

# MIXOGRAPH STUDIES. I. EFFECT OF CERTAIN COMPOUNDS ON MIXING PROPERTIES<sup>1</sup>

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## ABSTRACT

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The mixograph was used to study the effects of oxidants, sulfhydryl-containing reagents, compounds containing activated double bonds, and ascorbic acid on dough properties. Cysteine's effect of shortening mixing time was compared with that of other reducing compounds. Fumaric acid and related unsaturated compounds reduced mixing time (as previously reported), but caused rapid dough breakdown and thinning of the mixogram's tail. The action of *N*-ethylmaleimide, a sulfhydryl-blocking reagent, was similar to that of fumaric acid. Oxidants normally used in bread-baking did

not affect mixing time; however, the fast-acting oxidants (KIO<sub>3</sub>, azodicarbonamide, and KBrO<sub>3</sub> at pH 4.7) gave a rapid breakdown of dough and an extremely narrow mixogram tail. Slower-acting oxidants (ascorbic acid and KBrO<sub>3</sub> at pH 6.0) had little effect on the mixograms. Results did not confirm, as has been reported, that ascorbic acid reduced mixing time in an oxygen-limiting atmosphere. However, ascorbic acid in a CO<sub>2</sub> atmosphere did cause lower mixogram peak heights. Fast-acting oxidants were shown to interact with sulfhydryl compounds, which negated their effect on mixing.

It is generally accepted that oxidants increase the resistance of dough to extension, improve machining properties, and increase loaf volume. However, fast-acting oxidants such as potassium iodate are known to reduce the farinograph mixing tolerance (1,2). Potassium bromate, a slow-acting oxidant, has little or no effect during mixing except to increase water absorption (3).

The effects of certain sulfhydryl-containing compounds on dough-mixing are well documented. Since 1936, when Sullivan *et al.* (3) reported that glutathione reduced mixing time, action of those compounds during mixing has been described in several papers (4-8). Freilich and Frey (9) demonstrated that sulfhydryl compounds can overcome buckiness. Henika and Rodgers (10,11) patented cysteine-bromate-whey blends for short-time breadmaking.

To demonstrate the action of thiol-blocking reagents on dough-mixing, Mecham *et al.* (12) used the mixograph and Sullivan *et al.* (1) the farinograph. In 1971, patents were granted to Conn and Kichline (13) for the use of fumaric acid (FA) and unsaturated alcohols to reduce mixing time in conventional bread production. Commercial bakers, however, report that FA and the unsaturated alcohols do not reduce mixing time in continuous bread production systems. The action of those compounds in dough is unknown; however, the compounds reportedly react with thiol groups under certain conditions (14).

Ascorbic acid (AA) apparently acts differently from the mixing additives discussed so far. In conventional dough makeup, the influence of AA is similar to that of oxidants (15). L-ascorbic acid is purportedly oxidized by an enzyme to form dehydroascorbic acid, which acts as an oxidant (15). In the continuous bread production system, L-ascorbic acid reduces mixing speed requirements

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and produces softer doughs (15,16). Johnston and Mauseth (17) have patented the use of AA in continuous bread production. Zenter (18) has shown that neither reduction of disulfide bonds nor blocking of thiol groups can be attributed to AA. He suggests that AA acts as a hydrogen bond-breaking reagent similar to urea.

When a fast-acting oxidant and reducing agent are used together, logic would suggest that the reagents would react before they can have their desired effects on the dough system. This study was conducted to determine if such interactions occur.

### MATERIALS AND METHODS

A composite of experimentally milled hard red winter wheat flour (protein 12.3% and ash 0.44%) was used.

Solutions of each chemical were prepared fresh daily. Fumaric, maleic, and related acids were suspended in distilled water and neutralized with sodium hydroxide to pH 7.0. For the interaction studies, the two solutions to be studied were added to the water just before starting the mixograph.

A mixograph with a 35-g bowl was used (National Mfg. Co., 1218 N. 22nd Street, Lincoln, Nebr.), and procedures outlined for mixograph usage in AACC methods (19) were followed. A CO<sub>2</sub> atmosphere was achieved by sealing the mixograph chamber, displacing air with CO<sub>2</sub>, and maintaining an atmosphere that would not support combustion. Solutions used in the CO<sub>2</sub> atmosphere tests were made from boiled distilled water. The flour was purged to remove air and allowed to set for 2 hr under a CO<sub>2</sub> atmosphere.

