

## PREPARATION AND PROPERTIES OF ACID-MODIFIED CEREAL FLOURS<sup>1</sup>

J. C. RANKIN, J. H. SAMALIK, MARGARET M. HOLZAPFEL,  
C. R. RUSSELL, AND C. E. RIST

### ABSTRACT

Cereal flours were partially depolymerized by a dry-state method to give products having paste viscosities suitable for a number of industrial sizing and adhesive applications. Dry flours were treated with small amounts of dilute hydrochloric acid followed by neutralization with aqueous base. The effect of reaction times of 6 min. to 48 hr. at temperatures of 25°–45°C. was investigated. Flours treated with amounts of dilute acid equivalent to 0.80–2.40 weight-percent hydrogen chloride on a dry-flour basis were converted in 1–8 hr. at 28°–37°C. to products with suitable viscosities for tub-sizing of paper. These products contained less than 3% reducing sugar, had high apparent amylose content, and in laboratory-scale sizing applications imparted high-strength increases to paper.

Additional improvements in the flow and dispersion properties of flour were achieved by hydroxyethylation of flour in the dry state before or after acid modification. Acid modification alone and in combination with hydroxyethylation significantly improved the aqueous dispersibility of the starch and protein components of flour. In this respect the modified flours were similar to comparably modified starches. However, paste viscosity properties of the modified flours were more like those of hypochlorite-oxidized starches.

Storage of modified flours over a 3-month period had little effect on their paste viscosity properties.

Large amounts of hydrophilic, high polymers are required for adhesive, sizing, thickening, and flocculating purposes for paper, textiles, gypsum board, ore refining, and packaging. Industrial demands for such products are expanding and constitute a most attractive potential market for low-cost flour products made from cereal grains. However, compared to starch, the amount of flour used for such purposes is small because it lacks one or more of the requisite properties for many applications. For example, in surface sizing and coating of paper, the paste viscosity of unmodified flour is too high to meet requirements (1–3), and the protein in enzymatically modified flour does not disperse adequately in aqueous systems (4). For similar reasons flour is not a satisfactory sizing agent for textiles, whereas modified starches with reduced viscosity are used extensively (5). Reduced paste

<sup>1</sup>Manuscript received January 27, 1964. Contribution from the Northern Regional Research Laboratory, Peoria, Illinois. This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Mention of firm names or trade products does not constitute endorsement or rejection of the U.S. Department of Agriculture over others of a similar nature not mentioned.

viscosity at high solids concentration of starch is also one criterion for its effective application in manufacture of gypsum board (6). Starch is partially depolymerized by acid, enzymatic treatment, hypochlorite oxidation, and dextrinization. Wet processes for modifying starch are not satisfactory for flour because it becomes doughy in water and is difficult to process and recover. Consequently, a dry-state conversion treatment for modifying cereal flours was developed. Briefly, it consists in spraying a small amount of dilute aqueous mineral acid into dry flour, holding the acidified flour for a predetermined conversion time, and then dry-blending with base to neutralize the acid. In turn, these products can be hydroxyalkylated by our previously described methods (7-9) to broaden further their potential industrial applicability. The reverse order of the two treatments can be successfully carried out to produce similar products.

Evaluation studies on the modified flours included paste viscosity and dispersion measurements, sugar analyses, spectrophotometric determinations of the starch-iodine complex, and laboratory-scale experiments on tub-sizing of paper to test strength properties of the modified flours. Commercially modified starches were similarly tested for comparative purposes.

### Materials and Methods

*Materials.* Raw materials were commercial unmodified flours of wheat, yellow corn, and sorghum. Two air-classified flours (10), one a low- and the other a high-protein fraction, and a commercial unmodified wheat starch were also studied. Other commercial starches used for comparison were acid-modified corn starch, hydroxyethylated acid-modified sorghum starch, and two hypochlorite-oxidized corn starches of different viscosity grades.

Hydrochloric acid and sodium hydroxide employed were of reagent grade, and the purity of ethylene oxide compressed gas was listed as 99.5%.

The amount of acid used in conversion of flour is expressed as weight-percent anhydrous hydrogen chloride based on dry flour. The number of ml. and approximate normality of acid used per 100 g. of dry flour to achieve various levels of hydrogen chloride are as follows:

<i>Acid</i> <i>ml.</i>	<i>Approximate</i> <i>Normality</i>	<i>HCl in Flour</i> <i>wt.-%</i>
8-11	2	0.58-0.80
7-11	4	1.04-1.60
10-11	6	2.10-2.40

Before acid modification, flour and starches were dried to a moisture content of 3% or less by heating in a forced-draft air oven at 40°–100°C.

