Natural Maturing of Wheat Flour. I. Changes in Some Chemical Components and in Farinograph and Extensigraph Properties

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ABSTRACT

Freshly milled or green flour was stored for 90 days at 30°C. in air and in nitrogen. Concomitant changes in pH, microorganism population, protease activity, and SH and nitrogen contents of metaphosphoric acid solution solubles, ascorbic and dehydroascorbic acid contents, lipid peroxide, titratable acidity, and some rheological properties were measured. The significant change observed was the decrease in the SH content, and this seems to be directly responsible for the changes in rheological properties of the dough and presumably in the breadmaking quality. Increases in mold counts and acidity were observed, but these were quite small and probably not involved in the natural maturing reaction.

Natural maturing of freshly milled flour has been the concern of flour millers and cereal chemists for many years. Although many aspects of this phenomenon are known, there are some factors that require additional clarification.

The pertinent literature on this topic falls into three broad divisions; i.e., studies of the changes in 1) flour components, 2) rheological properties of doughs produced from the flour, and 3) breadmaking quality.

Studies of changes in flour components during the period 1920 to 1930 (1–7) showed that the amount of extractable lipid decreased, whereas acidity and maltose values increased during storage of flour under natural conditions. Barton-Wright (6) found deterioration in the quality of the washed-out gluten and attributed this to the formation of free fatty acids. More recent studies are those of Cuendet et al. (8), Greer et al. (9), and Tsen and Dempster (10). However, most of these studies were on flours stored for relatively long periods (e.g. 27 years in the study by Greer et al.) and hence they provide little information on the natural maturing that occurs during the first 2 months or so after milling.

There have been relatively few studies in relation to the changes in rheological properties of doughs resulting from storage of the flour. Smith and Andrews (11) and Cosgrove (12) showed that oxygen uptake by doughs during mixing increased after natural maturing.

Several studies have been made of the changes in breadmaking quality during storage of flour. Among the most important are those of Bailey and Johnson (2), Fisher et al. (3), Cathcart and Killen (5), and Cuendet et al. (8). Generally it was noted that changes during prolonged storage produced a decrease in loaf volume. Cuendet et al. (8) showed a significant negative correlation between loaf volume and acidity. Again it must be emphasized that these studies covered periods much longer than necessary to produce the optimal natural maturing.

From the literature survey it appeared that no detailed study has been made of changes in flour during the immediate post-milling period that has led to improvement of breadmaking quality. Such a study was undertaken in our laboratory. Results of the first part of this study are presented in this paper.

MATERIALS AND METHODS

Flours

Two flours were used, a long-patent of 0.40% ash and 12.8% protein and a second-clear of 0.51% ash and 13.1% protein. Both were commercially milled from Canadian HRS wheat and were not bleached or treated with maturing agents.

Storage Conditions

One set of flour samples was stored under air in double-layer polyethylene bags. For storage under nitrogen, the flour was kept in metal containers. Atmospheric oxygen was removed by three consecutive evacuations and flushings with oxygen-free nitrogen. The flour was stored at a constant temperature of 30°C.

Acidity

Acidity of the residual free lipid was determined by the following methods.

1. *Peroxide value*. One gram of sample and then 15 ml. of acetic acid and 1 ml. of KI-saturated aqueous solution were put into 10 ml. of chloroform. After 1 min. of shaking, the mixture was kept in a dark place. Water (75 ml.) was added and, after strong shaking, the mixture was titrated with 0.01N $Na_2S_2O_3$, with a few drops of soluble starch aqueous solution used as indicator (13, p. 135).

$$\text{Peroxide value} = \frac{(T - B) \times F}{S} \times 100$$

where:
B = titration ml. of 0.01N $Na_2S_2O_3$ for blank solution;
T = titration ml. of 0.01N $Na_2S_2O_3$ for sample solution;
F = factor of 0.01N $Na_2S_2O_3$; and
S = quantity of sample (g.).

2. *Acid value*. An accurately measured quantity of sample was dissolved in 50 ml. of ethanol and titrated with 0.5N KOH aqueous solution (13, p. 106).

$$\text{Acid value} = \frac{56.11 \times T \times N \times F}{S}$$

where:
T = quantity of KOH solution consumed by sample (blank value was deducted);
N = normality of KOH aqueous solution;
F = factor of KOH aqueous solution; and
S = quantity of sample.

