REACTIONS OF CYSTEINE, BROMATE, AND WHEY IN A RAPID BREADMAKING PROCESS[1]

R. G. Henika and N. E. Rodgers[2]

ABSTRACT

Reactions triggered by cysteine, bromate, and whey rapidly developed and matured a dough system independently of yeast fermentation. Cysteine (60 p.p.m.) reduced peak mix time of unfermented doughs 30–65%, depending upon flour strength, and 100 p.p.m. gave optimum extensibility and relaxation. Potassium bromate alone up to 40 p.p.m. improved bread quality slightly, whereas cysteine alone up to 100 p.p.m. significantly decreased it. Whey tempered both the depressing effect of cysteine and the bromate benefit. Interactions of cysteine, bromate, and whey proved complex at low levels of bromate, but above 20 p.p.m. bromate and with 4% whey, bread quality improved greatly as cysteine was increased from 20 to 80 p.p.m. Excellent loaf volume and grain quality, along with short mixing time and high extensibility without preliminary fermentation, were obtained with 80 p.p.m. cysteine, 4% whey, and 50–60 p.p.m. bromate.

This paper describes beneficial effects of cysteine, potassium bromate, and whey in a rapid breadmaking process using batch equipment. A later paper will cover reactions under continuous mix conditions.

A balanced combination of cysteine, bromate, and whey promotes rapid and complete mix development of unfermented dough and subsequent maturing with limited fermentation. Thus, controlled biochemical development and maturity replace preliminary fermentation reactions and eliminate long sponge or straight-dough fermentation steps. Fermentation reactions condition the yeast cell for optimum gas production and supplement the maturing action of the oxidant. A patent has been granted (1), practical aspects have been described (2,3), and the Federal Standards of Identity for bread and rolls have been changed to include cysteine (4).

Bromate has long been used as a dough conditioner to supplement fermentation mechanisms, and cheddar or Swiss cheese whey has shown increased acceptance as a dairy ingredient in yeast-fermented foods. But beneficial effects of cysteine seem contrary to reports in the literature. Balland in 1884 reported liquefaction of gluten by wheat germ (5), and Sullivan later showed that glutathione was the offender (6). Meanwhile, it was reported that wheat germ reduced baking

[1] Manuscript received October 8, 1964. Contribution from the Research and Development Laboratory, Foremost Dairies, Inc., San Francisco, Calif. Presented at the 48th annual meeting, Minneapolis, Minn., April-May 1963.

[2] N. E. Rodgers presently at Pillsbury Mills, Inc., Minneapolis, Minn.

quality (7), that both cysteine and glutathione greatly softened dough (8), and that glutathione reduced mix time and impaired bread quality (9). While many authors described these effects as deleterious (10, 11), a few suggested that cysteine could improve the baking quality of bucky flours (12) and improve bread texture (13). Swanson and Andrews confirmed that cysteine reduced mix time and still made good bread (14), but concluded later that it impaired gas retention (15).

Most studies showing deleterious effects of sulfhydryl compounds have been made with doughs involving extensive fermentation. The beneficial effects of cysteine reported here stem from sharply curtailing the role of fermentation in dough development and maturation.

Materials and Methods

Materials. Commercial flours milled in 1959 are described below. Water was adjusted to give peak consistency of 500 B.U. Cysteine was obtained from Nutritional Biochemical Corp. in the form of L-cys-

Description	*Peak Mix Time*	*Protein*	*Ash*
	min.	%	%
Strong Montana spring, highly refined, short patent	9	12.7	0.40
80% Hard spring and 20% hard winter, long patent, all around one-type, bromated	6	11.7	0.43
Idaho red winter, fancy, short patent, topping	4	11.1	0.39
50% Hard red winter and 50% hard white, northern bluestem, short patent	3	10.8	0.40

teine hydrochloride monohydrate, and all data are so reported. Other cysteine salts performed similarly on an equal-cysteine basis. Potassium bromate was reagent grade. The whey was a commercial, spray-dried, hydrated sweet cheddar cheese whey with heat-treatment similar to that given high-heat nonfat dry milk (NFDM). Table I compares the composition of whey with NFDM and flour. The figures were compiled from many sources, most reported less than 10 years ago, and each is an average from at least three authors. (Cheddar whey from one plant in Wisconsin over a 5-year period analyzed 72.5% lactose, 12.5% protein, and 8.02% minerals calculated to 4.0% moisture.)

