

Mixograph Studies. V. Effect of pH¹

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ABSTRACT

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Decreasing the pH of flour-water dough gave mixograms with decreased mixing stability. Increasing the pH of flour-water dough gave mixograms with longer mixing times and greater mixing stability. Tenox (a mixture of butylated hydroxytoluene and butylated hydroxyanisole) did not reverse the effect of low pH, showing that the mechanism by which low pH affects mixing stability is different from that by which activated double-bond compounds affect mixing stability. Fumaric acid and potassium iodate

effectively decreased mixing stability at pH 6.12, but not at higher or lower pHs. Thus, activated double-bond compounds are necessary only at a pH near that of flour-water (~pH 6.0). The effect of pH on the flour-water mixogram stability is reversible. The data are consistent with the theory that the thin-mixogram tail indicates a conformational change in the gluten proteins as a result of overmixing.

When flour-water doughs are overmixed, the dough appears wet and loses some of its resistance to extension. Previously, researchers (Hoseney et al 1980, Schroeder and Hoseney 1978, Sidhu et al 1980, Weak et al 1977) reported on the effect of fast-acting oxidants and activated double-bond compounds on overmixing. They concluded that disulfide bonds are broken during mixing, creating thiyl radicals that react with activated double-bond compounds. The grafting of those compounds to the protein apparently decreases the dough's resistance to extension.

Recently, Danno and Hoseney (1982) reported that overmixing can be reversed by sodium chloride or sodium dodecyl sulfate (SDS). Surprisingly, the effects of fast-acting oxidants and activated double-bond compounds were also reversed by those reagents. Danno and Hoseney (1982) explained their results by assuming that the glutenin proteins underwent a configurational change as a result of overmixing in the presence of activated double-bond compounds. Because of that assumed change, they suggested that positive charges on the protein became more available and that NaCl and SDS neutralized or shielded those charges, causing the protein to reverse its configurational change.

If that were true, then the protein would be sensitive to changes in charges caused by other reagents. For example, a change in the pH of the dough water would change the charge on the proteins and thus would affect dough stability. Studies reporting the effect of pH on dough-mixing properties do not agree upon its effects. For example, Watanabe et al (1955), Galal et al (1978), and Tanaka et al (1967) reported marked weakening after peak time; in contrast, Bayfield and Young (1964) did not show weakening of their farinograms but did report that the dough lost its cohesiveness and became sticky at pH 4.6. Bennett and Ewart (1962) studied the effect of acids on dough protein using the Simon Extensometer. They found a marked reduction in extensibility as a result of acid addition and attributed the effect to addition of hydrogen ions to

the dough. They also suggested a hypothesis for the action of acid on flour protein similar to that of Galal et al (1978) and Danno and Hoseney (1982).

We document the effect of pH (both acidic and basic) on dough-mixing characteristics and relate those changes to the effects noted with fast-acting oxidants and activated double-bond compounds.

MATERIALS AND METHODS

We used an untreated commercial flour containing 11.6% protein and 0.43% ash. Mixograms were produced on a 10-g