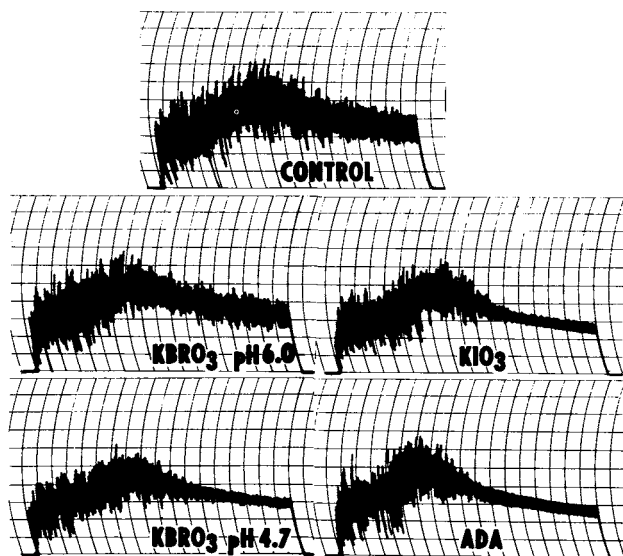
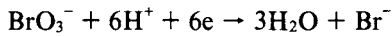


Fig. 1. Mixograms showing the effects of certain oxidants (30 ppm flour basis) on flour-water doughs.

## RESULTS AND DISCUSSION

The actions of some commonly used oxidants on flour-water mixograms are shown in Fig. 1. The major effect of potassium iodate ( $\text{KIO}_3$ ), azodicarbonamide (ADA), and potassium bromate ( $\text{KBrO}_3$ ) at pH 4.7 is to accelerate dough breakdown after the mixing peak (minimum dough mobility). The oxidants did not affect mixing time. It is generally accepted that oxidants increase the resistance to extension. However, resistance to extension decreases rapidly (as shown by the thinning of the mixogram tail, Fig. 1) after the peak has been reached.

Bromate ( $\text{BrO}_3$ ) accelerates dough breakdown substantially at pH 4.7, but not at pH 6.0 (Fig. 1). Hlynka and Chanin (20) found that optimum bromate requirements decrease with decreasing pH. The reduction of bromate ion requires hydrogen ions, as shown in this equation (21):



Bushuk and Hlynka (22) showed that the reaction rate of bromate in dough increases sharply when the pH decreases below pH 5.0. Bromate at the proper pH apparently is just as effective as the fast-acting oxidants. [The bromate curve ( $\text{KBrO}_3$ , pH 4.7) in Fig. 1 has a lower peak height than that of the control because of the buffer solution used to adjust pH.]

The pronounced effect of fast-acting oxidants on the rate of dough breakdown may indicate serious problems with mixing tolerance when those oxidants are used. The phenomenon also suggests a possible quality control procedure for the detection of fast-acting oxidants in flour. The procedure, which would require running mixograms of untreated and treated flour, could be an excellent way to detect oxidant-feeder malfunctions.

The effects of certain sulfhydryl-containing reagents on dough-mixing are shown in Fig. 2. Mixing time was reduced from 3.75 to 2.5 min with each treatment. Higher levels of cysteine are known to accelerate dough breakdown.

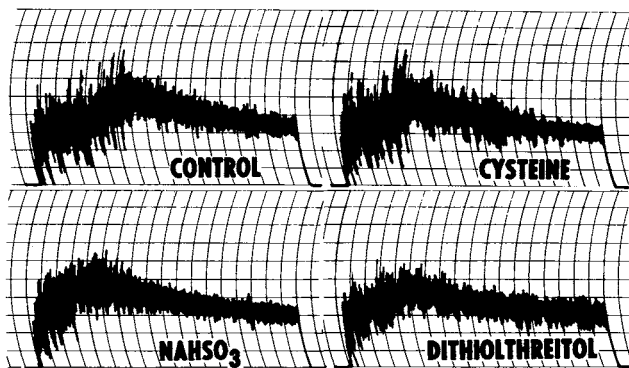


Fig. 2. Mixograms showing the effects of certain sulfhydryl agents (20 ppm flour basis) on flour-water doughs.

Jones *et al.* (7) found that dithiothrietol, at 200 ppm, reduced mixing time and greatly accelerated dough breakdown. In our work, dithiothrietol used at 20 ppm produced no rapid dough breakdown. Sodium bisulfite appeared not to decrease mixing tolerance as much as cysteine or dithiothrietol did.

