# THE EFFECT OF REMIXING ON THE STRUCTURAL RELAXATION OF UNLEAVENED DOUGH[1]

A. H. BLOKSMA[2] and I. HLYNKA

ABSTRACT

If unleavened doughs are tested in the Brabender extensigraph according to the structural relaxation procedure, they yield hyperbolic structural relaxation curves irrespective of whether they are or are not remixed before shaping. However, remixing causes a decrease in the structural relaxation constant and in the asymptotic load. The effect increases with increasing duration of remixing. The effect on the structural relaxation decreases when the time interval between remixing and shaping increases from 3 to 20 minutes; this is called recovery. Recovery may or may not be complete in 20 minutes, but under the conditions of the present experiments it does not proceed beyond that time interval.

Doughs to which 35 p.p.m. N-ethylmaleimide are added are least sensitive to remixing, closely followed by doughs with 12.5 p.p.m. iodate. Doughs with 20 p.p.m. bromate and doughs without additions but mixed in an atmosphere of oxygen show a large effect of remixing. With bromated doughs the effect of remixing increases considerably with reaction time. After recovery the rank order of doughs with different additions has remained essentially the same. Recovery of doughs with N-ethylmaleimide is even complete for reaction times shorter than 60 minutes. Doughs mixed in an oxygen atmosphere and remixed in nitrogen hardly show any recovery; if the remixing is done in an oxygen atmosphere, however, recovery is considerable.

Results obtained with the Brabender and Halton extensigraphs show that at least part of the effect of remixing is due to interference with subsequent structural activation during shaping of the test piece. Possibly differences between flour improvers that change rheological dough properties rapidly and slowly are more important than differences between oxidizing and thiol-blocking reagents.

Mechanical work on dough such as mixing, punching, dividing, or molding usually results in a change in its mechanical or rheological properties. Irrespective of the direction in which these properties have changed, the original properties are restored or recover gradually. The time intervals that are necessary for recovery have implications for the minimum time intervals between successive operations in practical breadmaking. These phenomena of change and recovery are illustrated at a more basic level by structural activation and relaxation (10). A dough can also stand a longer mixing time in the farinograph if periods of mixing alternate with periods of rest than if mixing is done continuously; the breakdown during mixing is reversed or

[1] Manuscript received August 27, 1959. Paper No. 181 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg 2, Canada.

[2] This author gratefully acknowledges a Postdoctorate Fellowship of the National Research Council of Canada for the year 1958-1959. Present address: Institute for Cereals, Flour and Bread T.N.O., Wageningen, The Netherlands.

compensated for during rest. The molecular processes that underlie these phenomena are unknown.

In the present study the change in rheological properties of unleavened doughs caused by remixing was investigated, with particular attention to the restoration of original properties, or recovery, after remixing. Remixing of yeasted doughs at the end of the fermentation period eliminates the adverse effect of excess bromate on loaf properties (12). In the present work other oxidizing flour improvers such as iodate and oxygen were also included, as well as the thiol-blocking reagent N-ethylmaleimide that does not possess oxidizing properties.

The structural relaxation method using the Brabender extensigraph has been useful in studies of flour improvement (5,7–10). In this method a series of test pieces with identical history is shaped and clamped in extensigraph sample holders, and stretched after various rest periods. A curve of the load at an arbitrary but constant extension vs. rest period is called structural relaxation curve; structural relaxation follows structural activation brought about by rounding and shaping the test piece. The effect of the history of the series on the structural relaxation curve provides information on processes that occur before shaping. This method proved to be equally useful for a study of remixing.