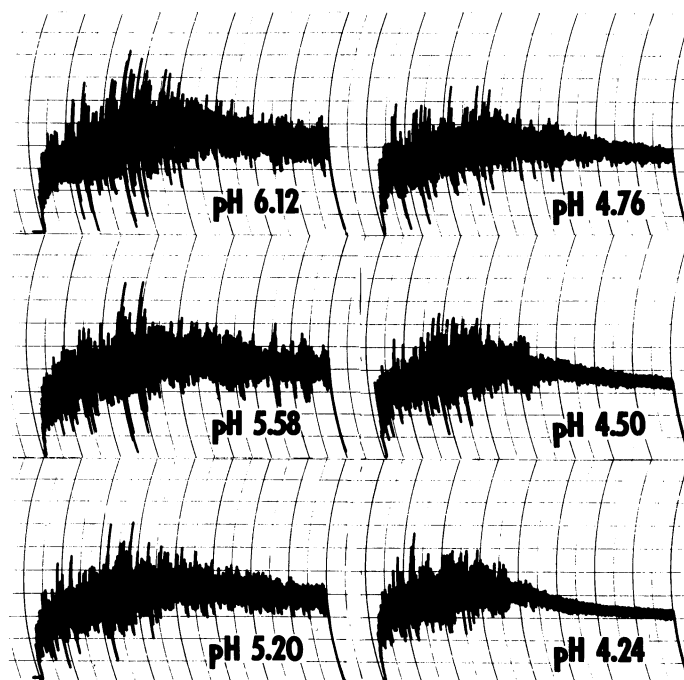


Fig. 1. Effect of acidic pHs on mixogram curves.

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mixograph as described by Finney and Shogren (1972). The pH of dough was adjusted down, with N lactic, acetic, or sulfuric acid replacing part or all of the dough water. The pH of dough was adjusted upward, with N sodium bicarbonate replacing part or all of the dough water. Fumaric acid was adjusted to pH 7.0 and added as part of the dough water. Tenox (tenox-4, Eastman Chemical Products, Inc., Kingsport, TN), a food-grade antioxidant containing 20% butylated hydroxytoluene and 20% butylated hydroxyanisole dispersed in 60% corn oil, was added directly into the mixing bowl. Gluten and starch were prepared as described by Schroeder and Hoseney (1978), except that defatted flour (petroleum ether-extracted) was used. Dough pH was determined by dispersing 10 g of dough in 100 ml of distilled water in a blender and measuring the pH of the resulting slurry.

RESULTS AND DISCUSSION

Flour-water dough gave a pH of 6.12. Adding increments of lactic acid to the mixing water decreased the pH of the dough and gave mixograms with decreased mixing stability (Fig. 1). At pH 4.24, the mixogram tail was very thin, similar to mixograms of flour with high levels of activated double-bond compounds or fast-acting oxidants added. The effect of other acids at about pH 4.2 is shown in Fig. 2. The apparent lesser effect of H₂SO₄ is explained as an

effect of the salts produced. This is shown clearly by adding an equivalent amount of Na₂SO₄ to acetic acid (Fig. 2).

Adding increments of sodium bicarbonate to the mixing water increased the pH of dough and gave mixograms of longer mixing time and much greater mixing stability (Fig. 3). The effect of pH on mixing stability was clear: at high pH, the dough was quite stable to overmixing; at lower pH, it was quite unstable. That effect can be explained by the change in charge on the proteins: at lower pH, the proteins have a more positive charge; those charges tend to repel each other and keep the protein from interacting with itself through

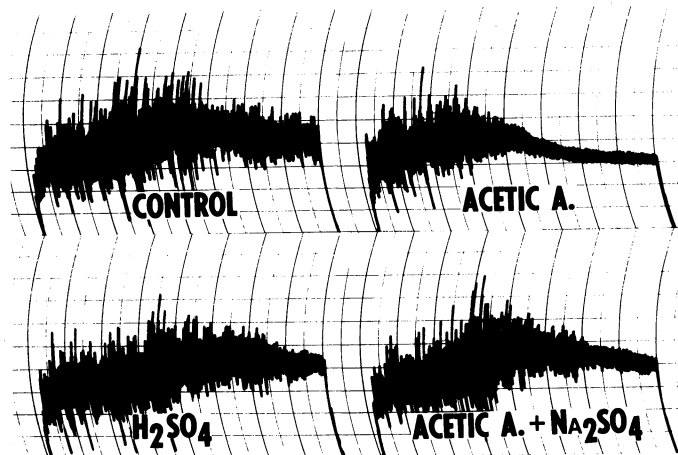


Fig. 2. Effect of acetic acid (pH 4.2), sulfuric acid (pH 4.2), and acetic acid plus an equivalent amount of Na₂SO₄ on mixogram curves.