In Fig. 3, the actions of certain activated unsaturated compounds (thiol blocking agents) are shown. Use of FA, maleic acid (MA), or N-ethylmaleimide (NEMI) reduced mixing times about 1 min, and caused a rapid dough breakdown after the peak, similar to that observed with fast-acting oxidants. Sorbic acid (curve not shown) was also effective; saturated acids such as succinic acid were not. At levels above 500 ppm, MA or FA caused no further reduction in mixing time; however, the rate of dough breakdown increased.

Activated, unsaturated acids are reportedly less effective in continuous-bread than in conventional-bread production. It is generally believed that oxygen is

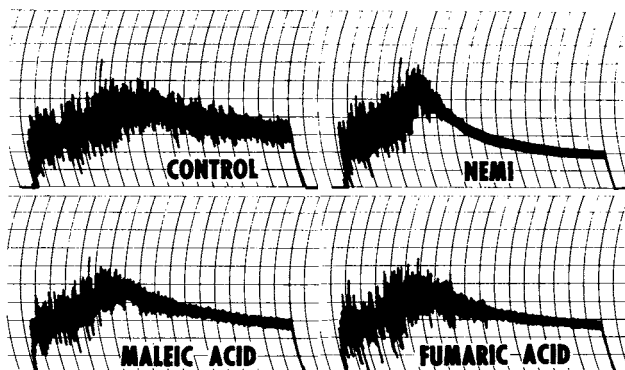


Fig. 3. Mixograms showing the action of compounds containing an activated double bond at flour dosages of 500 ppm for N-ethylmaleimide (NEMI) and 2000 ppm for maleic and fumaric acid.

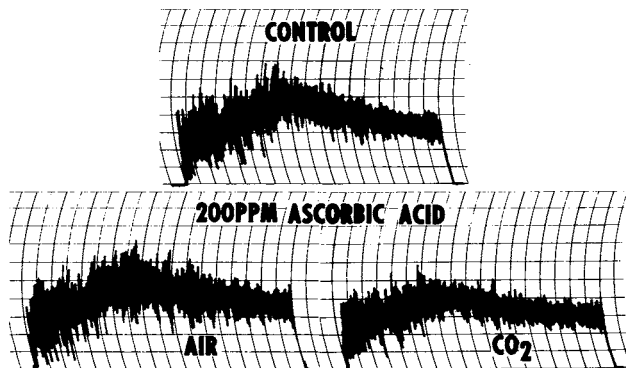


Fig. 4. Effect of ascorbic acid on dough in air and CO<sub>2</sub>.

more limiting in continuous systems. However, mixograms containing FA in air and  $\text{CO}_2$  atmosphere were essentially identical. Therefore, oxygen does not appear to be necessary for FA to reduce mixing time. Improved mixer efficiency (less time in the developer) in continuous-bread production could be responsible for decreased effectiveness of FA in the continuous system. The loss of effectiveness of FA in continuous-bread production may be related to interaction with other ingredients used in bread dough and not found in the flour-water doughs used in this work.

Mixograms of doughs mixed with AA in air and  $\text{CO}_2$  atmospheres are shown in Fig. 4. The only discernible effect of AA is a reduction of peak height. The lower curve height for dough mixed in  $\text{CO}_2$  with AA could be a manifestation of the "softer and drier doughs" described by Johnston and Mauseth (17) using AA in continuous-bread production. Even though no reduction in mixing time was

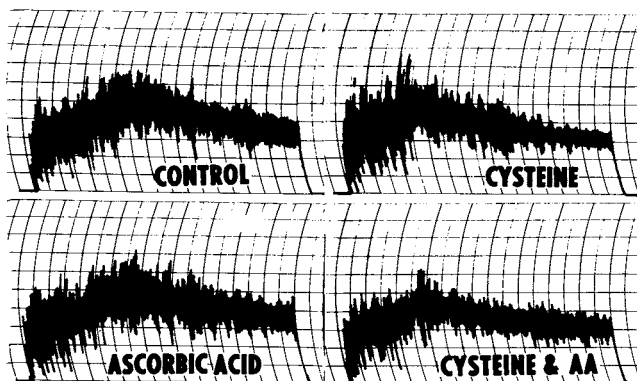


Fig. 5. Effect of cysteine (20 ppm) and ascorbic acid (200 ppm) together and separately.