*Preparative Method A.* Dried flour (202 g.) was placed in a stainless-steel 1-liter beaker provided with a heavy-duty mechanical stirrer having a blade that virtually scraped the bottom and sides of the beaker. The reactor was equipped with a Plexiglas cover, which contained appropriate holes for the stirrer, for addition of reagents, and for temperature measurements. Hydrochloric acid delivered dropwise from a buret was atomized and sprayed onto the flour with a stream of air over a 6-min. period as the flour was agitated at 340 r.p.m. Depending upon the viscosity desired, the depolymerization reaction was continued with agitation for 15 min. to 8 hr. at temperatures between 28° and 45°C. Acidified flour was also allowed to react without agitation for periods up to 24 hr. at 30°C. Temperature of the reaction was controlled by either heating or cooling the reaction vessel with an oil or water bath. The reaction was arrested by adding the calculated amount of dry powdered sodium hydroxide and mixing for 2 hr.

*Preparative Method B.* A Patterson-Kelley twin-shell blender, 8-qt. liquid-solids model (Serial No. EQ 15680), was charged with 2,092 g. of dry flour. The blender was equipped with an "intensifier" and liquid feed bar for spraying solutions of reagents into the mixing material. Tumbling action of the blender (24 r.p.m.) was started and hydrochloric acid was added over a period of 15 min. through the feed bar rotating at 3,400 r.p.m. At this point both agitations were stopped and the temperature of the charge was measured. Mixing in the blender at 24 r.p.m. was continued for 6 hr. at an average reaction temperature of 30°C. Acidified flours were also allowed to react at 25°C. without mixing for periods up to 48 hr. After the products were neutralized by the addition of aqueous sodium hydroxide through the liquid feed bar, its rotation was stopped, but tumbling was continued for 2 hr. more.

*Preparative Method C.* A portion of acid-modified flour from method A or B containing about 10% moisture was placed in a pressure-tight vessel and reacted with gaseous ethylene oxide by dry-state procedures previously reported (7,8). Salt formed during neutralization of the acid-treated flour served as catalyst for etherification.

*Evaluation Procedures.* Paste properties were determined in a standard model Brabender Amylograph recording viscometer, which was operated as previously reported (11). Commercial paper-sizing operations require aqueous dispersions of starch to possess workable viscosities in a range of solids concentration of 5 to 20% at 50° to

60°C. Therefore, a concentration of 20% (g. dry solids per 100 g. paste) was arbitrarily chosen for comparing the amylograph paste viscosities of acid-modified flours at 55°C. during the cooling cycle. The relative variation in amylograph paste viscosity at 55°C. was 8%, based on 11 replications with a single wheat flour having an average viscosity of 526 cp. To determine stability of pastes, their viscosity after various periods of aging at room temperature was measured with a Brookfield Synchro-Lectric Model LVF viscometer at 30 r.p.m. Both viscometers were calibrated in centipoises (cp.) with Bureau of Standards oils.

Dispersibility of starches, flours, and their composite protein in water was estimated by the following procedure: The sample to be tested (2.00 g. dry basis) was placed in a centrifuge bottle and 98 ml. of distilled water was added. The slurry was stirred mechanically at approximately 526 r.p.m. for 30 min. at 92°–100°C. The paste was cooled, and, after the water level was adjusted to its original volume, the sample was stirred once more for 5 min. without heat. After the aqueous dispersion was centrifuged for 15 min. at  $1,200 \times g$ , dispersible material was determined by evaporating a 25-ml. sample of supernatant in a tared dish to constant weight.

$$\text{Dispersibles, \%} = \text{residue wt.} \times 196$$

Kjeldahl nitrogen values (corrected for ash and moisture) for the residue and the original sample were used to calculate dispersible protein as follows:

$$\text{Dispersed protein, \%} = \frac{\text{g. of dispersed N}}{\text{g. N in sample}} \times 100$$

Dispersibility in water at room temperature was determined in the same manner except that quantities were increased by 50% to yield sufficient material for analysis. Standard deviation for total dispersibility and dispersed protein in 10 trials on a sample of acid-modified wheat flour was 2% for hot water measurements and 1% for cold water. Respective average values for total dispersibility and dispersed protein of the sample were 84 and 40% for hot water and 24 and 40% for cold water.

