time Range[b]	55°C.	25°C.
hours	*%*	*dl./g.*	*%*	*g./100 ml.*	*°C.*	*minute*	*cp.*	*cp.*
0[c]	. .	1.69	19	10	68	14	>1,825	>1,825
0.5	98	0.49	66	10	70	6	225	320
1.0	98	0.32	80	10	72	18	80	90
2.0	96	0.22	74	30	60	14	40	105

[a] Start of pasting is defined as the point at which the amylograph curve exhibits the maximum increase in rate of viscosity rise; i.e., the point at which the second derivative of viscosity with respect to time is at a maximum.
[b] Pasting range is the time from the start of pasting until maximum viscosity is reached.
[c] Unmodified starch.

Unsupported films were prepared from the products listed in Table I and commercial thin-boiling starches. Tensile strength of the films and intrinsic viscosities of the experimental and commercial modified starches were as follows:

Modified Starch[a]	*Intrinsic Viscosity*	*Tensile Strength*
	dl./g.	*kg./mm.*
Comm. 60-fluidity starch	0.65	2.14
Product from 0.5-hour reaction	0.49	4.28
Comm. hypochlorite-oxidized starch	0.40	3.31
Product from 1.0-hour reaction	0.32	4.49
Comm. 90-fluidity starch	0.23	Cracked on drying
Product from 2.0-hour reaction	0.22	3.66

[a] Unmodified starch with intrinsic viscosity 1.69 had tensile strength 4.30 kg./mm.

In all cases, films from experimental products had higher tensile strengths than those from the commercial starches having equal or higher intrinsic viscosity. One of the commercial samples failed to give a continuous film, although a laboratory preparation with similar intrinsic viscosity gave a relatively strong film.

TABLE II

INFLUENCE OF REACTION TEMPERATURE ON YIELD AND PHYSICAL PROPERTIES OF PRODUCTS OBTAINED AFTER 2-HOUR TREATMENT WITH 5% METHANOLIC CHLORINE

Reaction Temperature	Yield, Original Starch Basis	Intrinsic Viscosity	Clarity of 1% Paste	Amylograph Data				
				Pasting[a]			Viscosity	
				Concentration	Temperature at Start	Time Range	55°C.	25°C.
°C.	%	dl./g.	%	g./100 ml.	°C.	minutes	cp.	cp.
25	98	0.63	25	10	69	7	>1,825	>1,825
45	96	0.22	74	30	60	14	40	105
65[b]	56	0.06	74	50	45	10	250	450

[a] See Table I, footnotes a and b.
[b] Refluxed.

Data showing the effect of reaction temperature on yield and properties of products when the chlorine concentration was 5% and the reaction period was 2 hours are given in Table II. Yields were essentially quantitative except for the product prepared at the reflux temperature. This material was extensively degraded, as shown by low paste viscosity and low setback at high concentration. Films of the product cracked during drying.

The properties of materials obtained from 2-hour reactions at 45°C. and at three levels each of chlorine and hydrogen chloride are summarized in Table III. Of the two reagents, hydrogen chloride resulted in products with lower molecular weight as evidenced by lower yields, lower intrinsic and paste viscosities, and higher paste clarities. Pasting temperature and range were similar with both reagents but varied with reagent concentration. The partial insolubility of the product

TABLE III

EFFECT OF SUBSTITUTING HYDROGEN CHLORIDE FOR CHLORINE ON YIELD AND PHYSICAL PROPERTIES OF PRODUCTS OBTAINED FROM 2-HOUR REACTION AT 45°C. AT THREE LEVELS OF REAGENT CONCENTRATION

Reagent and Concentration	Yield, Original Starch Basis	Intrinsic Viscosity	Clarity of 1% Paste	Amylograph Data				
				Pasting[a]			Viscosity	
				Concentration	Temperature at Start	Time Range	55°C.	25°C.
	%	dl./g.	%	g./100 ml.	°C.	minutes	cp.	cp.
1% Cl_2	99	...[b]	31	10	67	8	1,475	2,075
1% HCl	99	0.76	51	10	66	8	200	550
3% Cl_2	99	0.41	71	10	70	6	100	150
3% HCl	98	0.35	81	20	66	8	150	1,900
5% Cl_2	96	0.22	74	35	61	15	>1,825	>1,825
5% HCl	90	0.12	89	35	61	16	90	590

[a] See Table I, footnotes a and b.
[b] 17.4% of product was insoluble in 1*N* potassium hydroxide.

obtained by the use of 1% chlorine will be discussed in the next section. Among materials soluble in 1*N* potassium hydroxide, laboratory products, whether prepared with chlorine or hydrogen chloride, were similar in setback, but their setback was higher than that of commercial products, as shown by the following values for paste viscosity at 25°C. and 10% concentration:

Modified Starch	*Intrinsic Viscosity*	*Brookfield Viscosity*		*Setback Ratio*[a]
		1 hour	*24 hours*	
	dl./g.	*cp.*	*cp.*	
Comm. 90-fluidity starch	0.44	176	473	2.7
Product from 3% chlorine	0.41	920	15,770	17.1
Product from 3% HCl	0.35	630	6,300	10.0

[a] Ratio of 24-hour value to 1-hour value.

