PREPARATION OF ACID-MODIFIED FLOUR FOR TUB SIZING[1]

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ABSTRACT

Soft white winter wheat flour was reacted with small amounts of 4*N* hydrochloric acid in a ribbon mixer to produce 30-lb. batches of a material similar to commercial products in paste viscosity and effectiveness as a tub-sizing agent. Although viscosity specifications were met by blending, viscosity varied from run to run with spraying quality, temperature, time, and acid concentration. An acid-modified flour was also prepared from gaseous hydrogen chloride.

While dextrins of various kinds are old to the art and science of cereal technology, they remain some of the most versatile products made from commercial starches. For many years dextrins have been used by the paper industry as sizes and in conjunction with clays, pigments, and other additives for paper coatings. Recently, Rankin *et al.* (1) found that whole flours could be modified with acid to give prod-

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ucts that appear promising when applied to paper as tub-sizing agents. Although these products cannot be called dextrins in the true sense, their method of preparation is based on similar principles. Different conditions are necessary owing to the presence of appreciable amounts of protein in the flours.

To extend the evaluation of acid-modified flours, sufficient material was required for application to paper in a mill run. A reactor was devised in which up to 40 lb. of flour could be acid-modified in one batch. This paper describes the reactor and preliminary results obtained.

Materials and Methods

Flour Modified. Commercial soft white winter flours milled from Genesse variety Michigan wheat were used. All of the runs except those shown in Fig. 3 were made on a single flour lot. Acid-modifica-

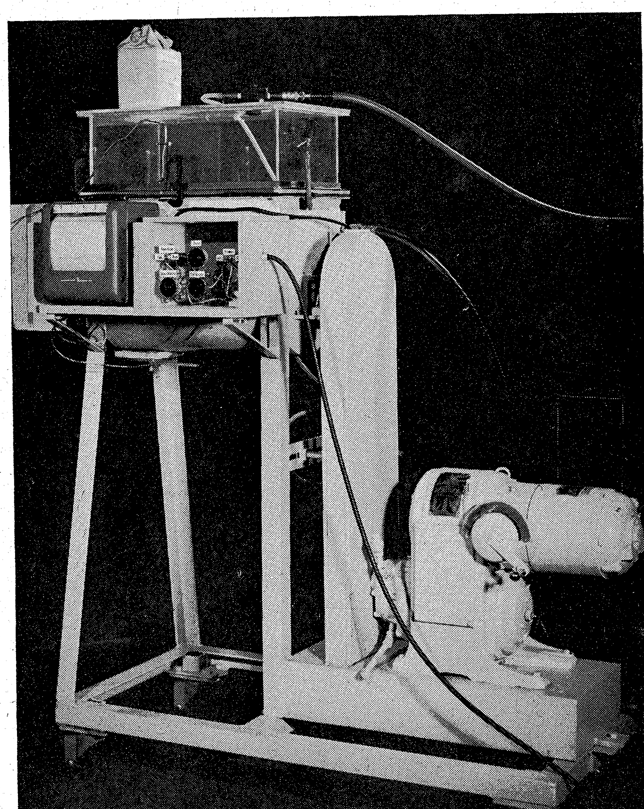

Fig. 1. Adapted ribbon mixer as reactor for acid modification of flour.

tion results shown in Fig. 3 were obtained on a second lot of the same type of flour received from the same source about 1 year later.

Equipment. A 1.3-cu. ft. double-ribbon mixer was adapted for use as a reactor (Fig. 1). A transparent plastic box 8 in. deep was made and mounted as a dome on the mixer top flange by means of C-clamps. Sealing was accomplished by foam rubber weather-stripping. A 4-in. stack was installed in the top of the dome and a bag filter tied to it. The spray is installed in an opening cut in the dome. The product is removed through a slide valve in the bottom of the mixer.

To follow closely the temperature changes during reaction, a thermistor probe connected to a circuit designed to give a linear voltage response to temperature change between 25° and 70°C. (77° to 158°F.) was inserted through the dome about 2 in. into the mixing flour. The temperature was recorded by a high-impedance millivoltmeter to give a continuous record of temperature change.

In the early runs, temperature control was achieved by spraying a small amount of water on the outside of the reactor. Because of the appreciable heat from the reaction of aqueous acid with dry flour, usually cooling was required near the end of the acid addition. A typical temperature chart is given in Fig. 2. This temperature profile may

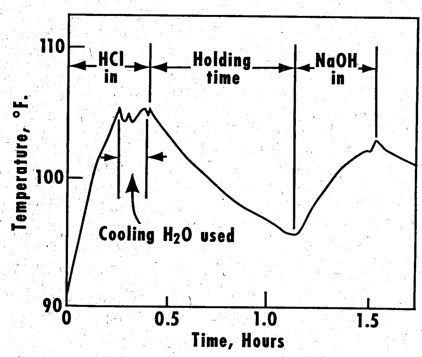

Fig. 2. Temperature changes during acid modification and alkali neutralization.

well be more typical of industrial-scale operation than would the "flat" temperature profile of a nearly isothermal system, because rapid heat exchange between a dry powder and a jacketed vessel wall is difficult to achieve in large vessels. In later runs, a water jacket was installed on the reactor and the temperature could then be kept uniformly low throughout the course of the reaction.