Ethylene oxide values were obtained by the Lortz procedure (12) and calculated as percent ethylene oxide in the final product on a dry, ash-free basis.

Carboxyl determinations were carried out in the manner described by Mattisson and Legendre (13) with a slight modification: the material was centrifuged and washed instead of filtered and washed.

The official AOAC method (14) for maltose equivalent in flour

was employed to measure the quantity of reducing sugars present in flour products.

Blue values (starch-iodine complex) were determined to estimate the amount of apparent amylose (15,16) present in the starch. Absorbance of a 1-cm. depth of solution of the starch-iodine complex was measured at 660  $m\mu$  with a Bausch & Lomb Spectronic 20 colorimeter. The percentage change in apparent amylose due to modification was calculated from absorbance values as follows:

$$\text{Change in apparent amylose, \%} = \frac{\text{Absorbance modified} - \text{absorbance unmodified}}{\text{Absorbance unmodified}} \times 100$$

Moisture content was obtained by drying the sample to constant weight at 100°C. *in vacuo* over phosphorus pentoxide.

Paper-sizing properties of selected products were determined as follows: The test sample (3.75 g. dry basis) was added to enough distilled water to make 150 g. of slurry. It was then cooked in a hot water bath (92°–100°C.) with mechanical stirring (approximately 526 r.p.m.) for 30 min. Water was again added to the paste to make 150 g. The 2.5% dispersion was used to size sheets (7 in. by 8 in.) of Kimberly-Clark magazine-grade raw stock paper by means of a jacketed size bath placed beneath a hand-driven set of rubber press rolls. Contents of the bath were maintained at 55°C. by circulating hot water through the jacket. Sheets of unsized paper were immersed in the size bath and excess paste was removed by passing the paper through the press with the same pressure applied on the rolls each time. The sized sheets were then drum-dried at 100°–140°C., conditioned, and tested for burst and tensile strength (17). The amount of size retained in the paper was determined by difference in dry weight of the unsized and sized sheet.

### Evaluation of Reaction Conditions for Preparing Modified Flours

Factors affecting conversion of flour were time and temperature of reaction, concentration of acid employed, methods of blending acid into flour, protein, and moisture contents of flour. Preliminary trials showed that (a) conversion temperatures much above 45°C. gave colored products, (b) use of concentrated hydrochloric acid in the available equipment was impractical because the very small amounts required for conversion could not be readily distributed uniformly throughout the flour and gave rise to dark specks, and (c) use of dilute hydrochloric acid required predrying of flour to a moisture content of 3% or less to avoid stickiness during conversion or in subsequent neutralization with aqueous base.

*Temperature.* The influence of this variable in the range of 28° to 45°C. on paper-sizing quality, apparent amylose, and reducing sugar contents of modified flours is shown in Table I. Effect of reaction tem-

TABLE I  
EFFECT OF REACTION TEMPERATURE ON PHYSICAL AND CHEMICAL PROPERTIES OF  
ACID-MODIFIED FLOURS

MATERIAL <sup>a</sup>	PREPARATION <sup>b</sup>		AMYLOGRAPH VISCOSITY, 20% PASTES AT 55°C. (Cooling cycle)	CHANGE IN APPARENT AMYLOSE	OFFICIAL AOAC, MALTULOSE	STRENGTH PROPERTIES OF TUB-SIZED PAPER <sup>c</sup>	
	Run No.	Temp. of Reaction				Burst Value	Breaking Length
		°C.	cp.	%	%	pt./100 lb.	m.
Base paper (control)	..	..	..	..	..	31.8	4,350
HO starch <sup>d</sup>	..	..	229	-50	0.1	43.8	5,083
SWW flour	..	..	981 <sup>e</sup>	0	0.3	42.8	5,170
HWW flour	1	45	161	-24	6.6	39.8	4,690
HWW flour	2	45	364	-25	4.9	39.6	4,740
SWW flour	3	37	621	-9	1.4	44.0	4,920
HWW flour	4	28	103	-3	2.6	44.5	5,120
SWW flour	5	28	267	+3	1.9	45.3	5,210

<sup>a</sup> Hard winter wheat (HWW); soft white wheat (SWW); hypochlorite-oxidized (HO).

