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BREAD STALING STUDIES. I. EFFECT OF PROTEIN CONTENT ON STALING RATE AND BREAD CRUMB PASTING PROPERTIES[1]

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ABSTRACT Cereal Chem. 54(2): 207-215

The effect of flour protein content (10.6, 11.0, 13.9, and 21.6% on a 14% mb) at two storage temperatures (21° and 30°C) on bread staling was investigated. Kinetic studies at the two temperatures indicated that regardless of the protein content in the flour, the basic mechanism of bread staling involves changes analogous to crystallization of the starch fraction of the crumb. The higher storage temperature and higher flour protein sample decreased the staling rate. The primary effect of protein in reducing staling rate was dilution of the starch and not the quality of the protein. Amylograms of crumb slurries obtained from the 11.0 and 13.9% flour proteins had pasting temperatures which decreased progressively as bread aged, and showed a minor peak at a lower temperature than the peak height at 95°C. The minor peak was most prominent for the bread produced from the 11.0% flour protein. Neither the minor peak nor the changes in the pasting temperature, however, were observed with the highest protein bread (21.6% flour protein). No appreciable changes were observed for either 15-min height or setback as the bread aged. The crumb showed a unique setback pattern which was not observed with starch, flour, or dough. During the setback at a certain temperature, a sharp increase in viscosity in the bread crumb slurries was noted. This temperature did not change as the bread aged. The highest protein bread showed a different setback pattern compared to the lower protein bread.

Numerous reports have shown that flour protein content is an important factor in the rate of bread staling. Steller and Bailey (1) found an inverse relation between protein content and bread staleness upon storage. However, the keeping quality of bread, as measured by crumb softness, did not appear to be a linear function of protein content. Working with synthetic dough systems, Bechtel and Meisner (2) and Prentice *et al.* (3) generally confirmed these views. They showed that increasing the protein level of the synthetic flours decreased the average crumb firmness and crumb firming rate. Ponte *et al.* (4), however, reported that the rate of bread firming was not significantly correlated to flour protein content.

Flour quality or strength has been reported (5) to be a prime factor in the

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TABLE I
Protein Content and Farinograph Data of Flours

Flour	Protein Content[a] %	Dough Development Time min	Stability min	Absorption at 500 BU %
A	11.0	5.0	5.5	60.6
A-1	10.6	5.5	12.5	57.2
B	13.9	8.5	16.0	62.5
C	21.6	16.5	21.0	74.0

[a]On a 14% moisture basis (N × 5.7).

keeping quality of bread. However, Prentice *et al.* (3) found that the rate of firming was not significantly different between synthetic flours containing the gluten from soft-wheat and from hard-wheat flours. Erlander and Erlander (6) reported that the ratio of starch to protein in the dough is critical in determining the rate of staling and that the structure of starch is such that some staling will always occur no matter how much protein is added to the dough.

The extent of starch gelatinization in bread was studied by Yasunaga *et al.* (7) on bread crumb slurries using the amylograph. They suggested that the amylograph could be used for staling study of bread. Staling studies reported by Banecki (8) using the amylograph showed that the peak viscosity of starches isolated from wheat bread decreased sharply during the first day but decreased less thereafter.

The purpose of this study was to investigate the effect of flour protein content on the rate and mechanism of bread staling at two storage temperatures and on the pasting properties of bread crumb.

MATERIALS AND METHODS

Flour Samples

Protein content and farinograph data of the four flours used are given in Table I. Flour A was a malted, unbleached commercial flour; flour A-1 was a blend of flour B and starch isolated from the same flour; flour B was a composite of hard red spring wheat flour, milled on a pilot mill (9); and flour C was a composite of the 5th break flour of hard red spring wheat, milled on a pilot mill (9). Flours A-1, B, and C were unbleached and untreated.

Bread Samples

Bread was made using a straight-dough procedure with a 3-hr fermentation, a 55-min proof period at 30°C, and a 25-min bake at 230°C.

The baking formula based on flour weight was as follows:

Flour (14% mb)	300 g
Sugar	5.0%
Salt	2.0%
Yeast	3.0%
Water	variable

The formula used was a lean one in order to minimize the possible effect of ingredients on staling. The dough was proofed and baked in 1-lb bread pans.

Aging of Bread

The bread was cooled at room temperature for 2 hr, then sliced and stored at 21° and 30° C in sealed containers to prevent moisture loss. Relative humidity of the storage chamber was maintained between 90 and 95%. The bread was tested for firmness using an Instron Universal Testing Instrument (Instron Corporation, Canton, Mass.) at 0, 1, 2, and 5 days. The limiting modulus was obtained from the bread stored at 2° C for 7 days.