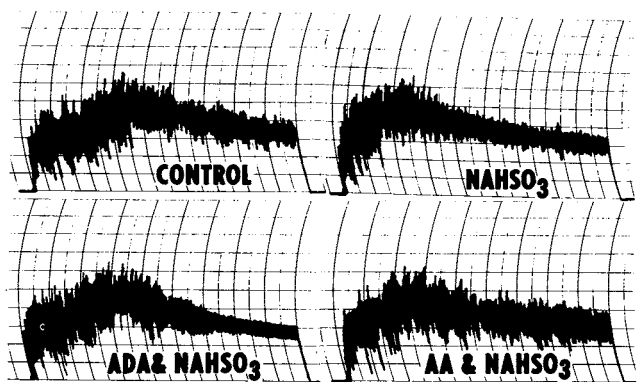


Fig. 6. Interaction of  $\text{NaHSO}_3$  (20 ppm) with ADA (30 ppm) and with ascorbic acid (200 ppm).

shown in the curve of AA in CO<sub>2</sub>, a softer dough could require less energy to mix.

The interaction of AA with cysteine (Fig. 5) resulted in the decrease in curve height (essentially the same as observed with AA in a CO<sub>2</sub> atmosphere). That indicates that AA, and not dehydroascorbic acid (AA in an air atmosphere), was responsible for lowering the curve height because the reducing agent would be

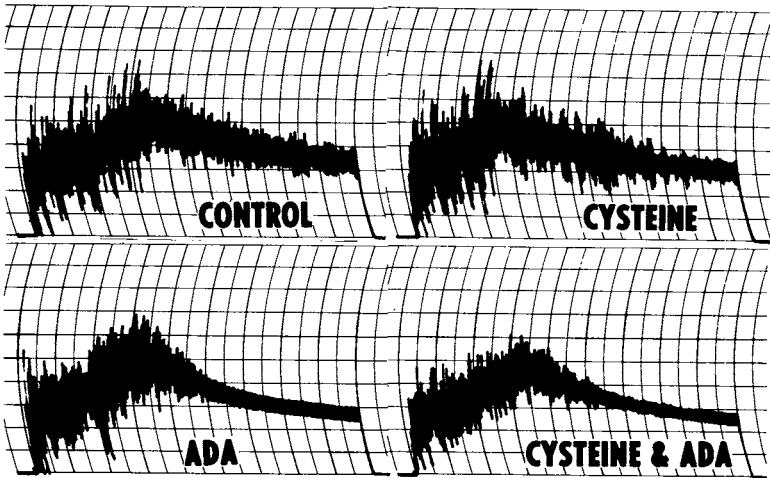


Fig. 7. Interaction of cysteine (20 ppm) and ADA (30 ppm).

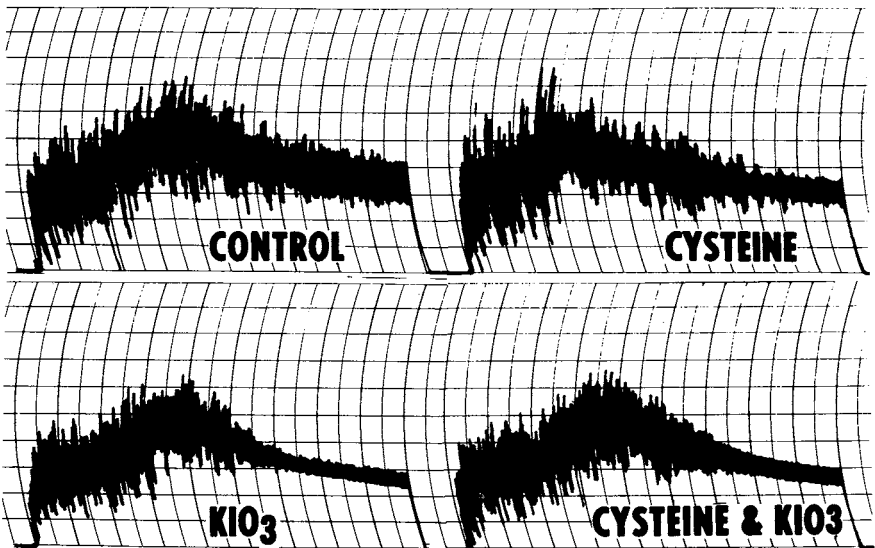


Fig. 8. Interaction of cysteine (20 ppm) and KIO<sub>3</sub> (30 ppm).

expected to prevent or slow the oxidation of AA. Hopkins and Morgan (23) found that glutathione prevented oxidation of AA even in the presence of copper. Grant (24) reported that cysteine was only slightly inhibitory on the oxidation of AA; however, his data were for flour-water slurries and not for doughs. Mixtures of AA and  $\text{NaHSO}_3$  or oxidants caused no change in mixogram peak height or mixing time.

