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POLYMERIC PRODUCTS FROM THE REACTION OF DIALDEHYDE STARCHES WITH CHLORINE IN METHANOL. PREPARATION AND PROPERTIES¹

W. C. SCHAEFER, C. R. RUSSELL, AND C. E. RIST

ABSTRACT

Periodate-oxidized corn starches, commonly called dialdehyde starches (DAS), were reacted with chlorine dissolved in methanol to give a new series of colorless polymers containing a variety of combinations of aldehyde, carboxyl, and methoxyl groups. The aldehyde content of the starting materials ranged from a trace (unmodified corn starch) to 1.9 groups per glucose residue. After reaction with methanolic chlorine, the D.S. of functional groups ranged from 0.01 to 0.34 for aldehyde groups, from 0.005 to 0.37 for carboxyl groups, and from 0.05 to 1.53 for methoxyl groups.

Intrinsic viscosities indicated that some polymer chain scission occurs during reaction with methanolic chlorine. However, microscopic examination of granules before and after treatment revealed no discernible changes in appearance, except with highly oxidized DAS.

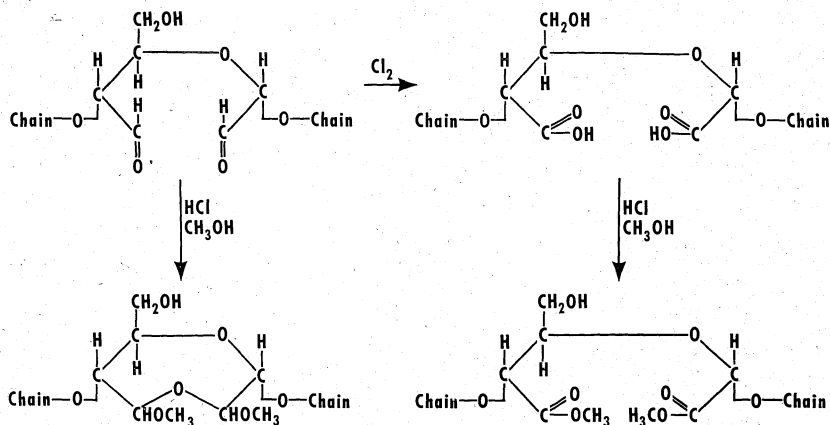
A wide range of aqueous paste characteristics of the reaction products was available, depending upon starting aldehyde content, reaction conditions, and pH during pasting. Properties of some products indicate a need for further studies in certain areas of potential application. For example, the product derived from unmodified starch may have value as a thin-boiling starch; the product from 5% DAS, as a coating adhesive; and that from 31% DAS, as a textile size.

The present study represents part of a research program directed toward the development of new products from cereal grain starches through chemical modification of dialdehyde starch (DAS, periodate-oxidized corn starch). Because DAS has recently become available commercially (2), its derivatives now deserve more than casual interest as to their potential commercial utility. Our goal is to prepare polymeric derivatives of DAS based on reaction of its aldehyde groups with chlorine in methanol.

The action of methanolic chlorine on DAS probably involves three

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reactions. First, part of the aldehyde groups are oxidized to carboxylic acids. Then, hydrochloric acid resulting from reduction of chlorine is available to catalyze ester and acetal formation through the reaction of methanol with newly formed carboxyl groups and remaining aldehyde groups. Possible reaction paths are as follows:



This illustration does not necessarily depict reaction mechanisms nor all the possible structures, but merely indicates the origin of functional groups which have been found in DAS products.

Derivatives have been obtained in a wide range from unmodified starch up to 93% DAS. This paper describes their preparation and properties, and discusses possible areas of application.

Materials and Methods

Materials. Starting materials in these reactions were prepared from commercial pearl starch in the pilot plant at the Northern Laboratory by the two-stage electrolytic process described by Pfeifer and co-workers (9). Each DAS was dried *in vacuo* at room temperature to less than 1% moisture before use. Chlorine was used as received in cylinders from the Matheson Company, Inc.² Methanol was reagent grade absolute. Zinc oxide powder, "Baker Analyzed" reagent, was used to evaluate the products as dispersing agents.