<sup>b</sup> Method A employed. Amount of acid and the reaction time were adjusted to give desired viscosities. Hydrochloric acid varied between 1.3 and 2.3% (calculated water-free HCl) based on weight of dry flour, and holding times of acidified flours were from 15 min. to 8 hr.

<sup>c</sup> Size in sheet = 3-4%; values for tensile tests were machine direction only.

<sup>d</sup> Carboxyl value, 2%.

<sup>e</sup> Paste concentration, 8%.

perature is compared for products of similar paste viscosity in runs 1 and 4 and in 2 and 5. Highest strength improvements are observed in paper sized with modified flours in which acid depolymerization is carried out on predried flour at a reaction temperature of 28°C. These products have viscosities in the range required for commercial tub-sizing of paper where pastes containing up to 20% solids are employed. However, much more dilute pastes gave the desired pickup of 3 to 4% size in laboratory applications because of relatively low press speed and pressure.

Strength properties of paper sized with products made at 28°C. were equal to or better than those of the hypochlorite-oxidized reference starch known to be a high-quality, commercial tub-sizing agent. Raising the reaction temperature to 37°C. reduced both apparent amylose content and sizing strength, even though the reaction was stopped before the product was depolymerized as fully as the 28°C. products. The comparatively high viscosity of the product prepared at 37°C. is not believed to be responsible for its reduced sizing strength, because unmodified flour gave as good or better results. Unmodified

flour is, of course, too viscous to be employed in commercial sizing where pastes of high solids content are required. In addition to superior sizing properties, the preferred modified flour samples also have the lowest sugar values and least change in the amount of apparent amylose as measured by the starch-iodine complex. Reducing sugars give low adhesive strength, have poor colloidal properties, and add little to paper sizing and coating. Preservation of the amount of apparent amylose (linear fraction of starch) is desirable because its high film strength confers strength properties to paper.

*Acidification and Mixing.* The effect of these variables on paste viscosity of flour is shown in Table II. Comparison of runs 9 with 10

TABLE II  
EFFECTS OF ACIDIFICATION AND MIXING METHODS, TIME, AND AMOUNT OF ACID ON CONVERSION OF HARD WINTER WHEAT FLOUR AT 30°C.

RUN No.	ACIDIFICATION		TREATMENT AFTER ACIDIFICATION		AMYLOGRAPH VISCOSITY, 20% PASTES AT 55°C. (Cooling cycle)
	HCl Added	Method of Addition	Method of Mixing	Holding Time	
	%			hr.	cp.
6	0.80	B	A	6	1,366
7	0.80	B	none	6	1,212
8	0.80	B	B	6	1,116
9	1.60	A	none	0	759
10	1.60	B	none	0	373
11	1.60	A	A	6	296
12	1.60	A	none	6	258
13	1.60	B	none	6	113
14	1.60	B	B	6	113
15	2.40	A	A	6	65
16	2.40	A	none	6	45

and 12 with 13 shows that the method of adding acid to flour has a marked effect on the rate of depolymerization as revealed in the paste viscosity values. Although introduction of acid by method B required 9 min. additional, something more than time must be involved because in runs 12 and 13 more than a twofold difference in viscosity still prevailed after imposition of a 6-hr. holding period. Apparently more effective distribution of acid is achieved by addition method B.

Comparison of runs 6 and 8, 7 and 8, 11 and 12, 13 and 14, and 15 and 16 shows that the type and extent of mixing after acidification had little effect on the reaction.

*Holding Time and Amount of Acid.* Either or both of these variables may be changed to produce products with the requisite viscosities for a wide variety of applications. This point is illustrated by runs 9, 12, and 16 in Table II, all of which were carried out with acid addition method A at 30°C. In run 9 a product with suitable viscosity (759 cp.) for use in gypsum board manufacture was produced with

1.6% acid with no holding time. A 6-hr. holding time (run 12) gave a product with a viscosity of 258 cp. appropriate for tub-sizing of paper. With the same holding period but with an increased amount of acid (run 16), a product was obtained having suitable viscosity (45 cp.) for use as an adhesive in high-solids coating of paper.

The relationship between paste viscosity and total reaction time, including time for both addition of acid and subsequent holding, for samples held without mixing is shown in Fig. 1.