The values of E_0, E_1, E_2, and E_5, which represent the firmness of the bread at 0, 1, 2, and 5 days, respectively, were subjected to Avrami analysis (10–12) to determine the rate constant and the Avrami exponent according to Cornford *et al.* (13) and McIver *et al.* (14):

$$\theta = \frac{E_L - E_t}{E_L - E_0} = \exp(-kt^n) \quad (1)$$

Thus:

$$\log\left(-\log_e \frac{E_L - E_t}{E_L - E_0}\right) = \log k + n \log t \quad (2)$$

or:

$$\log\left(\log \frac{E_L - E_0}{E_L - E_t}\right) = \log \frac{k}{2.303} + n \log t \quad (3)$$

Where θ is the fraction of uncrystallized material at time t, k is a rate constant and n is the Avrami exponent. E_t is the measured value of elastic modulus at time t and E_L is the limiting modulus. The reciprocal of the rate constant (1/k) is termed time constant. A detailed explanation of these various terms was given previously (13,14).

The Avrami exponent was obtained from the gradient of a graph of equation 2 and the rate constant was determined from a graph of $\log_e(E_L - E_t)$ *vs.* t (14).

Pasting Properties of Bread Crumb

At 0, 1, 2, and 5 days' storage, bread crumb was removed, freeze-dried, and ground on a Wiley mill to pass through a 60-mesh sieve.

The pasting properties of the freeze-dried and ground bread crumb from the different samples were investigated with a Brabender Amylograph®. Bread crumb (55 g) was suspended in 350 ml distilled water by agitation in a Waring Blendor at low speed for 1 min. The suspension was poured into the amylograph bowl and the blender was rinsed with 100 ml of additional water. The crumb suspension was heated uniformly from 25° to 95° C, held at 95° C for 15 min, and then cooled uniformly to 50° C.

The information obtained from the amylograph curve included pasting temperature, peak viscosity, 15-min height, and setback. Definitions of these terms were given previously (15).

RESULTS AND DISCUSSION

The results of the Avrami analysis on the aging of bread made from flour B are shown in Figs. 1 and 2. The Avrami exponents for bread stored at 21° and 30°C were 0.92 and 0.95, respectively (Fig. 1). The values of the rate constant at 21° and 30°C corresponded to 0.18 and 0.14 reciprocal days (Fig. 2), giving time constants of 5.44 and 7.18 days (Table II).

Table II shows the Avrami exponent and time constant for bread stored at 21° and 30°C. As evident from this table, the Avrami exponent was essentially unity at the two temperatures studied. The same value (*i.e.*, n = 1) was reported for wheat-starch gels (14,16,17), indicating that the mechanism of starch retrogradation is instantaneous nucleation followed by rod-like growth of crystals (18). The value of the Avrami exponent obtained for bread and for the wheat-starch gels suggests that the basic mechanism of bread staling involves changes analogous to crystallization of the starch fraction of the crumb, as reported by Colwell *et al.* (16).

By reexamining the results of Cornford *et al.* (13), Willhoft (19) found that by using equation 3 a large positive deviation from linearity occurred at less than 24 hr of storage, with n<1 at 27°C. Willhoft (19) postulated that during the first day of storage at 27°C an additional firming process occurs which is superimposed

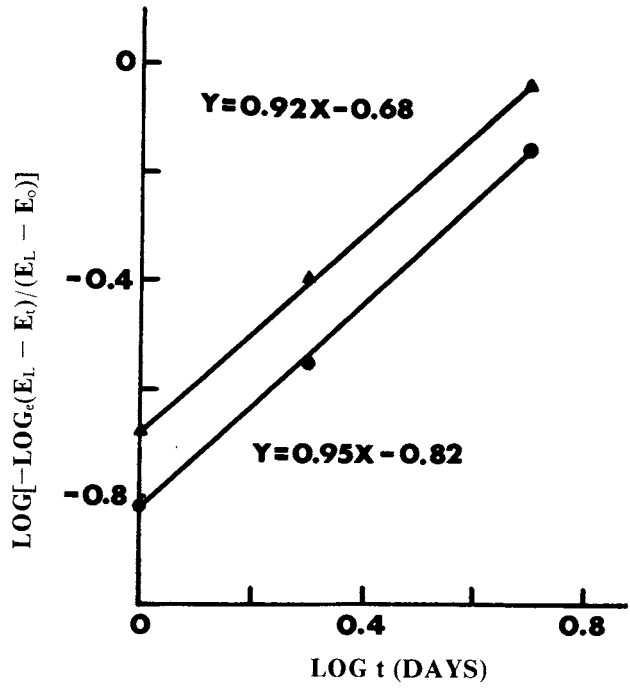

Fig. 1. Plot of log $\left(\log_e \frac{E_L - E_t}{E_L - E_0}\right)$ against log t of bread B (13.9% flour protein on a 14% mb) stored at 21° (▲) and 30°C (●).