Farinograph Tests. Flour, water to give 400-B.U. peak consistency, 1.75% salt, 4% whey, and cysteine were mixed at 86°F. to past peak development. Peak development time refers to the point of maximum dough consistency.

TABLE I
COMPARATIVE COMPOSITIONS OF WHITE BBEAD FLOUR, NONFAT DRY MILK, AND CHEDDAR WHEY

	FLOUR	WHEY	NONFAT DRY MILK
Gross composition (%)			
Moisture	14.0	4.0	3.0
Carbohydrate	73.0	71.8	51.4
Protein	11.52	12.7	36.3
Mineral	0.43	8.22	8.14
Fat	1.08	0.98	0.86
Energy (cal./100 g.)	357	344	362
Mineral composition (mg./100 g.)			
Potassium	144	2141	1567
Calcium	14.6	720	1262
Phosphorus	94.9	647	991
Sodium	2.6	896	620
Magnesium	25	139	117
Vitamins (mg./100 g.)			
Riboflavin	0.040	2.48	2.00
Thiamine chloride	0.074	0.458	0.35
Niacin	1.05	0.97	1.04
Choline	179	254	134
Inositol	54	265	201
Calcium pantothenate	0.43	4.81	3.41
Pyridoxine	0.19	0.25	0.50
Biotin	0.0012	0.030	0.046
Essential amino acids (g./100 g.)			
Isoleucine	0.563	0.777	2.27
Leucine	.887	1.16	2.96
Lysine	.284	0.883	2.87
Methionine	.194	0.186	0.931
Cystine[a]	.269	0.261	0.329
Methionine + cystine	.463	0.447	1.26
Phenylalanine	.665	0.341	1.86
Threonine	.364	0.707	1.61
Tryptophan	.133	0.166	0.50
Valine	0.558	0.640	2.44

[a] Can fulfill part of methionine requirement.

Extensigraph Tests. Cysteine was added to a typical white bread formula including yeast but not yeast food. The spring and winter, one-type flour was used. Doughs were mixed to peak in the farinograph and 150-g. aliquots given 0 to 40 min. rest at 86°F. After the doughs were rounded and moulded, they were relaxed 8 min. and stretched. This formula and procedure duplicated bakery conditions except for the absence of bromate.

Baking Tests. White bread was made with the same flour in a typical wholesale formula containing 3.0% yeast, an Arkady-type yeast food without bromate, and no dairy solids. Cysteine, bromate, and whey were added singly or in combination. Cysteine and bromate were not allowed to react with each other before being mixed in the dough. After mixing *without a preceding sponge step* to optimum development at 82°F., the doughs were divided immediately to give 1-lb. baked weight. After a 40-min. floor time, they were rounded by hand, relaxed 10 min., moulded, and then proofed to a specified height or for a constant time. The doughs were baked 20 min. at 445°F. and cooled 10 min.; loaf volume was measured by rapeseed displacement. The next day, the grain quality was measured by the use of oblique light and a code to ensure impartiality. A score of 7 was minimum acceptable wholesale grain quality, 9 desirable, and 10 excellent. Uniform, small, oval cells with thin walls were scored highest.

Results

In dough tests, fermentation was limited to mixing and subsequent testing steps. With finished bread, yeast action was limited to a 40-min. floor time in addition to that occurring during mixing, dough handling, and proof. This distinguished the short-time process from that of a no-time dough, a sponge and dough, a straight dough, and certain brew methods. The 40-min. floor time was based on the gas production limitations of present commercial yeast. This was the shortest time which, combined with mixing time and intermediate proof, allowed the yeast cells in a bread dough at 82°F. to reach a high and uniform rate of gas production at the time of moulding.

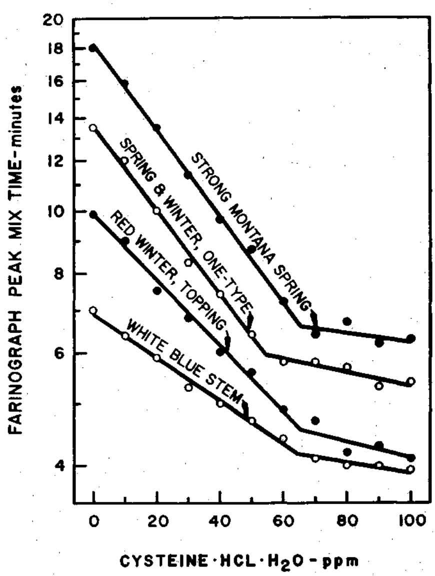

Fig. 1. Effect of cysteine on farinograph peak mix times of four types of bread flour.