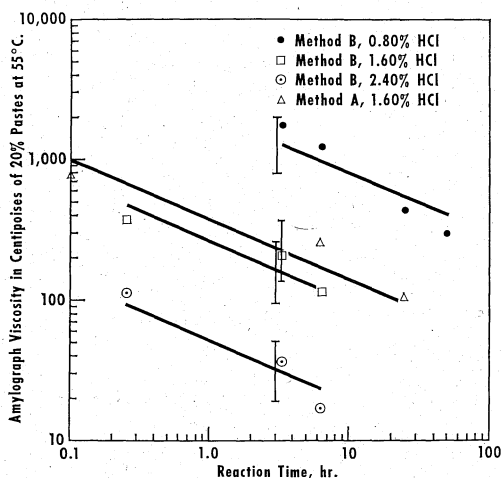


Fig. 1. Effect of amount of acid and acidification method on rate of change in viscosity of hard winter wheat flour. Reaction temperature, A = 30° and B = 25°C. The vertical bars (I) = confidence limits for the mean viscosity.

A log-log plot gave the best straight-line relationship. The least squares regression of  $\log v$  and  $\log t$  was computed for all acid conditions. Lines were tested for parallelism by using the residuals about the separate regression lines as an estimate of variation. The test indicated that the lines relating the two variables could be considered parallel. The common regression of viscosity on time was significant at the 1% level. The least-squares lines are shown in Fig. 1. The vertical bars on the figure indicate 95% confidence limits for the mean viscosity at approximately 3 hr.

*Effect of Protein.* Influence of protein content on conversion of flours to acid-modified products is presented in Table III. Method A with mixing was followed in all runs. Only the cereal flour, its protein content, amount of acid used for conversion, and its equivalent alkali for neutralization were varied. As protein content increases, larger quantities of acid are required to produce products whose cooked



TABLE III  
EFFECT OF PROTEIN ON CONVERSION OF FLOURS AT 28°C.<sup>a</sup>

STARTING MATERIAL <sup>b</sup>	PROTEIN CONTENT <sup>c</sup>	HCl ADDED	AMYLOGRAPH VISCOSITY, 20% PASTES AT 55°C. (Cooling cycle)
	%	%	cp.
Wheat starch	0.2	0.58	209
SWW flour (low-protein fraction)	3.5	1.04	219
Corn flour	6.7	1.40	180
SWW flour	8.8	1.48	267
Sorghum flour	10.8	1.56	209
HWW flour	14.3	1.60	258
HWW flour (high-protein fraction)	25.1	2.10	229

<sup>a</sup> Method A, 6-hr. holding time with mixing.

<sup>b</sup> Hard winter wheat (HWW); soft white wheat (SWW).

<sup>c</sup> Kjeldahl nitrogen,  $N \times 5.7$  for percentage protein in wheat;  $N \times 6.25$  for other cereals.

pastes give viscosities in a similar range.

*Hydroxyethylation of Acid-Modified Cereal Flours.* From 1 to 5% ethylene oxide reacted with modified flours in 2 to 10 hr. at 25° to 35°C. The reverse order of acid modification and hydroxyethylation was carried out under similar conditions with similar results. Data for the latter materials are not given because their properties are similar to those reported.

### Evaluation of Pasting Characteristics and Dispersion Properties of Modified Flours and Starches

As previously stated, starch is converted to various fluidities to meet viscosity requirements for a number of industrial applications. Starches are also modified to stabilize paste viscosity and enhance their utility. Another significant sign of the usefulness of modified starches is the degree to which they will disperse in water. The effect of pH and storage on their paste properties is also important. Modified flours were assessed by comparing their properties with those of commercial starches of comparable viscosity grade. The reference starches were known to be high-quality sizing agents and coating adhesives for paper and had excellent dispersion properties.

*Pasting Characteristics.* The amylograph viscosity curves of modified flours and starches obtained at a 20% paste concentration are illustrated in Fig. 2. With the exception of the acid-modified starch, commercially prepared starches have higher peak viscosities in the cooking cycle than do acid-modified and hydroxyethylated acid-modified flours. In the cooling cycle, paste viscosities of modified flour samples compare more closely with that of hypochlorite-oxidized starch than they do with the other modified starches. On cooling, paste viscosities of acid-modified flours do not increase nearly as much as with acid-