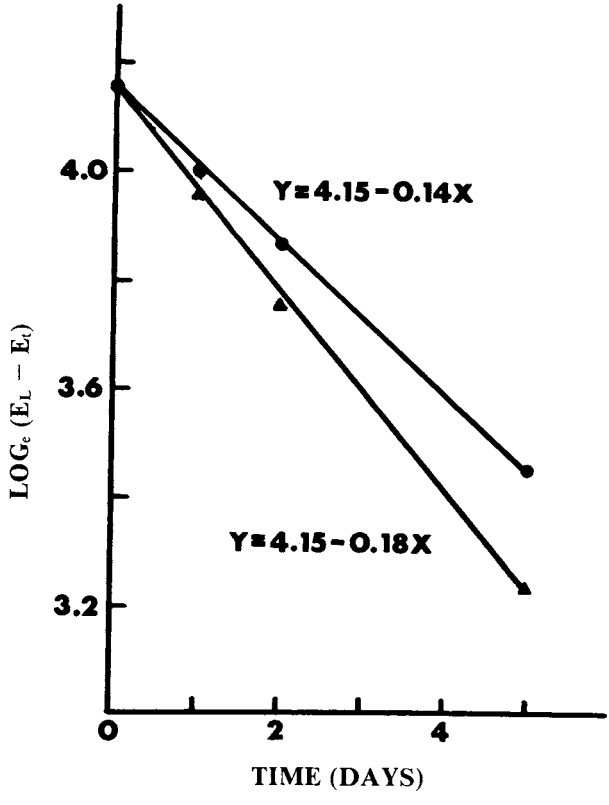

Fig. 2. Plot of $\log_e (E_L - E_t)$ against time of bread B (13.9% flour protein on a 14% mb) stored at 21° (▲) and 30°C (●).

TABLE II
Avrami Exponent and Time Constant of Bread Stored at 21° and 30°C

Bread	Storage Temperature °C	Avrami Exponent	Time Constant
A	21	0.92	3.74
	30	0.99	4.60
A-1	21	0.94	3.75
	30	0.93	4.56
B	21	0.92	5.44
	30	0.95	7.18
C	21	1.04	11.25
	30	0.99	18.73

on the growth of crystallinity of the starch fraction. However, the results shown in Figs. 1 and 2 and Table II do not support this hypothesis. From the results of Colwell *et al.* (16), the Avrami exponent of bread stored at 43° C also was found to be unity.

The time constant of bread made from different protein-containing flours demonstrates that the staling rate of bread is inversely related to the protein content of the flour (Table II). It is reported (20,21) that protein content is positively correlated to specific loaf volume, which has an inverse relation with compressibility of bread (4). Axford *et al.* (22) reported that the effect on firming rate with changes in specific loaf volume parallels that of the effect on the extent of crumb firming, provided that the storage temperature is constant. Although the actual rate of staling would be dependent on the specific loaf volume, the time constant (the time for any given fraction of material to be converted into the stale form) should be independent of the specific loaf volume (22). Since θ of equation 1 is a measure of the ratio of the amount of material unchanged at time t to the initial amount of material available for change, the time constant is independent of the concentration in the solid or condensed phase, which in any case will not be affected by changes in the loaf volume (22). Therefore, the time constants shown in Table II were not the function of specific volume, although the specific volume of the bread varied: 4.43–4.56, 4.26–4.46, 5.02–5.19, and 4.55–4.71 for breads A, A-1, B, and C, respectively.

Although flour A-1 showed greater strength than flour A (Table I), the time constants for the bread produced from the A-1 and A flour were identical (Table II). This suggests that the staling rate of bread is independent of protein quality, and supports the suggestion of Erlander and Erlander (6) who emphasized the importance of the ratio of starch to protein in the dough in determining the rate of bread staling.

It is unknown why the bread stored at the high temperatures aged at a slower rate (Table II). Colwell *et al.* (16) suggested that moisture transfer from the interior crumb to the outer layers of the bread might account for the reduced effect of the crumb firmness. Another possibility suggested by these authors is the formation of a more symmetrically perfect crystal structure at higher temperature, imposing limitations on the availablity of material for crystal formation.

Figure 3 shows amylograms for the slurries of freeze-dried and ground fresh crumb. That portion of the amylograms from 25° to 70° C is not included in the figure. Unlike the amylograms of flour or starch, bread crumbs A and B showed a minor peak at a lower temperature than the peak height at 95° C. The initial peak was most pronounced for the crumb slurry of bread A. These results agree with those of Yasunaga *et al.* (7) who reported that the minor peak was particularly prominent when the overall increase in viscosity was relatively low. The temperature at which the initial peak occurred did not change as the bread aged. The minor peak, however, was absent for the crumb slurry of bread C.