Reaction. A typical preparation was carried out as follows: 67 g. of chlorine were dissolved in a suspension of 153 g. of 10% DAS in 1,350 ml. of methanol at approximately 10°C. The mixture was warmed to 25°C. and stirred for 2 hours. The product was isolated by

²Mention 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.

filtration on medium fritted glass, and adhering HCl was neutralized to pH 6.5 with aqueous sodium bicarbonate. The product was then washed on the filter three times with water. The third filtrate was free of chloride ion. The purified product was then dried in a stream of moving air at room temperature.

The DAS-methanol slurry was precooled to approximately 10°C. in an ice-water bath to absorb heat evolved during the admission of chlorine. Sufficient chlorine was admitted to supply an excess over the amount necessary to provide one atom per aldehyde group, and the volume of methanol was regulated to give a chlorine concentration of 5% (w/v).

In determining the quantity of chlorine, allowance was made for the reaction of some of it with methanol (8). The rate of this side reaction was strongly dependent upon temperature. For example, the time required for loss of oxidizing activity from 5% methanolic chlorine was 40 minutes at 50°, 5 hours at 25°, and several days at 0°. Consequently, this side reaction can be minimized by keeping the temperature as low as possible.

Reaction time and temperature should be chosen in combinations that impart desirable pasting behavior to products. Details on the effect of these variables are discussed under "Results and Discussion."

Most products were isolated by filtration as in the typical example given. Some more highly modified products, however, were neutralized in methanol to avoid possible swelling in water. Samples that clogged the filter were washed by centrifugation. In some cases, as many as five washes were required to remove salts of neutralization.

Evaluation. Aldehyde content of starting materials was determined by either the borohydride method (10) or the hydroxylamine method (5); the products were analyzed by either the hydroxylamine method (5) or the later chlorite method (7). Carboxyl content of products was determined by titration of their cold pastes with 0.1*N* sodium hydroxide. With the products from the more highly oxidized starting materials, part of the alkali was added during the heating to facilitate pasting. Methoxyl content was determined by Zeisel's alkoxy method (4).

Intrinsic viscosities were determined at 25°C. with Ostwald-Cannon-Fenske No. 100 viscometers (3). Kinetic energy corrections were not applied. Samples were dispersed in 0.5*N* potassium hydroxide containing 25% urea (w/v) after they had been reduced with potassium borohydride to impart stability in alkali (11). Undispersed material was removed by centrifugation at 2500 × *g* for 30 minutes, and the amount

was determined gravimetrically. A more detailed description of this procedure will be published elsewhere.

Pasting behavior of the products was evaluated with the Brabender Amylograph-Viscograph, type AC. 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 Brabender units and in centipoises; conversion to cps. is based on calibration of the instrument with oils of known viscosity obtained from the National Bureau of Standards (6). Concentrations are expressed as percent by weight.

Viscosity behavior of pastes was further characterized with a Brookfield-Synchro-Lectric Model LVF viscometer. For studies of paste stability at 55° and at 25°C., viscosity measurements were made at 30 r.p.m. with the largest spindle giving a scale reading. Studies of the effect of shearing rate on viscosity involved all available spindle speeds—6, 12, 30, and 60 r.p.m.

Clarity determinations of cold pastes were made with a Coleman Junior Model 6A spectrophotometer, using Coleman Class B, 19 × 15 mm., selected round cuvetts. Any sedimented material was resuspended before readings were made. Results are expressed as percent transmission at 650 m_{μ} compared with a distilled water blank.

Paste pH measurements were made at 25°C. with a Beckman Zeromatic pH meter.

Microscopic observations of granular behavior were made with a hot-stage microscope at magnification of 100×. Samples were heated at the rate of 2° per minute. Observations at room temperature were also made on an unheated stage at 400× magnification.

Products were evaluated as dispersing agents by suspending zinc oxide powder in an equal weight of water containing 1% by weight of the material to be tested, and measuring the Brookfield viscosity at 30 r.p.m. For this evaluation, the products were pasted by stirring for 1 hour at 90°C. in the presence of sodium hydroxide equivalent to their cold paste acidity. Paste pH ranged from 4.5 to 5.0.