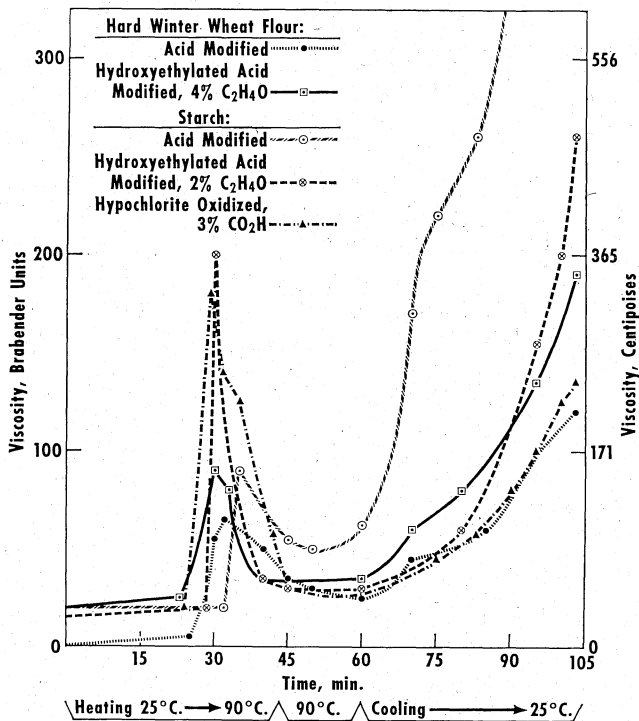


Fig. 2. Amylograph viscosities of 20% pastes of modified flours and starches.

modified starch. Thus, flours can be modified by present procedures to give products having relatively stable paste viscosities without considerable modification of the amount of apparent amylose present (blue value measurements, Table I).

*Paste Viscosity.* To achieve desired pickup and minimize selective absorption due to viscosity changes in a continuous paper tub-sizing operation, starch pastes must have stable viscosity. The stability of paste viscosity of modified flours is apparent from the values at different time intervals given in Table IV. The Brookfield viscosity determinations were made after pasting of the starchy material in the amylograph, as shown in Fig. 2. Since pasted modified flours have excellent viscosity stability, they should meet requirements for a number of industrial applications.

*Effect of Paste Concentration on Viscosity.* The influence of solids concentration on the paste viscosity of modified flours and starches is shown in Fig. 3. Here again, similarity in the behavior of modified flours and hypochlorite-oxidized starch is quite evident. Compared to the behavior of their starch counterparts, paste viscosities of the modi-

TABLE IV  
PASTE VISCOSITY OF MODIFIED FLOURS AND STARCHES

Product <sup>a</sup>	20% PASTE VISCOSITY <sup>b</sup>			
	Amylograph at 55°C. (Cooling cycle)	Brookfield at Room Temperature after Amylograph Run		
		1 hr.	24 hr.	1 week
	<i>cp.</i>	<i>cp.</i>	<i>cp.</i>	<i>cp.</i>
AM HWW flour	103	625	880	1,000
AM HWW flour <sup>c</sup>	142	600	1,180	1,540
AM SWW flour	621	3,520	6,000	6,500
AM SWW flour	142	705	960	880
AM SWW flour (low-protein fraction)	142	865	1,900	3,800
AM sorghum flour	94	460	710	685
AM starch	421	5,000	gelled	...
AM starch <sup>c</sup>	123	2,900	gelled	...
HO starch <sup>d</sup>	103	540	2,280	10,900

<sup>a</sup> Acid-modified (AM); hard winter wheat (HWW); soft white wheat (SWW); hypochlorite-oxidized (HO).

<sup>b</sup> pH of pastes 5-8.

<sup>c</sup> Hydroxyethylated, 2-4% C<sub>2</sub>H<sub>4</sub>O.

<sup>d</sup> Carboxyl value, 3%.