Spraying conditions are important in controlling agglomeration of the flour particles, which is an indirect measure of the homogeneity of the product. In this small reactor, the easiest way to obtain a fine spray at a rate low enough to ensure good dispersion throughout the flour was to use an air sprayer. An experimental sprayer was made by inserting a drawn glass orifice through rubber stoppers into a tee connection carrying compressed air. The orifice tip was positioned in the center of an annular air orifice to which the tee was attached. By longitudinal adjustment of the glass orifice through which the liquid was introduced and by regulation of the liquid head, a fair spraying action was achieved. Later a commercial spray (Spraying Systems Company, Set-up No. 104[2]) of similar design was purchased. The commercial spray is constructed of hard rubber and has machined orifices.

The commercial spray requires more air for operation than the experimental one, but very good control of rates is provided by its aspirating action.

Operating Procedure. Briefly, acid-modified flours were prepared by spraying from 9 to 11 ml. of 4*N* hydrochloric acid per 100 g. of flour into 30–40 lb. of flour that had been dried to less than 3% moisture content, holding the mixture at a temperature less than 37°C. (100°F.) for 30 min. to 2 hr., and then spraying in from 3 to 3.5 ml. of 14*N* sodium hydroxide per 100 g. of flour to stop the reaction and control the pH of pastes of the acid-modified flour.

Flour was also acid-modified by dry hydrogen chloride, by blowing the gas through a small orifice in the discharge valve of the reactor. The amount of gas used was determined by weighing the container before and after delivery. This method also gives a heat rise previously noted. Its advantages are that it yields a finer product with no more effort and that it eliminates drying, which is costly.

As an alternative to neutralization with 14*N* sodium hydroxide, dry ammonia gas was introduced in the same manner as the hydrogen chloride gas.

Analytical Procedures. Screen analyses of acid-modified flour were carried out by shaking 100 g. in a screen set consisting of 14-, 30-, 60-, and 140-mesh U.S. standard sieves for 40 minutes.

Viscosity measurements were made in a Brabender Amylograph; the viscosity reported is for a 20% solution of acid-modified flour when the temperature of the solution was 55°C. on the cooling cycle. The Brabender reading was converted to centipoises by a calibration curve.

The value of the product as a tub-sizing agent was estimated by a method developed by Ernst (3) using the tests of strength recom-

[2] The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over firms or similar products not mentioned.

mended by TAPPI. The results were analyzed by an analysis of covariance with retention as the independent variable, and the strength values were adjusted to a common retention (2).

Results and Discussion

Differences in acid-modified flour particle size distribution resulting from different spray qualities obtained with the two sprays used are shown in Table I. With the experimental spray, the particle distribution depended on the way in which the components were assembled and on the liquid orifice size, which was difficult to duplicate in glass. With the commercial spray, the distribution depended primarily on the spray rate, although reproducibility from run to run was not close.

TABLE I

SCREEN ANALYSIS OF ACID-MODIFIED FLOURS DEPENDS ON SPRAY QUALITY

Spray Design	Spraying Rate	Screen Analysis				
		Over 14 Mesh	14–30 Mesh	30–60 Mesh	60–140 Mesh	Through 140 Mesh
	cc. 4N HCl/min.	%	%	%	%	%
Experimental	34	0.4	2.4	9.6	28.9	58.6
Experimental	29	None	1.5	19.4	23.9	55.1
Commercial	43	None	0.1	2.1	28.7	58.9
Commercial	63	0.5	2.0	10.8	42.2	45.3

The data from a few typical runs with aqueous hydrochloric acid in which the temperature fluctuated in the manner shown in Fig. 2 are given in Table II. It will be noted that the final viscosity was not much lower in run 4 than in run 3, although the acid used and temperature

TABLE II

EFFECTS OF SOME VARIABLES ON PROPERTIES OF ACID-MODIFIED FLOUR

	Run Number					
	1	2	3	4	5	6
Variables						
Spray design	Exptl.	Exptl.	Comml.	Comml.	Comml.	Comml.
Acid, cc. of 4N/100 g.	10.1	9.0	9.0	9.2	9.5	10.0
Acid spray rate, cc/min.	41	29	28	43	41	48
Maximum temp., °F.	100	100	95	98	104	105
Holding time, min.	60	20	35	139	60	83
Results						
Viscosity, cp.[a]	380[b]	380[b]	656	621	488	426
Setback ratio[c]	gel	2.7	1.7	1.7	1.2	1.3

[a] Viscosity of a 20% solution at 55°C. as measured on the Brabender Amylograph cooling cycle.
[b] Estimated, to compare with other data measured on different machine.
[c] Ratio of viscosity of 20% solution held at 26°C. for 24 hours after preparation to viscosity when held for 1 hour.

were greater and the holding time was quadrupled. During 20 experiments, of which the data in Table II are typical, general trends were established, although the amount of change which occurred was not closely predictable. With the experimental spray, the viscosity varied from an estimated 170 to 370 cps. over a holding time range of 15 to 80 min. With the commercial spray, at higher average acid input and temperature, the viscosity range was from 430 to 660 over a time range of 30 to 139 min. Although spray rates were comparable for the two types of sprayers in some instances, the apparent rates of viscosity change differed greatly and seemed to be correlated with product particle size. Another correlate of particle size is the viscosity change on paste aging. Limited data suggest that setback is reduced by change in spray quality from the experimental to the commercial unit.