Evaluation as an adhesive for paper coatings involved the use of coating colors which contained 50% solids based on the total weight of color and 15% adhesive based on the dry weight of clay in the color. The product to be tested as adhesive was pasted by stirring at 90° to 95°C. for 35 minutes in the presence of sufficient sodium hydroxide to neutralize paste acidity. Brookfield viscosity measurements were made on the adhesive itself and on the coating color before ap-

plication. Coating colors were applied at pH 6.5 to commercial coating base paper with a Bird applicator which had 0.001-in. stock clearance. After application, coatings were evaluated with Dennison waxes and with the I.G.T. Printability Tester.

The biological oxygen demand (BOD) of reaction products was based on a 5-day incubation at 20°C. after seeding with raw sewage. Dissolved oxygen was determined by the Winkler method (1). Samples were partly neutralized with sodium hydroxide during paste preparation.

Results and Discussion

Functional Groups in Products. The changes in chemical properties of DAS upon reaction with methanolic chlorine for 2 hours at 25°C. are shown in Fig. 1. In general, the aldehyde content of products is

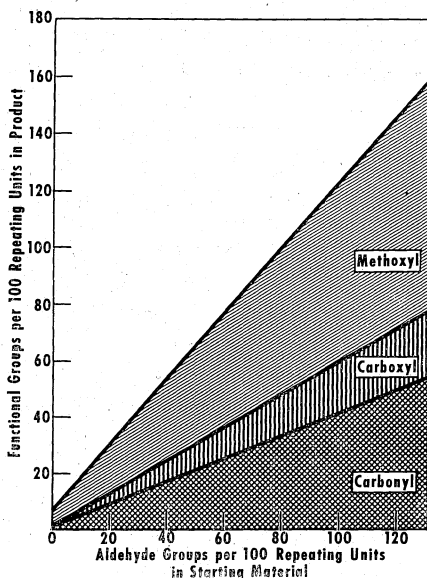


Fig. 1. Effect of methanolic chlorine on the chemical properties of dialdehyde starches. The content of functional groups is expressed as number per 100 repeating units; therefore, "percent dialdehyde" of starting material is equal to one-half the value given here.

slightly less than half of the starting amount, carboxyl ranges from 15 to 20% of starting aldehyde, and the number of methoxyl groups is approximately equal to aldehyde plus carboxyl.

Data for products from more completely oxidized DAS are not included in the figure. These products of necessity were prepared

under milder reaction conditions because of the greater reactivity of highly oxidized starting materials. For comparison, the product from 93% DAS (186 aldehyde groups per 100 repeating units) contained 34 aldehyde, 37 carboxyl, and 153 methoxyl groups per 100 repeating units after a 2-hour reaction at 15°C. The yield was 92% of the weight of starting material. In contrast to lower aldehyde preparations, this material became completely gelatinized during the reaction, enabling better contact between reactants. This loss of granule structure probably accounts for the proportionately higher methoxyl and carboxyl content and lower aldehyde content of the product. Analyses revealed that products contained no chlorine.

TABLE I
INTRINSIC VISCOSITIES^a OF SELECTED DIALDEHYDE STARCHES AND
THEIR RESPECTIVE PRODUCTS

STARTING MATERIAL	BEFORE REACTION		AFTER REACTION	
	Intrinsic Viscosity	Loss on Centrifuging	Intrinsic Viscosity	Loss on Centrifuging
Unmodified starch	1.50	<1	0.17	<1
Dialdehyde starch		%		%
3%	0.31	16	0.08	<1
5%	0.19	59	0.19	10
10%	0.08	23	0.07	34
31%	...	84	...	75
65%	...	79	...	84
93%	0.72	38	0.08	<1

^a These values are averages of two determinations. The standard deviation based on differences between 10 sets of duplicates (see ref. 12) was 0.029.

Intrinsic Viscosities. The data in Table I indicate that DAS underwent considerable chain cleavage during reaction with methanolic chlorine. These values were obtained before and after a 2-hour reaction at 25°C., except for 93% DAS, which was reacted at 15°C. Viscosity values are not given for samples having intermediate aldehyde content (both starting materials and products) because of their low solubility. These substances could be dispersed only under conditions which caused extensive degradation.