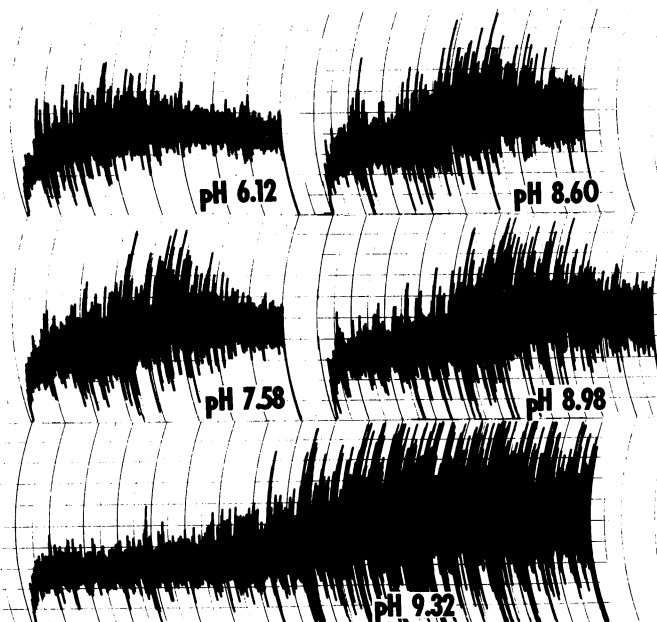


Fig. 3. Effect of basic pHs on mixogram curves.

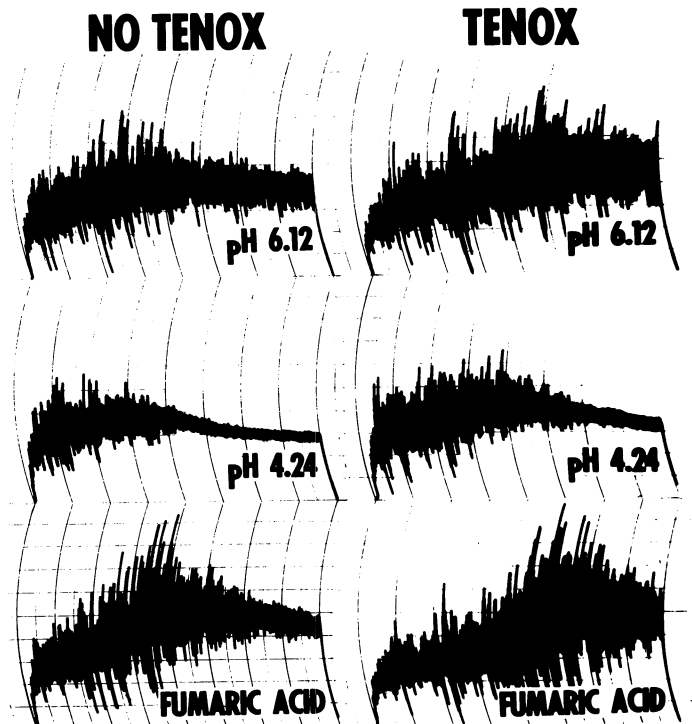


Fig. 4. Effect of tenox on mixogram stability.

DEFATTED GLUTEN PLUS STARCH

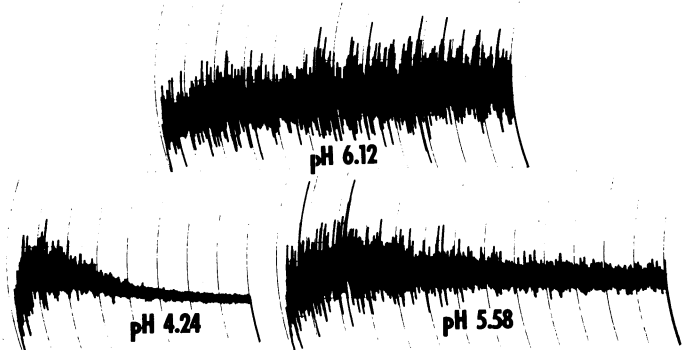


Fig. 5. Effect of acidic pHs on mixogram curves of gluten plus starch.