Changes in dough properties with increasing *duration of remixing* are reflected in a decrease in the parameters that describe the structural relaxation curves, the relaxation constant, and the asymptotic load. Using a constant duration of remixing, the influence of the *time interval between remixing and shaping* was studied. The decrease in structural relaxation constant as a consequence of remixing is largest for short time intervals between remixing and shaping; it becomes smaller with increasing time intervals up to about 20 minutes, when recovery appears to attain its maximum value. This observation made it possible to compare easily the maximum effect of remixing and the maximum recovery for doughs with different *flour improvers* and after different *reaction times,* by choosing the time intervals between remixing and shaping as short as possible and 20 minutes, respectively. In order to learn more about the interaction between remixing and structural activation, some experiments were done with a load-extension meter in which structural activation during shaping of the test piece could be minimized; for this purpose the Halton extensigraph was chosen.

## Materials and Methods

A commercially milled, straight-grade, untreated flour from Canadian hard spring wheat was used. It contained 13.2% protein (N × 5.7) and 0.46% ash on a 14% moisture basis. The farinograph water absorption was 64.5%.

Doughs were prepared from 200 g. flour (14% moisture basis), 2 g. sodium chloride, 114.2 g. (57.1%) water, with or without additions of potassium bromate, potassium iodate, or N-ethylmaleimide (NEMI). Flour was stored overnight in an atmosphere of nitrogen before use. Salts were reagent grade, and N-ethylmaleimide was obtained from Nutritional Biochemicals Corp., Cleveland, Ohio.

The procedure used is the structural relaxation method for the Brabender extensigraph, as described earlier (9). The essential modification is that, except in control experiments, part of the mixing was done after a portion of the reaction time had elapsed. This second part of mixing, or remixing, divided the reaction time into two intervals: the first interval from the end of initial mixing to the end of remixing, and the *second interval* from the end of remixing until the end of shaping.

Doughs were mixed and remixed in the GRL mixer (15) in an atmosphere of nitrogen after evacuation of the mixing bowl. In some experiments mixing was done in oxygen. Evacuation of the bowl prior to remixing inflates a dough to several times its original volume; this inflation, however, has no significant effect on the structural relaxation. The sum of initial mixing and remixing times was always 210 seconds. It may be argued that before remixing a dough was not exactly in the same state as its control dough, since the latter obtained a longer initial mixing. Because variations in the duration of initial mixing time have only a slight effect on structural relaxation (6), similar results would have been obtained with the same initial mixing times for remixed and control doughs.

An incidental modification of the method is that two test pieces of 150 g. were scaled just prior to shaping; this reduced the number of remixing operations by a factor of two. The time needed for weighing, rounding, and shaping prevented the use of second intervals shorter than 3 minutes.

Eight test pieces were stretched after various rest periods ranging from 4 to 45 minutes for the lowest and from 7 to 120 minutes for the highest resistances. Corrected loads at 7 cm. kymograph paper displacement were read. From the scatter of the experimental points around the linear transformation of the structural relaxation curve, standard errors of estimate for the relaxation constant C and the asymptotic load $L_a$ were calculated by means of formulas from correlation analysis (11). They were 100 to 200 g.-minutes for C, generally increasing with C, and 4 g. for $L_a$. The reproducibility of C was in agreement with this standard error. Day-to-day variations in $L_a$, however, were larger than corresponds with this standard error.

The Halton extensigraph was used with relaxometer dough holders and accessories for loading them as described earlier (14). Three test pieces of 100 g. were scaled prior to loading the sample holders. Further, the procedure was as described above for the Brabender extensigraph. This method avoids the vigorous working of dough during rounding and shaping in the latter machine. For comparison, in some experiments the test pieces were rounded 30 times on the Brabender extensigraph rounder.

Dough temperature was maintained at 30°C. during all operations.

## Results

*Brabender Extensigraph — General Observations.* With the Brabender extensigraph, plots of the product of load and rest period vs. rest period yielded straight lines, irrespective of whether doughs were remixed or not, independently of the second interval. Remixing does not alter the fact that the structural relaxation curve can be described as a hyperbola. Therefore the effect of remixing can be adequately recorded by changes in the structural relaxation constant C and the asymptotic load $L_a$. Remixing did not significantly affect the relation between the load at 7 cm. and the extensibility of doughs.