Reaction Time and Temperature. A reaction period of 2 hours at 25°C. allowed the chlorine oxidation to proceed to a desirable extent without causing decreased yield due to degradation of starting material. Under these conditions, products were obtained from DAS having up to 65% dialdehyde in yields of 95 to 99% of the weight of starting material. High yields prevailed at 25°C. until the reaction period was extended past 24 hours, but beyond 2 hours there was no significant increase in the number of functional groups introduced

TABLE II
INFLUENCE OF REACTION TEMPERATURE ON YIELD AND PROPERTIES
OF PRODUCTS DERIVED FROM 5% DIALDEHYDE STARCH

REACTION TEMPERATURE	YIELD, PERCENT OF STARTING MATERIAL	FUNCTIONAL GROUPS PER 100 REPORTING UNITS			PASTING ^a		PASTE pH	CLARITY OF 5% PASTE ^a	BROOKFIELD VISCOSITY ^{a,d}
		Aldehyde	Carboxyl	Methoxyl	Tempera-	Time			
					ture at Start ^b	Range ^c			
°C					°C	minute	%	cp	
10	98	7.6	1.0	2.5	71	25	3.1	41	3260 (10%)
30	95	4.2	2.2	4.5	60	23	2.7	60	800 (10%)
40	64	3.6	2.1	8.8	45	9	3.4	50 ^e	36 (20%)

^a Samples were pasted with sufficient sodium hydroxide to neutralize one-fourth of the carboxyl groups.

^b 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.

^c Pasting range is the time from the start of pasting until maximum viscosity is reached.

^d Viscosities were measured at 25°C. 1 hour after pastes were removed from amylograph. Values in parentheses indicate solids content of pastes.

^e Paste was discolored.

into the product.

The influence of reaction temperature on the yield and properties of products is shown in Table II. These data were obtained with products from 6% DAS reacted for 2 hours at three selected temperatures. Increased reaction temperature gives lower aldehyde content and higher methoxyl content, lower and shorter pasting range, increased clarity until discoloration interferes, and lower viscosity. However, any advantages that arise from increased reaction temperature must be balanced against decreased yield, which becomes prohibitive at 40°C.

This drop in yield becomes more pronounced with increasing extent of modification. The following yields, based upon weight of starting material, were obtained with a 2-hour reaction at 37°C.:

Product Derived from	Yield, Dry Basis %	Product Derived from	Yield, Dry Basis %
Pearl starch	97	10% DAS	87
0.5% DAS	98	20% DAS	75
3% DAS	98	31% DAS	76
6% DAS	98	65% DAS	41

Effect of Substituting Hydrochloric Acid for Chlorine. The contribution of chlorine toward changing the properties of DAS is shown in Table III. Data are given for products obtained by reacting 6% DAS with 5% methanolic chlorine and with 5% methanolic HCl for 2 hours at 25°C. The original properties of 6% DAS are also included for comparison. The chlorine product had higher paste clarity and lower viscosity than its HCl counterpart. Since their aldehyde and methoxyl contents are similar, this improvement must be related to

TABLE III
 OXIDIZING ACTIVITY OF CHLORINE IS LARGELY RESPONSIBLE FOR THE PASTE
 CHARACTERISTICS OF PRODUCTS
 (These data were obtained with 5% dialdehyde starch as starting material)

REAGENT	FUNCTIONAL GROUPS PER 100 REPEATING UNITS			PASTING ^a		PASTE pH	CLARITY ^b	BROOKFIELD Viscosity ^{b, c}
	Aldehyde	Carboxyl	Methoxyl	Tempera- ture	Time			
				at Start	Range			
Chlorine	3.2	2.6	5	°C	minute		%	cp
HCl	2.0	0.2	7	58 ^d	7 ^d	4.7 ^d	43 ^d	58 ^d
None (5% DAS before reaction)	11.2	0.2	0	60	6	4.9	9	945
				75	5	4.5	10	11,200

^a See Table II, footnotes b and c.

^b Solids content, 10%.

^c Viscosities were measured at 25°C. 1 hour after pastes were removed from amylograph.