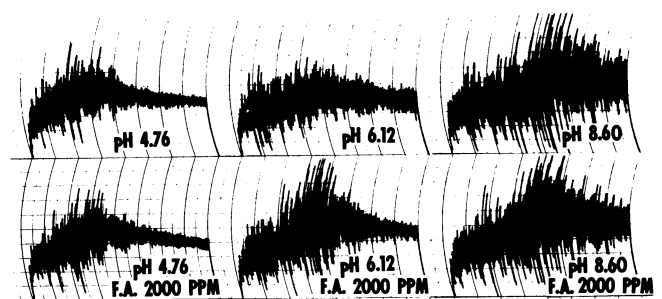


Fig. 6. Effect of fumaric acid at certain pHs on mixing stability.

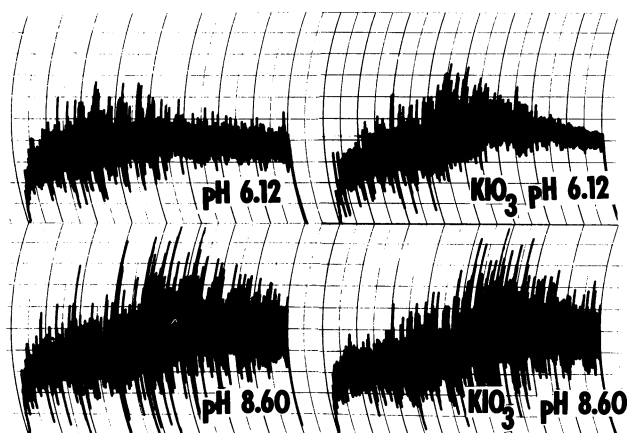


Fig. 7. Effect of potassium iodate (KIO_3) and certain pHs on mixing stability.

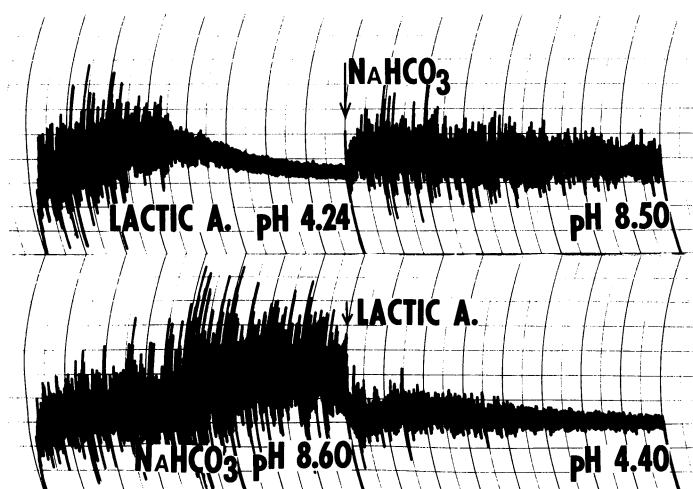


Fig. 8. Reversing the effect of lactic acid with sodium bicarbonate and reversing the effect of sodium bicarbonate with lactic acid as measured with the mixograph.

secondary bonds. As shown in Fig. 2, however, specific salt effects may also occur. As the pH was increased, the amount of positive charge declined, and essentially no negative charge was generated because practically all of the carboxylic acid group on the gluten protein side chains occur as their amides (Kasarda et al 1976). Thus, as the pH increased, the protein had less charge and could associate more closely, giving a very strong dough. The lack of charge also caused the protein to hydrate more slowly and therefore to require a longer mixing time.

Danno and Hosoney (1982) speculated that the extremely thin mixogram tail resulted from a conformational change in the glutenin proteins. They also concluded that an activated double-bond compound was necessary for rapid dough breakdown. Schroeder and Hosoney (1978) showed that tenox would reverse the effect of activated double-bond compounds. Thus, if the low pH were producing the thin mixogram tail by increasing the number of thyl radicals (S^{\cdot} , not SH) formed or by increasing the

reactivity of activated double-bond compounds, then adding tenox would reverse the effect. In fact (Fig. 4), the tenox did not have a noticeable effect at pH 4.24. This suggests that the more positive charges on the protein causes the assumed conformational change and that the addition of the activated double-bond compound would not be necessary, at least not at low pH. To test that theory, gluten and starch (flour minus the water solubles that contain the activated double-bond compounds) were mixed in the mixograph at certain pHs (Fig. 5). Clearly, the thin mixogram tails can be produced at low pH, even though no activated double-bond compound is in the system.