Protease Activity

This was determined by the procedure of Egami (14). A slurry comprising 10 g. flour, 1.25 g. hemoglobin, and 50 ml. of 0.1M phosphate buffer (pH 6.0) was autolyzed for 2 hr. at 40°C. Trichloroacetic acid, 0.5 ml. (0.4M), was then added and the mixture was centrifuged for 5 min. at 2,800 × g. Folin reagent (10 ml.) and 2 ml. of 0.4M sodium carbonate were added to 0.5 ml. of the supernatant and the

color was developed for 20 min. at 40°C. The solution was cooled and its absorbance at 660 mμ was determined on a spectrophotometer. Tyrosine content of the solution was caluclated as follows:

$$\text{Tyrosine } (\gamma) = \frac{A - 0.003}{0.0537} \times \text{dilution}$$

where A is absorbance, 0.003 is the blank, and 0.0537 is extinction coefficient for tyrosine. Protease activity was expressed as tyrosine per g. flour.

Soluble SH and Nitrogen Contents

Flour (50 g.) was suspended in 100 ml. of 2% metaphosphoric acid solution, stirred at 1,000 r.p.m. for 1 min. in a homogenizer, and centrifuged for 15 min. at 1,700 × g. The SH content of the supernatant was determined by the amperometric titration procedure of Sokol et al. (15). Nitrogen content of the water-solubles was determined by the Kjeldahl method.

Ascorbic and Dehydroascorbic Acid Contents

Flour (20 g.) was suspended in 40 ml. of 10% metaphosphoric acid solution, mixed in a homogenizer for 3 min. at 1,000 r.p.m., and centrifuged for 15 min. at 1,700 × g. Ascorbic and dehydroascorbic acid in the supernatant were determined by a modified Roe method (16).

Viscosity of Aqueous Flour Suspensions

Flour suspensions were prepared by stirring 30 to 90 g. flour in 100 ml. of water at 1,000 r.p.m. in a homogenizer. The viscosity of the slurry at 20°C. was determined with a rotational viscometer.

Farinograph Consistency

The 300-g. bowl and variable amounts of water at 30°C. were used. For mixing under nitrogen or oxygen, the dry flour was mixed in a stream of appropriate gas for 5 min. before addition of water saturated with the gas being used.

Structural Relaxation

This property was investigated according to the technique developed by Hlynka and co-workers (17,18,19). Doughs containing 2% sodium chloride were prepared by mixing 300 g. flour to 60% absorption in a 300-g. farinograph bowl. Doughs were mixed for 1 min. at normal speed (63 r.p.m.), rested for 5 min., and then mixed for 3 min. additional at normal speed (63 r.p.m.). The test pieces were shaped immediately after mixing and were given rest periods varying from 10 to 100 min. at 30°C.

RESULTS AND DISCUSSION

Changes in pH and in Population of Microorganisms

The pH of flour-water slurries decreased continually over the 90-day storage period from 6.1 to 5.6 for both grades of flour stored in air. The pH of flour stored under nitrogen remained essentially constant. Flour stored in air showed a significant increase in the mold population (mainly *Aspergillus flavus* and *A.*

candidus), but the bacterial count, which was of the order of 1×10^4 per g., remained constant.

Protease Activity

This was measured to test the Jørgensen (20) protease hypothesis for the mechanism of flour maturing. The activities of the long-patent and second-clear flours were 10 and 12 units respectively and remained unchanged during storage in air and in nitrogen.

Soluble SH and Nitrogen Contents

The SH contents of the water-solubles are given in Table I. Both flours showed a marked decrease in SH during storage time in air, and a much smaller decrease during storage under nitrogen. The amounts of nitrogen in the water-solubles was 0.2 and 0.3% in the long-patent and second-clear flours respectively for both atmospheres. These values remained the same with storage time.