*Duration of Remixing.* Remixing decreases both C and $L_a$. Fig. 1 shows the dependence on the duration of remixing of this effect for doughs with various additions of bromate. After the longer durations of remixing, doughs were sticky and difficult to handle. On the basis

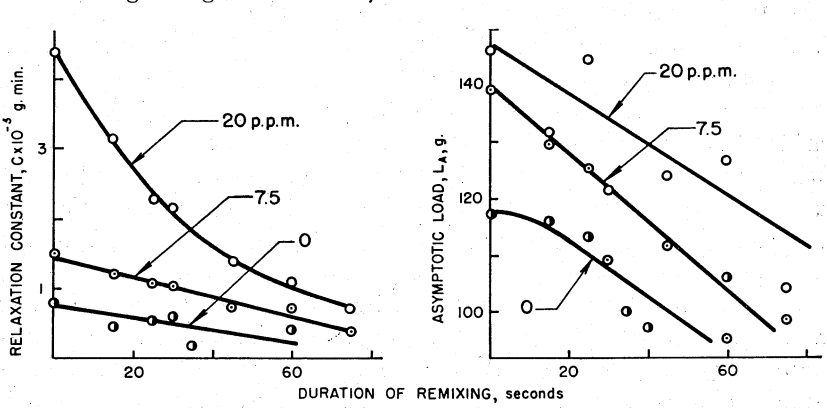


Fig. 1. Dependence of the structural relaxation constant (left) and the asymptotic load (right) on the duration of remixing for doughs without and with 7.5 and 20 p.p.m. bromate. First interval 177 minutes, second interval 3 minutes.

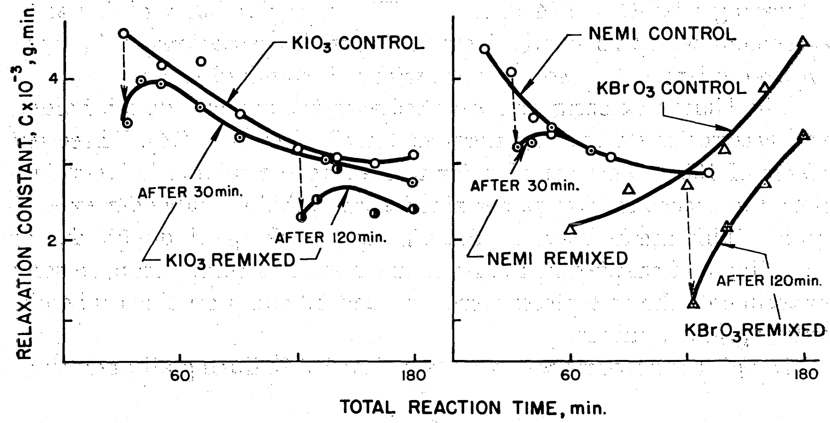


Fig. 2. Dependence of the srtuctural relaxation constant on the second interval (between remixing and shaping) for doughs containing 12.5 p.m.m. iodate (left), 20 p.p.m. bromate (right), or 35 p.p.m. N-ethylmaleimide (right). First intervals (between initial mixing and remixing) were either 30 (iodate and NEMI) or 120 minutes (iodate and bromate). Total reaction time, which is the sum of the constant first and the variable second interval, is plotted along the abscissa. Dashed arrows indicate the immediate effect of remixing.

of these results a duration of remixing of 60 seconds was chosen for all experiments reported below.