The high setback of the laboratory products may be a result of fat extraction by the methanol in the reaction mixture, because addition of 1% soap on a starch-weight basis greatly reduced setback. For example, when the 3%-chlorine product was pasted at 10% concentration in the presence of soap, the 1-hour viscosity was 170 and the 24-hour value was 240, giving a setback ratio of 1.4.

Products Obtained at Low Chlorine Concentrations. A series of modified starches was prepared by reaction at 45°C. for 2 hours with varying concentrations of chlorine in methanol. At chlorine concentrations between 0.05 and 1.0%, cross-linking reactions apparently predominated over chain scission. The solid curve in Fig. 2 indicates the amount of product that was insoluble in 1*N* potassium hydroxide. The broken-line curve indicates that hydrogen chloride gave similar,

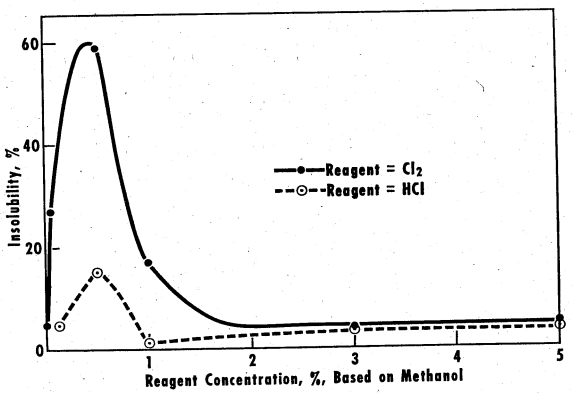

Fig. 2. Influence of reagent concentration on insolubility of reaction products in 1*N* potassium hydroxide. "Insolubles" defined as percent removed by centrifugation at 2,500 × *g* for 30 minutes.

but less extensive, cross-linking. This apparent cross-linking is analogous to the formation of thick-boiling starches in aqueous systems upon treatment with low concentrations of chlorine.

Partial insolubility in potassium hydroxide also resulted when starch was reacted for 2 hours at 45°C. with 5.0% chlorine in methanol containing 5.6% sodium hydroxide. This amount of sodium hydroxide was equivalent to the amount of hydrogen chloride liberated upon reduction of the chlorine. The resulting product was 33% insoluble in 1*N* potassium hydroxide.

Incomplete alkali solubility (Fig. 2) was accompanied by low setback, as shown by the following Brookfield Viscometer data obtained with 5% pastes at 25°C.:

Reagent	*Viscosity*		*Setback Ratio*[a]
	1 Hour	*24 Hours*	
	cp.	*cp.*	
0.05% chlorine	6,400	7,800	1.22
0.5% chlorine	380	609	1.60
1.0% chlorine	950	1,320	1.39
5.0% chlorine, 5.6% NaOH	120	275	2.29

[a] Ratio of 24-hour value to 1-hour value.

Cross-linking apparently reduced granular swelling, as evidenced by the low paste viscosity of the least-soluble product, i.e., the product obtained with 0.5% chlorine.

Paste clarity of 1% pastes of these products ranged from 27 to 44%, except that the product that had been reacted in the presence of sodium hydroxide had a paste clarity of 60%. This product had an alkali number of 27.6, in contrast to the others which were similar to the laboratory products presented in Fig. 1.

Amylograph curves of these products indicated that their pasting temperatures were essentially unchanged from that of unmodified starch, but the time required to reach peak viscosity was reduced to 8 minutes.

"Percolation" and "Dry" Reactions with Chlorine and Methanol. Exploratory studies of percolation and dry reactions gave products having properties listed in Table IV. Essentially quantitative yields were obtained by both procedures. The percolation product was characterized by its low solubility in potassium hydroxide. Low solubility was accompanied by low setback ratio, as was observed in other products that gave evidence of cross-linking. This product also had a low alkali number.

TABLE IV

PROPERTIES OF PRODUCTS OBTAINED BY "PERCOLATION" AND "DRY" REACTIONS

Reaction Conditions	Intrinsic Viscosity	Clarity of 1% Paste	Alkali Number	Brookfield Viscometer Data [a]		
				Viscosity		Setback Ratio [b]
				1-Hour	24-Hour	
	dl./g.	%		*cp.*	*cp.*	
Percolation reaction	...[c]	44	11.7	11,900	17,900	1.50
Dry reaction, dry starch	0.72	75	17.0	440	12,900	29.4
Dry reaction, undried starch	0.56	75	25.7	675	6,600	9.8

[a] Concentration, 10 g./100 ml.
[b] Ratio of 24-hour value to 1-hour value.
[c] 63.6% of product was insoluble in 1*N* potassium hydroxide.

Data for the "dry" reaction products indicate that predrying of starting material results in a product having higher intrinsic viscosity, lower alkali number, and higher setback than when the starting material contains equilibrium moisture. The differences in intrinsic viscosity and alkali number indicate that predrying the starch results in a larger polymer and increases resistance to alkali. The latter property is probably due to more complete conversion of aldehyde groups to acetals.

Amylograph curves indicated that these three products commenced pasting at 69°C. The "percolation" product reached maximum viscosity in 8 minutes; both "dry" products reached maximum viscosity in 12 minutes.

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