The final viscosity should be decreased by adding larger amounts of acid or by increasing the temperature or holding time if the reaction conforms to the usual processes of chemical kinetics. The degree and manner of viscosity change are important to a proper understanding of the process. After addition of a water jacket to the reactor, the

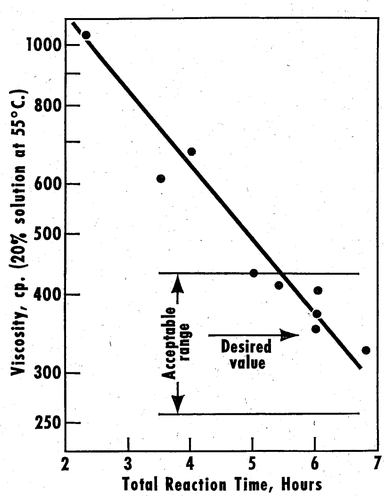

Fig. 3. Effect of time on product viscosity. Reaction at 80°F. with 11 cc. of 4N HCl per 100 g. of dry flour.

temperature could be held within ± 0.5°C., thus eliminating the first temperature peak shown in Fig. 2. Also after this improvement, viscosity correlated well with holding time (Fig. 3). These data were obtained under very carefully controlled conditions so that reproducibility of viscosity was good, and thus could be brought into an "acceptable" range near the tentatively desired value shown. The importance of temperature is demonstrated by the 3.5-hr. run. In this case the temperature reached 36°C. (97°F.) for a brief period during acid addition, thus reducing the viscosity below the value expected had the temperature been kept below 28°C. (82°F.) as in the other runs. These data also contrast with run 6 in Table II where, with less acid, only an hour and a half was required for the reaction to be essentially complete.

An exact viscosity can be achieved by blending an acid-modified flour of high viscosity with one having a lower viscosity. However, when acid-modified flours of unequal viscosities are blended, the resulting viscosity follows a geometric rather than an arithmetic law, as shown in Fig. 4. Here the viscosities obtained by blending two such

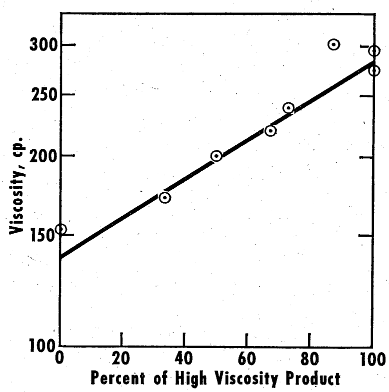

Fig. 4. Results from blending high- and low-viscosity products prepared by the wet spray method.

products in various proportions are plotted as a semilog function. Viscosities of blends of two or more products have been predicted within analytical error by calculating the logarithmic average.

Because the method used for estimating the tub-sizing effect of the products is not very precise, small differences in product quality were difficult to determine. Table III compares strength values for paper tub-sized with typical acid-modified flour produced by the general, nonisothermal pilot-plant procedures described and with a commercial product. The strength values of the standard untreated paper and the paper sized with a fine fraction of acid-modified flour produced by the wet spray technique are also included. The values of strength have been adjusted to constant retention of the size by the paper to give more comparable results. Although some real differences may exist

TABLE III

STRENGTH OF PAPER SIZED WITH ACID-MODIFIED FLOURS

Sample	Strength Values[a]		
	Burst	Tensile, Breaking Length	Fold, Double
	pts./100 lb.	*meters*	
Control paper	32	4,350	40
Acid-modified flour (4*N* HCl) treated flour	43	4,820	90
Fine fraction of above (+140 mesh)	45	4,830	80
Acid-modified flour (dry HCl)	43	4,900	70
Acid-modified flour (dry HCl, neutralized with dry NH_4OH)	45	5,010	100
Commercial product (hypochlorite-oxidized starch)	42	5,070	60

[a] Adjusted to a retention of 3%.

between the different products or between the average of the products and the commercial product, the differences are so small that they were not statistically significant in this series of tests. Properties of the product, other than paper strength improvement, are also important in its application as a tub size. These properties should be found in mill-run tests.

This preliminary experience with acid modification of a cereal flour shows that much more needs to be known to apply it to commercial use. While not a thorough study of the problems involved, the present investigation has indicated important areas for development.

Acknowledgments

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