*Second Interval.* The influence of the length of the second interval (between remixing and shaping) was studied in a series of experiments with constant first interval (between initial mixing and remixing). Figure 2 shows how the effect of remixing on C depends upon the second interval for doughs with 12.5 p.p.m. iodate, 20 p.p.m. bromate, or 35 p.p.m. N-ethylmaleimide. The effect of remixing is largest for the shortest second interval that was practicable, that is 3 minutes. This maximum effect is indicated in Fig. 2 by dashed arrows. The effect decreases considerably when the second interval increases from 3 to 20 minutes as is shown by the approach of the lines for the remixed and the control doughs with increasing total reaction time; with a sufficiently long second interval between remixing and shaping, dough shows recovery. In the experiments with N-ethylmaleimide for second intervals of more than 20 minutes, the line for remixed doughs coincides with that for control doughs. With bromated doughs the line for remixed doughs is parallel with that for control doughs after more than about 20 minutes' second interval. Lines for remixed doughs, containing iodate, show recovery during the first 20 minutes after remixing, after which the lines run more or less parallel with that for control doughs, though at a much closer distance than with bromated doughs. This means that, whether recovery is complete or not, it does not proceed after more than about 20 minutes after remixing. Results not reported here in detail, from experiments with constant total reaction time and various first and second intervals, support these conclusions.

*Type of Improver and Reaction Time.* Figure 2 showed already

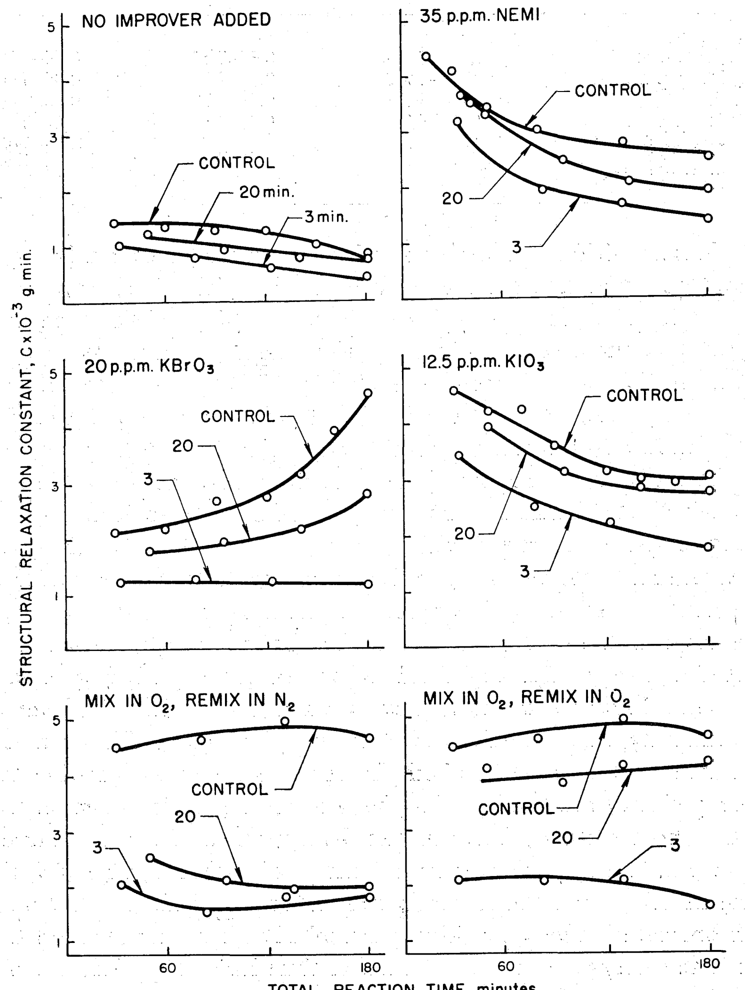


Fig. 3. Dependence of the sensitivity to remixing and of the recovery on the type of improver and reaction time. The curves for 3 minutes' second interval (between remixing and shaping) are supposed to indicate the sensitivity to remixing, and those for 20 minutes the maximum recovery. Total reaction time, which is the sum of the variable first interval (between initial mixing and remixing) and the constant second interval, is plotted along the abscissa.