^d Sample was pasted in the presence of sodium hydroxide equivalent to its cold paste acidity in order to make final paste pH similar to that of other samples.

the increased carboxyl content of the chlorine product, which, upon neutralization, should permit better dispersion.

Brabender Amylograph Curves. Curves for representative products obtained after a 2-hour reaction with 5% methanolic chlorine at 37°C. are given in Fig. 2. The curve for the product from unmodified starch, which has a low hot-peak viscosity but sets up to a high viscosity with cooling, is representative of products obtained from starting materials that had very low starting aldehyde content. Products from DAS in the neighborhood of 5% dialdehyde gave the highest peak viscosities in proportion to their cold viscosities. The curve for the 20% DAS is

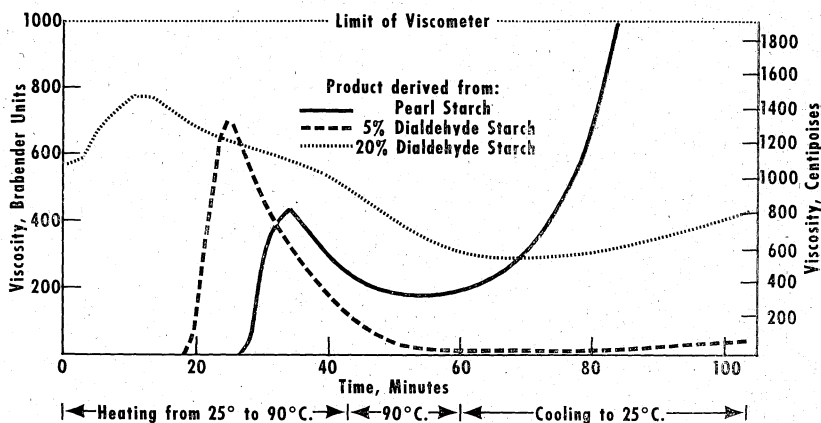


Fig. 2. Effect of starting aldehyde content on amylograph curves. The solids content of products was adjusted to give viscosities within the range of the instrument. The concentration of the unmodified starch derivative was 30% by weight; that of 5% dialdehyde starch, 20%; and that of 20% dialdehyde starch, 6.5%. The amount of alkali was adjusted to provide maximum viscosity for each product, as indicated in Table IV.

typical of those from higher DAS. All of them swelled at room temperature and gave curves similar in shape. The chief difference was that their over-all viscosity decreased slightly with increasing aldehyde content.

Pasting behavior of products was strongly influenced by alkali. Products from DAS having 6% dialdehyde or less gave the highest paste viscosity in the presence of alkali equivalent to one-fourth of their cold paste acidity. More alkali gave a higher peak on the amylogram, but caused excessive thinning of the final paste.

Products from 10 to 20% DAS were more resistant to hot water, hence they required additional alkali to lower their pasting temperature to a more desirable value. This effect is illustrated for the product from 10% DAS in Fig. 3. In this case pasting began at 42°C. when the amount of added alkali was equivalent to the cold paste acidity. With

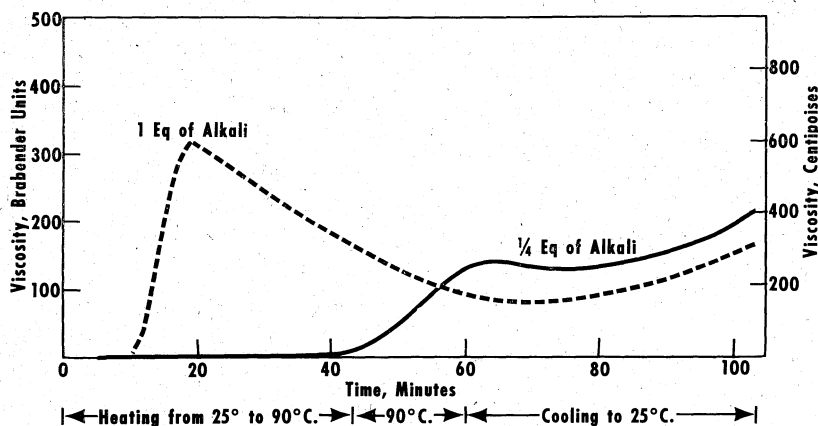


Fig. 3. Effect of alkali on the amylograph curve of the product obtained from 10% dialdehyde starch. The solids content of both samples was 7.5%.

one-fourth as much alkali, the pasting temperature was 90°C.