Differences in loaf volume and grain quality were due primarily to differences in gas retention, not gas production.

Development Time. Figure 1 shows the effect of cysteine on farinograph development of flours in a simple dough containing salt and whey. A logarithmic decrease in peak time with increasing cysteine characterized all flours. Despite widely variant properties of the native flours, the logarithmic trend extended uniformly to 53–63 p.p.m. cysteine. Beyond, the effect sharply diminished. Cysteine also increased peak consistency slightly, 75 p.p.m. being equivalent to reducing absorption 0.5%. The curve for each type of flour is remarkably reproducible from lot to lot and year to year. Addition of potassium bromate up to 100 p.p.m. does not change the cysteine effect.

Considering that peak consistency was held constant, it seems that the cysteine required to saturate the development reactions is quite constant, regardless of large differences in protein content. In the bakery, this reduction in development time is similar to the relative difference in peak development times of a straight or brew dough and a remixed sponge and dough (2).

Extensibility. Cysteine increased dough extensibility and effectively retarded loss of extensibility during floor time. Figure 2 indicates a threshold at 50 p.p.m., above which cysteine significantly increased

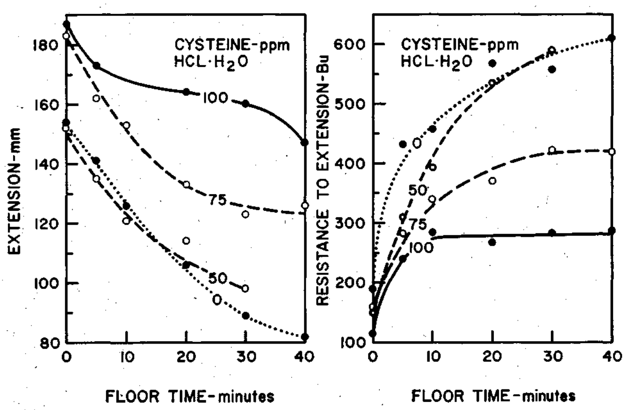

Fig. 2. Effect of cysteine on extensigraph properties of unbromated "straight" doughs at various floor times.

extension. At the higher levels, extensibility did not decrease with floor time. It is important, both theoretically and practically, that the threshold level which improved extensibility was only slightly higher than the maximum level which effectively reduced mix time. Resistance to extension showed a similar threshold level. While these data are based on doughs without bromate, we have found that, at 82°F., potassium bromate does not materially change the resistance pattern until late in the floor time. At this time, resistance increases above the amount found with high levels of cysteine alone.

The high extensibility, rapid relaxation, and maintenance of extensibility during floor time in the extensigraph have been confirmed in the bakery, where these properties allow rapid and easy dough-handling, either by hand in a retail shop or by high-speed make-up in a wholesale plant.

Bread Properties. Although the above dough studies show beneficial effects of cysteine on mix time and machinability, breads made from such unbromated doughs have inferior volume and grain quality. Figure 3 shows that, in bread without bromate and whey, loaf volume declined linearly with increasing cysteine. Adding 4% whey tempered

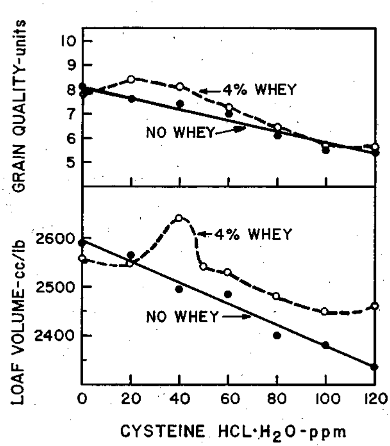

Fig. 3. Effect of cysteine and whey on bread properties of "straight" doughs in the absence of bromate. Doughs given 40 min. floor time and proofed 60 min.

depression of loaf volume and grain quality, but the high cysteine level required for proper development and extensibility made poor bread.

In contrast, Fig. 4 shows that, without cysteine or whey, levels of potassium bromate above that used in long fermentation methods improved loaf volume and grain quality somewhat. However, even at the optimum level, the grain quality was not satisfactory and the doughs took too long to mix and were too bucky to handle at high speed. The addition of whey tempered the improving effect of bromate.