TABLE I

RELATIVE VALUES OF THE STRUCTURAL RELAXATION CONSTANT C FOR REMIXED DOUGHS

| IMPROVER | RANGE OF VALUES FOR C FOR CONTROL DOUGHS | C FOR REMIXED DOUGH DIVIDED BY C FOR CONTROL DOUGH AFTER THE SAME TOTAL REACTION TIME | |
|---|---|---|---|
| | | 3 Minutes' 2nd Interval | 20 Minutes' 2nd Interval |
| | *g/minute* | | |
| NEMI, 35 p.p.m. | 2500–3800 | 0.55–0.85 | 0.75–1.00 |
| $KIO_3$, 12.5 p.p.m. | 3000–4300 | 0.55–0.75 | 0.85–0.90 |
| None | 750–1400 | 0.45–0.70 | 0.70–0.90 |
| $KBrO_3$, 20 p.p.m. | 2200–4500 | 0.25–0.60 | 0.60–0.80 |
| $O_2$ (remixing in $O_2$) | 4400–5000 | 0.30–0.45 | 0.80–0.90 |
| $O_2$ (remixing in $N_2$) | | | 0.40–0.55 |

that doughs with bromate are much more sensitive to remixing and recover to a lesser extent than do doughs with N-ethylmaleimide. The results of a more extensive study of the effect of the type of improver and the reaction time on the sensitivity and recovery are shown in Fig. 3. In these experiments various first intervals were followed by second intervals of either 3 or 20 minutes. Curves for a second interval of 3 minutes show the maximum effect of remixing. On the basis of the results above it is assumed that the 20 minutes' curves indicate the maximum recovery. The course of control curves in Fig. 3 is in agreement with earlier work (5,7,8); the effect of N-ethylmaleimide on structural relaxation has not yet been published. The control experiments with N-ethylmaleimide, bromate, and iodate cover similar ranges of values for the structural relaxation constant C. However, doughs mixed in oxygen had slightly higher values for C, and doughs without improvers much lower values. To overcome this difficulty, relative values of C as read from Fig. 3 are summarized in Table I. Doughs with N-ethylmaleimide are least sensitive to remixing, closely followed by doughs with iodate. This is demonstrated by the short distance between the 3 minutes' and control curves in Fig. 3 and the high figures in column 3 of Table I. The larger distance in Fig. 3 and the lower figures in Table I indicate that doughs with bromate are very sensitive, particularly after long reaction times; this is the only case in which reaction time has a large effect. Doughs mixed in oxygen are also very sensitive. The position of the 20 minutes' curves in Fig. 3 and the figures in column 4 of Table I show that after recovery the rank order of doughs with different improvers is essentially the same as after a second interval of only 3 minutes. Recovery is even complete for doughs with N-ethylmaleimide after reaction times of less than 60 minutes. Doughs mixed in oxygen and remixed in nitrogen hardly show any recovery; after remixing in oxygen, however, recovery is considerable.

*Dough with Both Iodate and Bromate.* The behavior of doughs with both 6.25 p.p.m. iodate and 10 p.p.m. bromate is intermediate between that of doughs with either 12.5 p.p.m. iodate or 20 p.p.m bromate alone. After short reaction times the behavior is more like that of doughs with iodate, and after long reaction times more like that of bromated doughs.

*Asymptotic Load.* The asymptotic load $L_a$ generally follows the behavior of the structural relaxation constant C but in a less consistent way as is illustrated in Fig. 1. $L_a$ of iodated doughs is not significantly affected by remixing. In agreement with earlier work (7,8), a large effect of oxygen on $L_a$ was found.

*Halton Extensigraph.* Structural relaxation curves obtained with the Halton extensigraph for doughs with 20 p.p.m. bromate and after 180 minutes' reaction time showed a much larger scatter of experimental points than did curves obtained with the Brabender extensigraph. Moreover, they did not fit the usual equations for a hyperbola. However, qualitative information on the interaction of remixing and structural activation could be obtained. Rounding of the test pieces raises the structural relaxation curve, presumably by structural activation, and remixing with a 4 minutes' second interval lowers them. The effect of structural activation is much more marked in control doughs than if it follows remixing.