The initial peak was not observed with amylograms of freeze-dried doughs obtained after mixing and after fermentation (results not shown). Banecki (8) demonstrated that the enzymatically isolated starches from the bread crumb did not show the initial peak. These results imply that the minor peak may be due to association of starch with other flour constituents during baking.

The 15-min height was highest for the crumb slurry of bread B, followed by

that for bread A and for bread C (Fig. 3). Since the extent of gelatinization which takes place during baking depends largely on available water (7), the lower 15-min height for bread crumb C was expected because of its higher baking absorption. Despite higher absorption, the amylogram obtained from bread crumb B showed a higher 15-min height than that from bread crumb A. This would be due to the malt treatment on flour A.

The setback pattern of the samples (Fig. 3) indicates that there is a certain temperature which caused a sharp increase in viscosity, which was not observed in freeze-dried dough obtained after mixing or after fermentation (results not shown). The slurries of bread crumb A and B showed quite similar setback patterns, while bread crumb C had a different pattern. The storage of bread did not change the temperature at which the viscosity increased rapidly during setback.

The amylograms of bread crumb slurries (Table III) show that the 15-min height and setback were essentially unchanged with bread storage, except with bread produced from A and B flours and stored at 30°C for 5 days.

The pasting temperature of bread crumb slurries A and B progressively decreased as bread aged, while that of bread C remained essentially constant (Table III). It was reported (23) that the concentration of starch is inversely related to the pasting temperature. Hence, the progressive decrease of the pasting temperature with bread storage would imply a higher starch concentration in the stale bread crumb. However, this would not be the case, since the starch concentration (retrograded plus unretrograded) in the crumb would remain

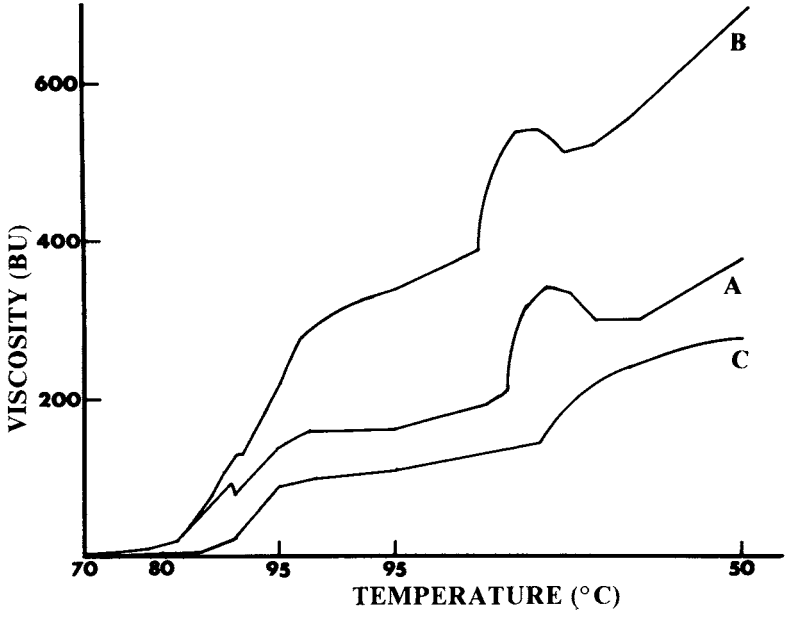

Fig. 3. Amylograms of fresh bread crumbs A, B, and C. Flour protein contents of A, B, and C were 11.0, 13.9, and 21.6%, respectively, on a 14% mb. That portion of the amylogram from 25° to 70°C is not shown.

TABLE III
Data on Amylograms of Bread Crumb Slurries

Bread	Storage Time day	Storage Temperature °C	Pasting Temperature °C	15-Min Height BU	Height at 50° C BU
A	0	...	77.5	170	380
	1	21	64.0	170	380
		30	65.5	160	360
	5	21	61.0	170	350
		30	62.0	130	320
B	0	...	77.5	340	700
	1	21	68.5	330	680
		30	68.5	360	720
	5	21	59.5	360	700
		30	61.0	320	630
C	0	...	86.5	110	280
	1	21	86.5	110	270
		30	88.0	110	270
	5	21	88.0	110	260
		30	88.0	110	260

constant. Furthermore, since the stale bread can be refreshened merely by heating to 50°–60° C (24), it is assumed that the retrograded starch was fully reversed before reaching the pasting temperature. Possibly the characteristics of the retrograded starch granules are such that when heated in excess water they swell more readily than the starch granules in fresh bread, which would cause a lower pasting temperature.

The absence of changes in the pasting temperature upon storage of bread C (Table III) indicated there must be a critical starch content in dough to cause changes in pasting temperature.

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