The interaction of  $\text{NaHSO}_3$  and ADA is shown in Fig. 6. The excess ADA completely oxidized the reducing agent so that mixing time was not reduced. The effect of the oxidant also was reduced, as shown by less thinning of the mixogram tail. The interaction of excess oxidant with cysteine is shown in Figs. 7 and 8.

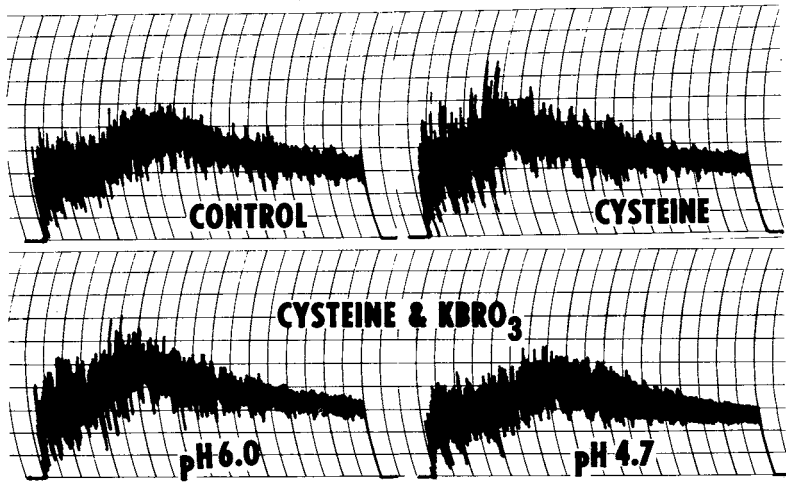


Fig. 9. Interaction of cysteine (20 ppm) and  $\text{KBrO}_3$  (30 ppm) at pH 6.0 and 4.7.

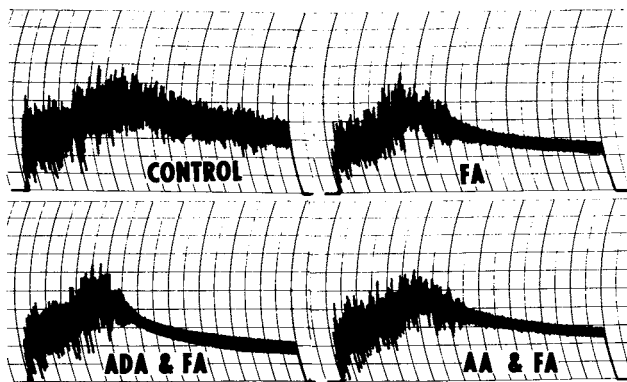


Fig. 10. Interaction of fumaric acid (2000 ppm) with ADA (30 ppm) and with ascorbic acid (200 ppm).

Both  $\text{KIO}_3$  and ADA reacted with cysteine so that no reduction in mixing time occurred. Figure 9 shows very little interaction of bromate and cysteine at pH 6.0 but, at pH 4.7, the reduction of mixing time caused by cysteine was lost.

Currently, some commercial baking procedures use both reducing agents and oxidants at mixing. If our findings hold true for complete dough, then combining oxidants and reductants during dough-mixing apparently defeats the purpose of using either an oxidant or a reductant. In straight-dough processing, using both bromate and cysteine would enable maximum effective usage of the additives because the pH would be high enough not to trigger the bromate reaction. As fermentation reduced the pH of the dough, bromate would start to affect dough properties. Thus, because of bromate's pH dependence, both reductant and oxidant perform their designated tasks without interaction. Preferment or sponge-dough systems in which bromate and cysteine are added at the same time will use the dough conditioners less effectively, because the reagents react with each other. A mixograph was run in which cysteine was added at the start of mixing and  $\text{KIO}_3$  added after the peak. The mixogram tail still thinned even though cysteine dosage was in excess of  $\text{KIO}_3$ . Timing of the addition to dough might possibly solve the problem of oxidant and reductant interaction. An oxidant could be added at the mixing peak or shortly before, because little cysteine would be available to interact with the oxidant.

Figure 10 shows mixograms of FA added with ADA or AA. Apparently FA does not interact with ADA or AA.

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