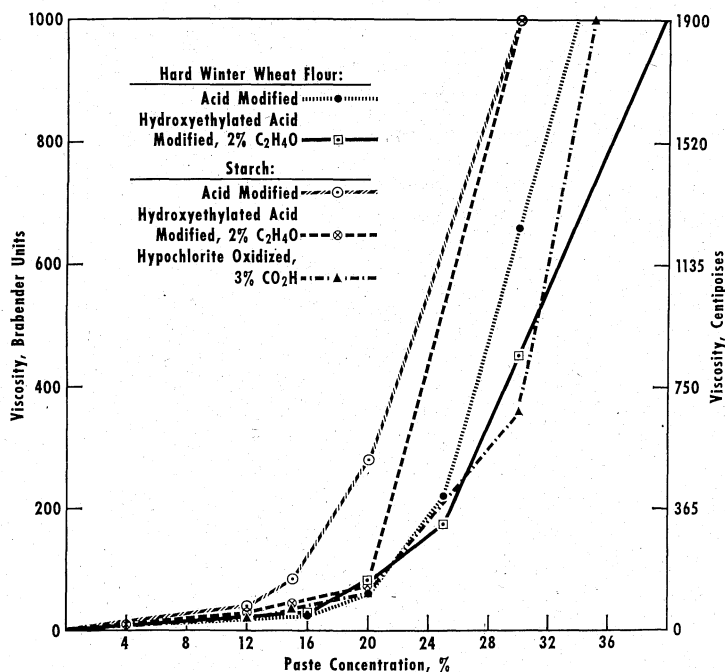


Fig. 3. Effect of solids concentration of modified flour and starch pastes on amylograph viscosity at 55°C. during cooling cycle.

fied flours rise much less rapidly with increasing solids concentration, and thus the flours may have advantages in high-solids sizing and coating applications.

*Storage Stability.* Modified flours stored at room temperature in closed containers for 3 months showed virtually no change in pH and in amylograph and Brookfield viscosities.

*Dispersibility.* As shown in Table V, acid modification of cereal

TABLE V  
DISPERSIBILITY OF MODIFIED FLOURS AND STARCHES AT 2% AQUEOUS CONCENTRATION<sup>a</sup>

SAMPLE <sup>b</sup>	DISPERSIBLES		DISPERSED PROTEIN	
	Hot Water <sup>c</sup>	Cold Water	Hot Water <sup>c</sup>	Cold Water
	%	%	%	%
U HWW flour	26	7	23	16
U SWW flour	24	8	34	33
U sorghum flour	18	3	4	3
U yellow corn flour	22	3	6	3
AM HWW flour	76	20	50	40
AM HWW flour <sup>d</sup>	91	27	45	32
AM SWW flour	87	19	52	41
AM SWW flour (low-protein fraction)	96	15	77	40
AM sorghum flour	78	15	7	4
AM yellow corn flour	85	24	13	5
AM starch	78	3	..	..
AM starch <sup>d</sup>	84	2	..	..
HO starch <sup>e</sup>	100	6	..	..

<sup>a</sup>pH of pastes 4-8.

<sup>b</sup>Unmodified (U); acid-modified (AM); hard winter wheat (HWW); soft white wheat (SWW); hypochlorite-oxidized (HO).

<sup>c</sup>Hot water (92°-100°C.).

<sup>d</sup>Hydroxyethylated, 2% C<sub>2</sub>H<sub>4</sub>O.

<sup>e</sup>Carboxyl value, 3%.

flours increases the total amount of flour dispersible and also improves the dispersibility of the protein. Such improvement is true in hot-water tests and, in most cases, in cold-water tests as well. Etherification of the acid-modified product further enhances the amount of dispersible flour. Hot-water dispersibility of flour products is comparable to that of acid-modified starch and its hydroxyethylated derivative but less than that of hypochlorite-oxidized starch. Cold-water dispersibilities of flour products are greater than those of the modified starches. However, modified flours are prepared by dry procedures, whereas the starch products are made by wet methods, which remove water-soluble material and might account for some of the difference. The kind of cereal grain that the flour comes from also affects protein dispersibility. Percentage of dispersed protein in both modified and unmodified sorghum and corn flours is considerably less than that in the wheat flour counterparts.

TABLE VI  
EFFECT OF pH ON PASTE VISCOSITY AND DISPERSIBILITY OF MODIFIED  
FLOURS AND STARCHES

PRODUCT <sup>a</sup>	pH	20% PASTE VISCOSITY			2% HOT-WATER DISPERSIBILITY	
		Amylograph at 55°C. (Cooling cycle)	Brookfield at Room Temperature after Amylograph Run		Dis- persibles %	Dispersed Protein %
			1 hr.	24 hr.		
		<i>cp.</i>	<i>cp.</i>	<i>cp.</i>	%	%
AM HWW flour	4	94	670	1,440	76	54
	7	113	615	1,540	80	40
	10	84	355	640	98	96
AM HWW flour <sup>b</sup>	4	65	275	590	82	54
	7	65	370	510	91	45
	10	17	145	195	100	92
AM starch	4	441	3,760	gelled	78	..
	7	94	14,200	gelled	93	..
	10	36	13,000	gelled	98	..
AM starch <sup>b</sup>	4	229	1,080	6,500	85	..
	7	132	2,900	gelled	98	..
	10	36	960	8,200	100	..
HO starch <sup>c</sup>	4	.. <sup>d</sup>	280	1,180	95	..
	7	74	540	2,280	98	..
	10	.. <sup>d</sup>	129	160	98	..