## Discussion

The present experiments confirm the observation of Freilich and Frey (12) that remixing after fermentation is a means of canceling the effect of excess bromate. Figure 1 illustrates that remixing reduces the structural relaxation constant C and the asymptotic load $L_a$ to values that correspond with a lower bromate level. Freilich and Frey, by using long fermentation time, adopted good conditions for a demonstration of the effect of remixing; according to the present experiments, doughs with bromate after a long reaction time are most sensitive to remixing.

Two observations can easily be understood. The first is the difference between doughs initially mixed in oxygen, and remixed in nitrogen and in oxygen, respectively, followed by a second interval of 20 minutes between remixing and shaping. Remixing in nitrogen reduces the duration of the improvement reaction but not of degradative processes. Remixing in oxygen brings the improver concentration up again to its original level, thus favoring the improvement reaction. The second observation is the behavior of doughs with both 6.25 p.p.m. iodate and 10 p.p.m. bromate, which is in agreement with the fast reaction of iodate and the slow reaction of bromate (5).

Recovery attains its maximum about 20 minutes after remixing. Of course the validity of this conclusion is confined to unleavened doughs from the present flour with the present water content and at 30°C. It is in remarkably good agreement with the recovery times of 25 minutes used in test baking (1) and 15–20 minutes in practice (2).

The decrease in extensigram height caused by remixing illustrates a decrease in rigidity of dough. Assuming that the rigidity is due to crosslinks between peptide chains, it is logical to suppose that remixing breaks some of the crosslinks, and that new crosslinks are formed during the first 20 minutes of the second interval. Since the energy applied to the dough during remixing is in the order of only 10 gcal. per $cm.^3$, or about 13 kcal. per mole amino acid residue, part of which is converted into heat, breaking of primary chemical bonds cannot occur to a large extent. Chain entanglements could be the crosslinks disappearing by remixing. During rest they may be re-formed as a consequence of Brownian motion. This explanation is related to those usually given for thixotropy and structural viscosity.

In the present experiments there are two operations that affect the rigidity of dough. Rounding and shaping cause an increase in the rigidity, which is referred to as structural activation (7); presumably this is due to the formation of crosslinks to an extent that depends upon chemical reactions in the preceding reaction time. The second operation is remixing, which decreases the rigidity. These operations are followed by the processes structural relaxation and recovery, during which their effects gradually decrease. Results of the present experiments indicate that structural activation, followed by relaxation, and breakdown, due to remixing, and followed by recovery, do not proceed independently. The experiments with the Halton extensigraph demonstrate that remixing has a smaller effect if structural activation is minimized. This fact finds its counterpart in the observation that the effect of remixing is largest in bromated doughs after a long reaction time; previous investigations (5,7-10), including work with bromated doughs in the Chopin extensigraph (3,16), has shown that under these conditions structural activation is more obvious than in any other of the present experiments. Moreover, in some cases the effect of remixing could not be observed by palpating doughs before rounding and shaping, whereas extensigrams, obtained after shaping, showed it clearly. Finally, there is no indication that the progress of recovery in the course of time obeys an equation related to the hyperbolic equation for structural relaxation. Therefore, one cannot expect that structural relaxation curves after remixing and second intervals shorter than 20 minutes, could be described as hyperbolas if breakdown, due to remixing, and recovery were merely superposed on structural activation and relaxation. The fact that all experimental data could very well be described by the hyperbolic equation also suggests that structural activation was affected by previous remixing. It cannot be decided on the basis of the present experiments whether a complete omission of structural activation would result in no effect of remixing. The hypothesis that remixing interferes with subsequent structural activation is not necessarily contradictory to the assumption made above, that the effect of remixing is due to chain disentanglement. It is possible that the work of rounding and shaping results in structural activation only if there is a sufficient number of chain entanglements.