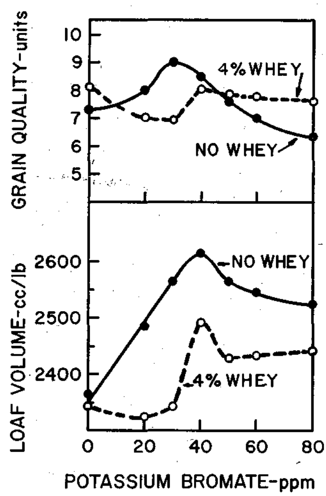

Fig. 4. Effect of bromate and whey on the bread properties of "straight" doughs in the absence of cysteine. Doughs given 40 min. floor time and proofed 3.2 cm. above edge of pan.

Figure 5 shows the effects of simultaneously varying cysteine and bromate in the presence of 4% whey. In the range of 0–20 p.p.m. bromate, substantial reversals in volume and grain quality occurred as the cysteine level was increased. Above 20 p.p.m. bromate, the gen-

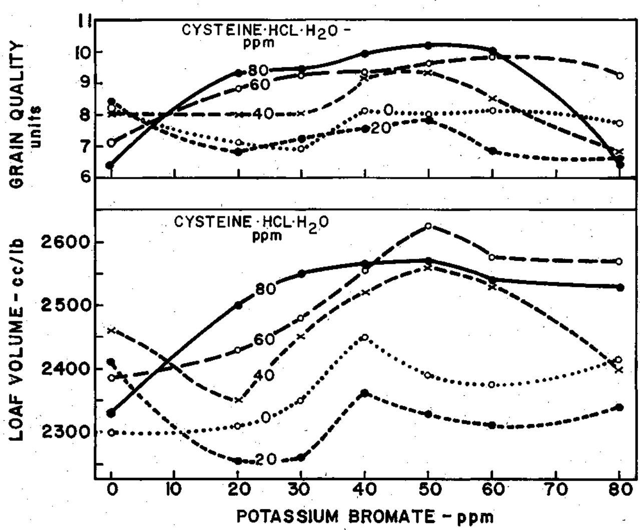

Fig. 5. Effect of cysteine and bromate on bread properties of "straight" doughs containing 4.0% whey. Doughs given 40 min. floor time and proofed 3.0 cm. above edge of pan.

eral pattern was one of seeming synergistic improvement of both volume and grain with increased cysteine. Although not shown, the pattern at 100 and 120 p.p.m. cysteine was similar to that at 80 p.p.m. If a dough improver is defined as an ingredient which significantly improves loaf volume and grain quality, then, under these conditions, both cysteine and bromate should be called dough improvers.

The quality optima at 50 p.p.m. potassium bromate and 80 p.p.m. cysteine shown in Fig. 5 are significant, since they combine a concentration of cysteine affording a minimum mix time and the point of best machinability with the level of oxidant yielding optimum maturity. In commercial bakeries, both optimum bromate and cysteine level vary somewhat with the kind of yeast-raised item and the flour strength.

Figure 6 shows how whey improved volume and grain quality with 80 p.p.m. cysteine and various levels of bromate. Although it tempered

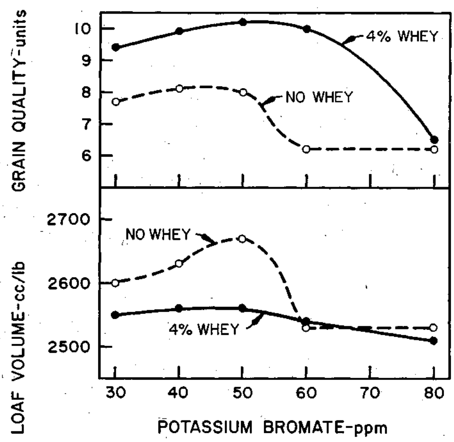

Fig. 6. Effect of whey and bromate on bread properties of "straight" doughs containing 80 p.p.m. cysteine. Doughs given 40 min. floor time and proofed 3.0 cm. above edge of pan.

the depressing effect of cysteine without bromate in Fig. 3 and the improving effect of bromate without cysteine in Fig. 4, whey rather unexpectedly showed considerable bread improvement when used with both cysteine and bromate. It also increased the bromate requirement 10 p.p.m. and, in commercial practice, markedly increased mixing and maturity tolerances. Several lots of high-heat NFDM which showed good baking properties in the sponge and dough process significantly delayed maturation reactions with cysteine and bromate, to give poor loaf volume and open grain. Adjusting oxidant level did not improve the performance of NFDM.