Products from higher DAS, like those from the lower-oxidized starting materials, were more sensitive to alkali. Highest paste viscosity, therefore, was again obtained with alkali equivalent to one-fourth of the cold paste acidity. All paste characteristics reported, unless otherwise stated, were obtained with added amounts of alkali as indicated in Table IV.

Under these conditions, pasting temperatures dropped progressively with increasing aldehyde content of starting material up to the 20% level (Table IV). Above this level, there was an abrupt rise in pasting temperature which accompanied the lowering of alkali content back

TABLE IV
SUMMARY OF PASTING BEHAVIOR

PRODUCT DERIVED FROM	FRACTION OF CARBOXYL GROUPS NEUTRALIZED	PASTING ^a		PASTE pH
		Temperature at Start	Time Range	
		°C	minute	
Unmodified starch	¼	67	6	3.1
Dialdehyde starch				
0.5%	¼	62	6	2.9
4%	¼	57	9	2.5
6%	¼	53	6	2.5
10%	all	42	8	4.6
20%	all	29	8	4.7
31%	¼	64	23	3.3
65%	¼	48	30	3.5
93%	¼	40	24	3.2

^a See Table II, footnotes b and c.

to one-fourth of the cold paste acidity. This drop in alkalinity also prolonged the time of pasting. The pH values in Table IV reflect the varying amounts of alkali used.

Comparative pasting studies of starting materials and products were not possible at all levels of oxidation, because the more highly oxidized starting materials do not paste readily in hot water. However, at the lower levels where comparisons are possible, amylograms (not shown) indicated that treatment with methanolic chlorine at 37°C. lowered pasting temperatures approximately 20°C.

Brookfield Viscosity Studies. Supplementing the preceding pasting data were studies made with the Brookfield Viscometer to determine variations in viscosity with starting aldehyde content, stability of paste viscosity, and the critical concentrations of the products. The derivatives studied were prepared at 37°C., except the 93% product, which was reacted at 15°C.

Pastes were prepared at four selected concentrations by stirring the products in distilled water at 90°C. for 1 hour in the presence of sodium hydroxide (Table IV). They were then cooled to 55°C., held at that temperature for 2 hours, then cooled to 25°C. Apparent viscosities at 30 r.p.m. were measured at the beginning and at the end of the 55° holding period and at 25°C. after 1 hour, 24 hours, and 1 week. Measurements were also made at 6, 12, 30, and 60 r.p.m., 24 hours after pasting, to observe the effect of shearing rate on viscosity.

The effect of starting aldehyde content on the paste viscosity of products at a concentration of 18% is summarized in Fig. 4. The points on the 55° curve were obtained at the end of a 2-hour holding period, and the 25° data were obtained 1 hour after cooling to that temperature. Since these data include any setback that occurred be-

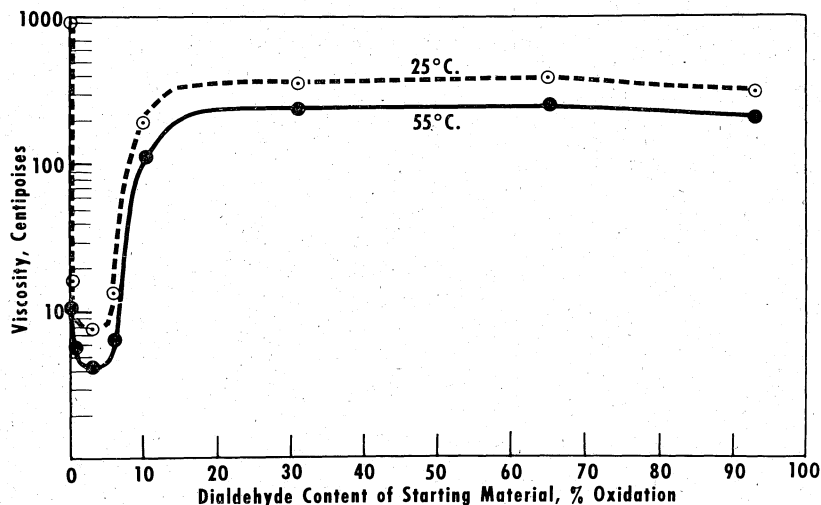


Fig. 4. Effect of starting aldehyde content on Brookfield viscosities at 18% solids.