Changes in Ascorbic and Dehydroascorbic Acid

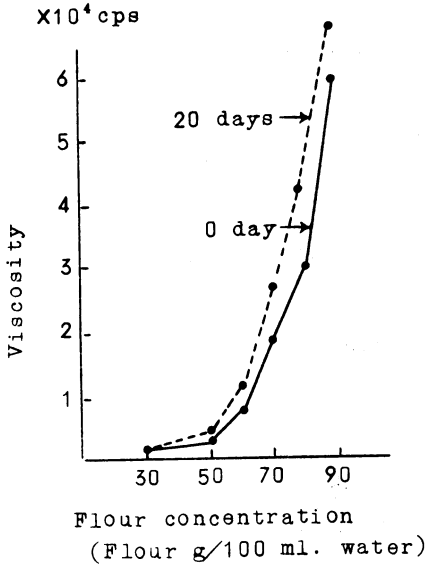
Although there have been no reports in the literature of the presence of these substances in flour, an attempt was made to detect their presence, since they might be involved in the changes during natural maturing. These substances were determined by Roe's modified method (16), and it is quite possible that the method gives a positive result for substances other than ascorbic or dehydroascorbic acid. According to this method, the long-patent flour contained about 0.15 mg. % of ascorbic acid and 1.4 mg. % of dehydroascorbic acid. These values did not change during storage.

Lipid Peroxide and Acidity

The long-patent flour stored in air and in nitrogen for 60 days was examined in this experiment. Initially the peroxide value of the flour was 5 mg. I_2 per 1 g. flour lipid and this did not change during storage. On the other hand, titratable acidity increased rapidly from 0.4 to 2.8 mg. KOH per 1 g. flour lipid during storage in nitrogen. The increase in acidity parallels the increase in mold counts, and these two parameters might be directly related.

TABLE I. CHANGE IN 2% METAPHOSPHORIC ACID-SOLUBLE SH OF FLOUR DURING STORAGE

Storage Period	Long-Patent		Second-Clear	
	Nitrogen	Air	Nitrogen	Air
days	μeq./g. flour			
0	0.21	0.21	0.30	0.30
3	0.20	0.17	0.30	0.28
6	0.20	0.14	0.28	0.23
10	0.19	0.10	0.27	0.17
20	0.19	0.09	0.27	0.10
30	0.17	0.08	0.26	0.10
60	0.18	0.08	0.27	0.11
90	0.18	0.09	0.26	0.11



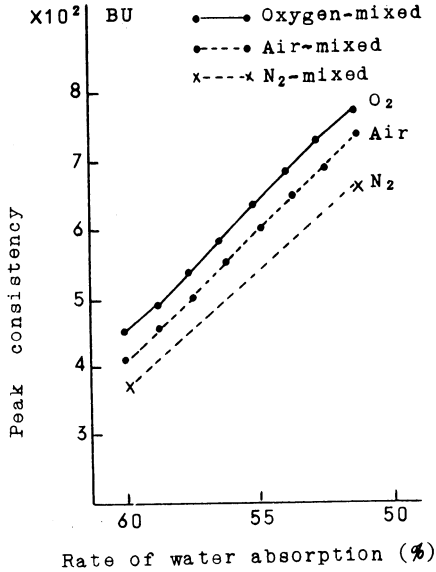


Fig. 1 (left). Viscosity of aqueous slurries of freshly milled flour (solid lines) and flour stored in air for 20 days (dashed lines).

Fig. 2 (right). Variation of peak farinograph consistency with absorption for flours stored in air and in nitrogen for 0, 10, and 30 days.

Changes in Viscosity of Flour Suspensions

Viscosities of flour-water suspensions varying in flour and water ratio from 60:100 to 80:100 were determined for fresh flour and for flour stored 20 days in air and nitrogen. Results for air-stored sample are shown in Fig. 1. The viscosity of the stored sample is higher than that of the fresh sample; this difference becomes increasingly greater when the flour:water ratio increases above 60:100. Flour stored under nitrogen (results not shown) did not show this increase in viscosity.

Changes in Peak Farinograph Consistency

Changes in this parameter were examined over a range of water absorption from 50 to 60%. It was found that peak consistency over this range of absorption was inversely related to absorption. Accordingly, the effects of storage time and atmosphere will be expressed in terms of this linear relationship.

Results for long-patent flour mixed in air are shown in Fig. 2. The slope of the plots does not change with storage time or atmosphere. However, the intercept increases with storage time. This increase is accentuated by storage in air. A parallel effect can also be demonstrated by mixing fresh flour in nitrogen, air, and oxygen. Again, the slope does not change significantly, but the extrapolated intercept increases with increasing oxygen content in the mixing atmosphere.