Full-size production runs in a large wholesale bakery were made with a product containing whey, cysteine, and bromate ("Reddi-Sponge"). Formula and procedure were similar to that given above (3% yeast, no sponge step, 82°F. dough temperature, 40-min. floor time, etc.). Mixing and machining properties were excellent. Bread scores from a well-known independent testing laboratory on triplicate samples of bread from this product and process and sponge and dough bread made at the same time are given in Table II. Note that

TABLE II

EXPERT SCORES OF COMMERCIAL WHITE BREAD MADE BY THE SPONGE AND DOUGH METHOD AND THE NEW SHORT-TIME METHOD WITH A CYSTEINE-WHEY-BROMATE PRODUCT

	PERFECT [a]	SPONGE AND DOUGH [b]	NEW METHOD [c]
External			
Volume	10	9.5	10
Crust color	8	7.5	8
Symmetry	3	3	3
Bake	3	2	2.5
Crust char.	3	2.5	2.5
Break	3	2	2
	30	26.5	28
Internal			
Grain	10	8	8.5
Crumb color	10	8	8.5
Aroma	10	9.5	9
Taste	15	13.5	13.5
Mastication	10	9	9
Texture	15	13	14
	70	61	62.5
Total	100	87.5	90.5

[a] All white bread scored past 3 months: average score = 85; highest score = 89.5.
[b] Weight, 16¾ oz.; length, 9 in.; compressimeter softness, 10.0 g./2.5 mm.
[c] Weight, 16½ oz.; length, 9 in.; compressimeter softness, 10.0 g./2.5 mm.

the sponge bread had a higher score than average and that the cysteine-whey-bromate bread not only had a score even higher but a score higher than any received during the previous 3-month period.

These data show that a proper combination of cysteine, whey, and bromate can completely develop and mature a dough without a long fermentation step, before or after mixing, to give top-quality bread. Savings in time, labor, space, and equipment are thus effected.

Discussion

The real dough-conditioning benefits of a 4-hr. sponge step are not really appreciated until one tries to make high-quality bread without it. These benefits are 1) reduced time to reach peak development during mixing, 2) increased extensibility at low temperatures without stickiness, and 3) significantly improved gas retention upon subsequent maturing. Not only are these properties essential, but their timing and sequence are critical. Successful breadmaking requires synchronizing these properties with optimum gas production.

The data in this report show that cysteine reduced development time 40%, markedly increased extensibility, and significantly improved gas retention upon proper oxidation in the presence of whey, with fermentation limited to that needed for optimum gas production. It is difficult to determine whether cysteine and bromate reactions are concurrent or separated in time at different phases of dough development and maturation. Cysteine and bromate react rapidly with each other in water solution, but the absence of any effect of bromate on the flour protein-cysteine reaction in the farinograph suggests an independent role for cysteine in bread dough.

The threshold concentration effect of cysteine in changing dough extensibility (Fig. 2) indicates a reaction beyond mechanical development. The relatively small shift in bromate optimum from 40 to 50 p.p.m., associated with low and high cysteine concentrations (Fig. 5), overtly precludes any extensive mutual destruction of the oxidizing and reducing agents by direct reaction. Moreover, this situation suggests an independent role for bromate.

In speculating on the role of cysteine, it is interesting to explore the possibility that, for proper dough development, not only must the disulfide-linked matrix of flour protein be unfolded, but also, oxidative reclosure must be delayed until the foundation structure of the bread is established upon moulding. This seems somewhat contrary to theories suggesting that the oxidant acts as a dough improver by suppressing disruption or translocation of disulfide bonds through –SH interchange. Consider, for example, the following family of reactions:

(a) $RSH + PSSP \rightarrow PSH + RSSP$
(b) $RSH + RSSP \rightarrow PSH + RSSR$
(c) $KBrO_3 + 3RSH + 3PSH \rightarrow 3RSSP + KBr + 3H_2O$
(d) $KBrO_3 + 6RSH \rightarrow 3RSSR + KBr + 3H_2O$
(e) $KBrO_3 + 6PSH \rightarrow 3PSSP + KBr + 3H_2O$

where RSH is cysteine or a fermentatively-derived –SH compound and P is flour protein.