tween the time of pasting and the time of measuring viscosity, the phenomenal drop in going from 0 to 3% dialdehyde on the 25° curve is primarily caused by the higher setback of the product obtained from unmodified starch (see Table V).

TABLE V
EFFECTS OF STARTING ALDEHYDE CONTENT AND PASTE CONCENTRATION
ON SETBACK AT 55° AND 25°C.^a

Solids Content (wt./wt.) %	55°C.		25°C.		
	Initial	2-hour	Initial	1-day	1-week
Product from unmodified starch					
9	2.0	2.1	4.1	62	220
18	9.0	11	930	1,300	>100,000
27	110	6,400	77,000	>100,000	>100,000
35	31,000	77,000	>100,000	>100,000	>100,000
Product from 0.5% dialdehyde starch					
9	2.3	1.9	3.3	4.2	8.8
18	5.6	5.8	16	1,100	11,500
27	21	70	13,500	>100,000	>100,000
35	390	20,000	>100,000	>100,000	>100,000
Product from 3% dialdehyde starch					
9	1.4	1.5	2.5	2.6	2.6
18	4.1	4.2	7.7	11	17
27	16	13	30	640	16,000
35	44	50	760	>100,000	>100,000
Product from 6% dialdehyde starch					
9	1.8	1.5	3.2	3.4	3.5
18	5.6	5.8	13	14	15
27	26	27	68	74	280
35	140	120	350	1,400	>100,000

^a Paste viscosities are given in cp. based on Brookfield Viscometer readings as indicated in the text.

Setback of paste viscosity upon standing was appreciable only with products from DAS of low aldehyde content. Data for these products are given in Table V at four concentrations and two temperatures. In all cases, except one, products from 3% DAS gave the lowest initial viscosity, but the 6% product had the lowest setback.

Products from 10% and higher DAS are not shown because, with one exception, their pastes exhibited no significant setback at either 55° or 25°C. The exception was the derivative from 93% DAS.

The reversibility of setback was determined on pastes of the lower oxidized products. Viscosity measurements were made at 55°C. on samples which had stood 1 week at 25°C. The following apparent viscosities were obtained at 30 r.p.m. after the pastes were stirred momentarily.

Product Derived from	Solids Content			
	9%	18%	27%	35%
Unmodified starch	50	5,240	>100,000	>100,000
3% DAS			270	4,240
6% DAS				12,000

Comparison of these values with those in Table V indicates that, in general, the viscosities of the reheated samples were considerably higher than the original 55°C. values.

Critical concentration, i.e., the concentration at which flow characteristics change from Newtonian to non-Newtonian, was determined graphically by plotting Brookfield viscosities at 6 and at 60 r.p.m. against concentration. The concentration at which the two curves join, and thus the concentration at which the viscosity became independent of shearing rate, was taken as the critical concentration. Values in the following table are based on data obtained at 25° on 1-day-old pastes:

Product Derived from	Critical Concentration %
Unmodified starch	4.5
6% DAS	30
10% DAS	6
31% DAS	10
93% DAS	8

These values are in keeping with the variations in viscosity with starting aldehyde content presented in Fig. 4.

Granular Phenomena. An insight into the pasting properties of the products was obtained by observing their behavior on a hot-stage microscope. The samples were heated in the presence of the same amounts of alkali as shown in Table IV.

Granules of the products from unmodified starch and 0.5% DAS, which gave relatively small peak viscosities at high concentration, fragmented and dispersed rapidly without swelling. Both 4 and 6% products, however, swelled extensively before disintegrating, accounting for the high peak viscosities. In contrast, 10 and 20% products did not swell so extensively before disintegrating; consequently, they had proportionately lower peak viscosities.