The actual values of this parameter are 2,160, 2,320, and 2,420 B.U. for nitrogen-, air-, and oxygen-mixing respectively. It seems that it might be possible to

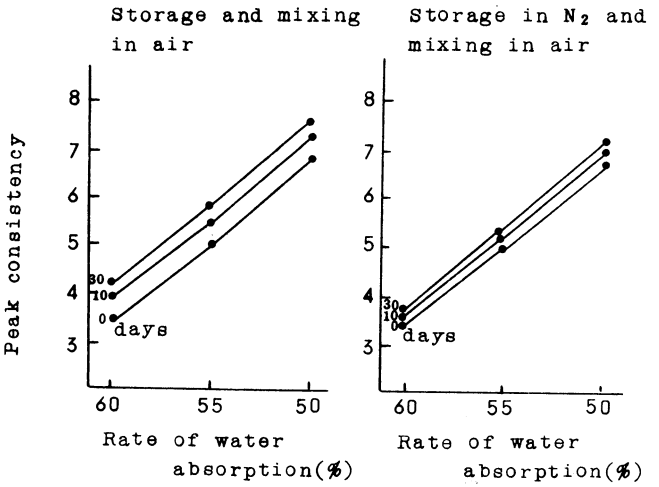


Fig. 3. The change of relaxation constant and asymptotic load with storage time.

express the relative maturity of the flour in terms of this intercept value (see Figs. 3 and 4); however, further work is necessary with a larger number of flours to establish this relationship.

Changes in Structural Relaxation

Derived structural relaxation results are shown in Fig. 5. On the left, the relaxation constant is plotted against storage time. For the three types of dough investigated (stored and mixed in air, stored in nitrogen, and mixed in air and in nitrogen), the relaxation constant increases with storage time. This increase is accentuated by mixing in air, indicating that oxygen incorporated during mixing is superposed on the effects resulting from changes during storage. Changes in the asymptotic load for the same doughs (right in Fig. 5) seem to occur during the first 10 days of storage. Again the changes are accentuated by mixing in air.

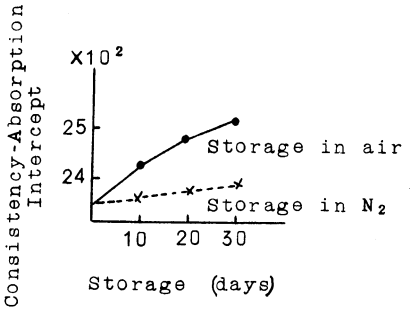


Fig. 4. Variation of peak consistency vs. absorption intercept with storage time in air and in nitrogen.

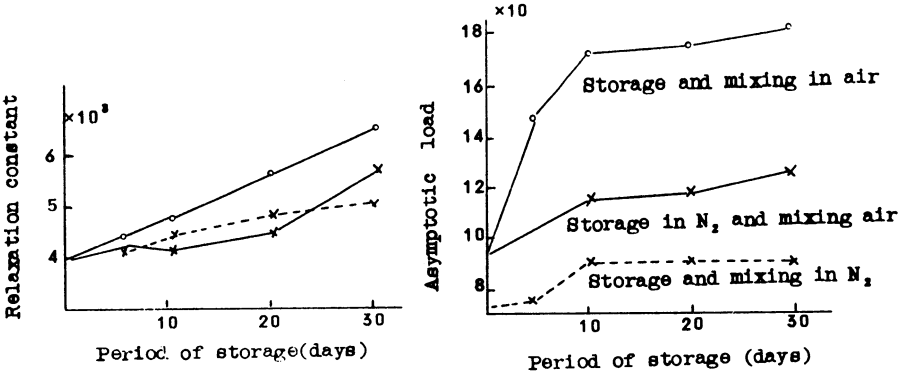


Fig. 5. Variation of relaxation constant and asymptotic load with storage time for doughs from flour 1) stored in air and mixed in air, and 2) stored in nitrogen and mixed in air and in nitrogen.

CONCLUSIONS

The major change that occurs during natural maturing of freshly milled flour is the gradual decrease in the SH content of the metaphosphoric acid solution components of flour. This change, in turn, affects the rheological properties of the dough in a way that might be either beneficial or detrimental to breadmaking quality. The above phenomena, i.e., decreases in labile SH content and changes in rheological properties of dough during natural maturing, are influenced by oxygen in air. The changes in mold count and fat acidity were related to the maturing reaction.

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