From the above discussion, it appears that activated double-bond compounds are necessary for rapid mixogram breakdown only at pHs equaling those for flour-water systems. When no activated double-bond compounds are available, such as in gluten plus starch (Fig. 4), the dough does not break down with longer mixing. As shown in Fig. 6, fumaric acid effectively decreased the mixing stability at pH 6.12 but not at pH 4.76 or 8.60. That also appears to be true for the action of fast-acting oxidants on mixing stability. At pH 6.12, KIO_3 decreased mixing stability (Fig. 7), but it had no noticeable effect on the mixogram at pH 8.60.

If, as suggested here, the effect of pH on the mixogram curve is only a change in the gluten protein conformation, then changing the pH after the dough is mixed would reverse the effect. Therefore, doughs were mixed at one pH for 8 min, and then sufficient acid or base was added (1 ml) to adjust the pH without grossly altering the dough consistency. As shown in Fig. 8, the effect of both acid and base at the pHs used was clearly reversible.

LITERATURE CITED

- BAYFIELD, E. G., and YOUNG, W. E. 1964. Flour brew studies. V. Effect of brew fermentation time. *Bakers Dig.* 38(1):69.
- BENNETT, R., and EWART, J. A. D. 1962. The reaction of acids with dough proteins. *J. Sci. Food Agric.* 13:15.
- DANNO, G., and HOSENEY, R. C. 1982. Effect of sodium chloride and sodium dodecyl sulfate on mixograph properties. *Cereal Chem.* 59:202.
- FINNEY, K. F., and SHOGREN, M. D. 1972. A ten-gram mixograph for determining and predicting functional properties of wheat flour. *Bakers Dig.* 46(2):23.
- GALAL, A. M., VARRIANO-MARSTON, E., and JOHNSON, J. A. 1978. Rheological dough properties as affected by organic acids and salt. *Cereal Chem.* 55:683.
- HOSENEY, R. C., RAO, H., FAUBION, J., and SIDHU, J. S. 1980. Mixograph studies. IV. The mechanism by which lipoxigenase increases mixing tolerance. *Cereal Chem.* 57:163.
- KASARDA, D. D., BERNARDIN, J. E., and NIMMO, C. C. 1976. Wheat proteins. Page 158 in: *Advances in Cereal Science and Technology*, Vol. 1. Y. Pomeranz, ed. Am. Assoc. Cereal Chem., St. Paul, MN.
- SCHROEDER, L. F., and HOSENEY, R. C. 1978. Mixograph studies. II. Effect of activated double-bond compounds on dough-mixing properties. *Cereal Chem.* 55:348.
- SIDHU, J. S., NORDIN, P., and HOSENEY, R. C. 1980. Mixograph studies. III. Reaction of fumaric acid with gluten proteins during dough mixing. *Cereal Chem.* 57:159.
- TANAKA, K., FURUKAWA, D., and MATSUMOTO, H. 1967. The effect of acid and salt on farinogram and extensigram of dough. *Cereal Chem.* 44:675.
- WATANABE, C., WATANABE, T., AND UEMURA, M. 1955. Researches on wheat milling and qualities of wheat flour. XI. On the effect of electrolyte on the rheological behavior of wheat flour dough. Preliminary report: On the effect of pH. *Shokuryo Kagaku Kenkyusho Kenkyu Hokoku* 10:15. Cited by Tanaka et al (1967).
- WEAK, E. D., HOSENEY, R. C., SEIB, P. A., and BAIG, M. 1977. Mixograph studies. I. Effect of certain compounds on mixing properties. *Cereal Chem.* 54:794.

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