Beginning with 20% DAS, all of the higher-oxidized products displayed granule swelling at room temperature, as would be expected from their amylograph curves. Incomplete rupturing of granules occurred with products from 30 and 65% DAS. The 93% product, which had been completely gelatinized during reaction, was in the form of amorphous particles. These particles swelled during heating, but most of them remained as discrete entities and were not completely dispersed.

Microscopic observations were also made at room temperature on an unheated stage, both of the starting DAS and of their respective products. Up to 65% DAS, neither appearance nor birefringence of granules was discernibly altered by reaction at 25°C. The product obtained from 93% DAS, as mentioned earlier, was completely gelatinized even when the reaction temperature was lowered to 15°C.

Clarity of Pastes. Figure 5 gives paste clarity of representative start-

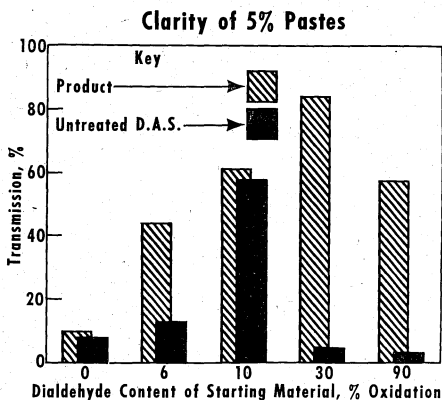


Fig. 5. Comparison of paste clarity of starting materials and products at representative levels of starting aldehyde content.

ing materials and products at 5% solids content. Measurements were made at room temperature 24 hours after the samples were pasted, by stirring in water at 90°C. for 1 hour in the presence of alkali in the

same amounts indicated in Table IV. Clarity improvement was greatest for DAS of highest aldehyde content.

Dispersant Effect. Performance as a dispersing agent was evaluated by noting the effect of products on the viscosity of 50% (w/w) aqueous zinc oxide pastes. The following data show an abrupt improvement in performance with products from DAS more than 6% oxidized:

<i>Medium</i>	<i>Brookfield Viscosity</i> <small>cp</small>
Distilled water control	>100,000
Sodium chloride	>100,000
Product from: pearl starch	1,400
6% DAS	2,400
10% DAS	21
31% DAS	25
93% DAS	17

Adhesive in Paper Coatings. The reaction product of 6% DAS, chosen for testing because of its low paste viscosity, gave encouraging results in a preliminary evaluation as a coating adhesive (Fig. 4). In comparison with commercially available starch derivatives used as coating adhesives, the 6% product gave higher values on the I.G.T. Printability Tester and similar wax pick values. Brookfield viscosity of the coating color was similar to that obtained with commercial products. Therefore, satisfactory machine performance would be expected for the 6% product.

Biological Oxygen Demand. The biological oxygen demand (BOD) of derivatives decreased with increasing modification. Five-day values for BOD, adjusted for solids content and expressed as percent of the value for untreated starch, are as follows:

<i>Substrate</i>	<i>Relative BOD</i> %
Unmodified starch	100
Product from: 6% DAS	78
31% DAS	28
93% DAS	8

Since waste treatment is becoming increasingly costly to many industrial users of starch and its derivatives and since BOD is often a deciding factor in determining the end use of a product, the data for the product from 31% DAS are especially interesting. It has a BOD 72% lower than that of unmodified starch and has high paste clarity (see Fig. 5), a characteristic that is usually accompanied by good bonding strength.

Conclusions

Dialdehyde starches, after reaction with methanolic chlorine, re-

tained approximately 40% of their original carbonyl functionality and contained carbonyl, carboxyl, and methoxyl groups in approximately a 2:1:3 ratio. These changes in functionality, along with concurrent reduction in molecular weight, gave products which had lower pasting temperatures, lower paste viscosity, less setback, and higher paste clarity than their respective starting dialdehyde starches. Products derived from 20% and higher dialdehyde starches were swollen by cold water. These changes in paste characteristics should, in general, increase the potential utility of dialdehyde starches in applications requiring a hydrophilic colloid.

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