During mechanical mixing, reactions *a* and *b* show cysteine opening up the flour protein molecule. If the access of RSH to disulfide bridges within the protein matrix were limited initially, reaction *a* would predominate and a temporarily blocked situation is created so the S–S bond cannot be restored in its original position. If reaction *c* takes precedence over *d* and *e*, –SH groups can be oxidatively blocked and a folded protein configuration further opened up. In the expanded state, the protein matrix can be reoriented into films by mechanical action on the dough.

Once the dough structure has evolved and residual –SH groups move into favorable position in the expanding dough, the S–S bridges by reaction *e* can firm up the matrix into a stable, gas-retaining, cellular structure. With progressive unfolding, faster infiltration of the protein by RSH is facilitated and reaction *b* may be favored, followed subsequently by consolidation through reaction *e*.

The combined action of oxidant and RSH in reaction *c* may be similar to the oxidantlike properties of –SH-blocking agents as reported (16,17). A notable difference is that the RSSP-type block can be reductively dissociated, whereas the other types of block are not reversible.

Whatever the mechanisms, a combination of whey, cysteine, and bromate triggers and synchronizes the developing and maturing mechanisms independently of the yeast-fermentation reactions. The separation of gas-retention and gas-production properties not only makes possible a very short process for making yeast-fermented bread, rolls, and sweet goods, but also has special benefits in conditioning pizza and extending the shelf-life and improving the quality of frozen bread. A subsequent paper will show how these reactions function in a similar manner under continuous-mix conditions to significantly improve dough and bread properties.

Literature Cited

1. HENIKA, R. G., and RODGERS, N. E. Process for making yeast-leavened bakery products and composition therefor. U.S. Patent No. 3,053,666 (Sept. 11, 1962).
2. HENIKA, R. G., and ZENNER, S. F. Baking with the new instant development process. Baker's Dig. **34:** 36–48 (June, 1960).
3. Production shortcuts with a new approach in fermentation. Baking Ind., August 6, 1960, pp. 25–27.
4. Use of L-cysteine in bread; effective date. Federal Register, Feb. 13, 1962, p. 1318.
5. BALLAND, A. Alterations qu'a prouvent les farines en veillissant. Ann. Chem. Phys. 6 Ser. t. **7:** 533–554 (1884).
6. SULLIVAN, BETTY, HOWE, MARJORIE, and SCHMALZ, F. D. On the presence of glutathione in wheat germ. Cereal Chem. **13:** 665–669 (1936).
7. GEDDES, W. F. III. Influence of germ constituents on baking quality and their relation to improvement in flour induced by heat and chemical improvers. Can. J. Research **2:** 195–213 (1930).
8. BALLS, A. K., and HALE, W. S. Further studies on the activity of proteinase in flour. Cereal Chem. **13:** 656–664 (1936).
9. JØRGENSEN, H. On the existence of powerful but latent proteolytic enzymes in wheat flour. Cereal Chem. **13:** 346–355 (1936).
10. POLLOCK, J. M., and GEDDES, W. F. Soy flour as a white bread ingredient. II. Fractionation of raw soy flour and effects of the fractions in bread. Cereal Chem. **37:** 30–54 (1960).

11. FREILICH, J., and FREY, C. N. Dough oxidation and mixing studies. VI. Effects of oxidizing agents in the presence of reducing matter. Cereal Chem. **21:** 241–251 (1944).
12. READ, J. W., and HAAS, L. W. Baking quality of flour as affected by certain enzyme actions. III. Purified amylase and the relative proteolytic activity of amylolytic agents. Cereal Chem. **14:** 58–73 (1937).
13. OFELT, C. W., and LARMOUR, R. K. The effect of milk on the bromate requirements of flours. Cereal Chem. **17:** 1–18 (1940).
14. SWANSON, C. O., and ANDREWS, A. C. Factors which influence the physical properties of dough. VI. Effect of cysteine and some other substances on mixogram patterns. Cereal Chem. **21:** 140–149 (1944).
15. SWANSON, E. C., and SWANSON, C. O. Modification of the gas production and gas retention properties of dough by some surface-active, reducing, and oxidizing agents. Cereal Chem. **23:** 590–600 (1946).
16. SOKOL, H. A., and MECHAM, D. K. Review of the functional role and significance of the sulfhydryl group in flour. Baker's Dig. **34:** 24–30, 74 (Dec. 1960).
17. BUSHUK, W., and HLYNKA, I. The effect of iodate and N-ethylmaleimide on extensigraph properties of dough. Cereal Chem. **39:** 189–195 (1962).