The large differences in sensitivity to remixing and in recovery between doughs with different improvers demonstrate that the improvers act in different ways. The addition of N-ethylmaleimide or iodate results in doughs with little sensitivity and good recovery, whereas bromate and oxygen are associated with high sensitivity and poor recovery. Remarkably, the dividing line between these two groups of flour improvers does not coincide with the distinction between oxidizing and thiol-blocking reagents. The behavior of the oxidizing potassium iodate is very similar to that of the only thiol-blocking reagent used in these experiments, N-ethylmaleimide. This is another argument in favor of the idea that flour improvement is due to disappearance of thiol groups rather than to the formation of disulfide cross-links (4,13). Although the position of oxygen in this respect is not completely clear, the dividing line between improvers inducing high and low sensitivity to remixing seems to be correlated with the slope of the plot of C vs. reaction time, that is, with the rate of change of rheological properties induced by them. Rapidly acting flour improvers seem to result in slightly sensitive doughs, whereas slowly acting reagents lead to highly sensitive doughs. The poor recovery of bromated doughs cannot be due to the presence of residual bromate, since then doughs with both iodate and bromate would also have shown poor recovery after short reaction times.

## Literature Cited

1. ANDERSON, J. A. Grain Research Laboratory 1958 Report, p. 6.
2. ANONYMOUS. Full-flavored bread from Patterson's new process. Baker's Digest **33** (3): 48–49 (1959).

3. BENNETT, RUTH, and COPPOCK, J. B. M. Measuring the physical characteristics of flour: a method of using the Chopin Alveograph to detect the effect of flour improvers. J. Sci. Food Agr. **3:** 297–307 (1952).
4. BLOKSMA, A. H. Die Bedeutung von Thiol- und Disulfidgruppen im Kleber für die Backfähigkeit. Getreide u. Mehl **8:** 65–69 (1958).
5. DEMPSTER, C. J., CUNNINGHAM, D. K., FISHER, M. H., HLYNKA, I., and ANDERSON, J. A. Comparative study of the improving action of bromate and iodate by baking data, rheological measurements, and chemical analyses. Cereal Chem. **33:** 221–239 (1956).
6. DEMPSTER, C. J., and HLYNKA, I. Some effects of the mixing process on the physical properties of dough. Cereal Chem. **35:** 483–488 (1958).
7. DEMPSTER, C. J., HLYNKA, I., and ANDERSON, J. A. Extensograph studies of structural relaxation in bromated and unbromated doughs mixed in nitrogen. Cereal Chem. **30:** 492–503 (1953).
8. DEMPSTER, C. J., HLYNKA, I., and ANDERSON, J. A. Extensograph studies of the improving action of oxygen in dough. Cereal Chem. **31:** 240–249 (1954).
9. DEMPSTER, C. J., HLYNKA, I., and ANDERSON, J. A. Influence of temperature on structural relaxation in bromated and unbromated doughs mixed in nitrogen. Cereal Chem. **32:** 241–254 (1955).
10. DEMPSTER, C. J., HLYNKA, I., and WINKLER, C. A. Quantitative extensograph studies of relaxation of internal stresses in non-fermenting bromated and unbromated doughs. Cereal Chem. **29:** 39–53 (1952).
11. EZEKIEL, M. Methods of correlation analysis, chap. 18. Wiley: New York (1930).
12. FREILICH, J., and FREY, C. N. Dough oxidation and mixing studies. II. Effects of remixing after fermentation. Cereal Chem. **16:** 495–502 (1939).
13. GOLDSTEIN, S. Sulfhydryl- und Disulfidgruppen der Klebereiweisse und ihre Beziehung zur Backfähigkeit der Brotmehle. Mitt. Gebiete Lebensm. u. Hyg. (Bern) **48:** 87–93 (1957).
14. HLYNKA, I. Some observations on the "research" extensometer. J. Sci. Food Agr. **6:** 763–767 (1955).
15. HLYNKA, I., and ANDERSON, J. A. Laboratory dough mixer with an air-tight bowl. Cereal Chem. **32:** 83–87 (1955).
16. HLYNKA, I., and BARTH, F. W. Chopin alveograph studies. II. Structural relaxation in dough. Cereal Chem. **32:** 472–480 (1955).