<sup>a</sup> Acid-modified (AM); hard winter wheat (HWW); hypochlorite-oxidized (HO).

<sup>b</sup> Hydroxyethylated, 2% C<sub>2</sub>H<sub>4</sub>O.

<sup>c</sup> Carboxyl value, 3%.

<sup>d</sup> Amylograph gave no measurable viscosity.

*Effect of pH on Viscosity and Dispersibility.* Data in Table VI show that increasing the pH of flour pastes from 4 to 7 had little effect on paste viscosity. However, when the paste pH was raised to 10, both amylograph and Brookfield viscosity decreased. In most cases, modified starches showed greater changes in pasting characteristics over the pH range of 4-10 than did flour products, but alkali had little effect in stabilizing paste viscosity for acid-modified and hydroxyethylated acid-modified starches. The flour and starches exhibited increased dispersibility with increasing pH. However, pastes of both modified flours and starches darkened from the alkali at a pH above 9.0.

#### Acknowledgment

We are indebted to H. C. Katz for his technical assistance during portions of the investigation; to A. J. Ernst for testing paper treated with modified flours; to Mrs. Bonita Heaton for ethylene oxide, ash, and nitrogen determinations; and to Dr. F. W. Kwolek, Biometrical Services, ARS, for statistical advice.

#### Literature Cited

1. FLETCHER, C. H. Starches for coating adhesives. Paper Trade J. 142 (42): 32-35 (1958).
2. KERR, R. W. Some aspects of starch chemistry in relation to tub-sizing. Paper Trade J. 115 (23): 30-34 (1942).
3. SEAMAN, J. The use of starch in the British paper industry. Stärke 11 (6): 166-169 (1959).

4. COMPTON, J. H. Wheat starch and wheat flour. TAPPI Monograph Series, No. 3, p. 102 (1947).
5. MONAGHAN, J. F. Processing and finishing cottons, vol. I, p. 159. Frank P. Bennett: Boston, Mass. (1935).
6. WIMMER, E. L., and MEINDL, F. Art of manufacturing cold water dispersible adhesives. U.S. Patent 2,894,859 (1959).
7. RANKIN, J. C., and MEHLTRETTER, C. L. Process for preparing hydroxyalkylated cereal flour. U.S. Patent 2,900,268 (1959).
8. RANKIN, J. C., MEHLTRETTER, C. L., and SENTI, F. R. Hydroxyethylated cereal flours. *Cereal Chem.* **36**: 215-227 (1959).
9. SCHWARTZ, S. M., RUSSELL, C. R., and SENTI, F. R. Preparation and properties of hydroxypropyl wheat flour. Abstr., 44th annual meeting, AACC, Washington, D.C., May 1959.
10. STRINGFELLOW, A. C., PFEIFER, V. F., and GRIFFIN, E. L. Air classification milling results for wheat and other cereal flours. *Baker's Dig.* **36** (4): 38-40, 42, 76 (1962).
11. RANKIN, J. C., RALL, J. G., RUSSELL, C. R., and SENTI, F. R. Preparation and properties of hydroxyethylated high-amylose corn starch. *Cereal Chem.* **37**: 656-670 (1960).
12. LORTZ, H. J. Determination of hydroxyalkyl groups in low-substituted starch ethers. *Anal. Chem.* **28**: 892-895 (1956).
13. MATTISSON, M. F., and LEGENDRE, K. A. Determination of the carboxyl content of oxidized starches. *Anal. Chem.* **24**: 1942-1944 (1952).
14. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official methods of analysis (8th ed.), pp. 213-214. The Association: Washington, D.C. (1955).
15. MCCREADY, R. M., and HASSID, W. Z. The separation and quantitative estimation of amylose and amylopectin in potato starch. *J. Am. Chem. Soc.* **65**: 1154-1157 (1943).
16. WOLFF, I. A., HOFREITER, B. T., WATSON, P. R., DEATHERAGE, W. L., and MACMASTERS, MAJEL M. The structure of a new starch of high amylose content. *J. Am. Chem. Soc.* **77**: 1654-1659 (1955).
17. TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY. Testing methods - recommended practices - specifications, T403m (1953); T404m (1950). The Association: New York, N.Y.

