# Bread Staling<sup>1</sup>

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## **ABSTRACT**

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Bread staling studies, although conducted for many years, have still not completely answered all of the questions associated with this phenomenon. Although almost everyone agrees that starch retrogradation is the most important single factor causing crumb firmness, the importance of other contributing factors and the means of retarding firming remain open to question. In this review, various aspects of bread staling are discussed. Recent studies conducted on the effect of surfactants on total watersolubles, soluble starch, and amylose content in bread crumb are presented, as are the effects of baking procedure and surfactants on the pasting properties of bread crumb.

Several reviews have been written on the topic of bread staling, including ones by Zoebel (1973), Willhoft (1973b), Maga (1975), Kim and D'Appolonia (1977e) and Knightly (1977).

To discuss all of the studies that have been conducted in relation to bread staling is beyond the scope of this review. The concensus among the various workers and studies still appears to be that changes in starch play the major role in bread firmness.

Bread staling, however, is an extremely complex phenomenon

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and is difficult to define in straightforward terms. Broadly speaking, bread staling refers to all changes that occur in bread after baking. Changes occur in both the crumb and the crust of the bread. The increase in crumb firmness has probably been used to the largest extent by investigators following bread staling. Other changes, however, such as loss of flavor, decrease in water absorption capacity, amount of soluble starch and enzyme susceptibility of the starch, increase in starch crystallinity and opacity, and changes in x-ray diffraction patterns have also been used.

This article discusses briefly some thoughts in the area of bread staling as well as some recent studies conducted in our laboratory.

Because the major component of bread is the flour, the various biochemical components found in the flour are important. Bread itself consists predominantly of proteins, starch, and water in the approximate ratio 1:6:5 (Willhoft 1973b). In addition, pentosans and lipids, although minor components of wheat flour, have been studied extensively to determine their functional properties in bread baking.

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Figure 1 shows some of the transitional compounds that exist in wheat flour in addition to proteins, carbohydrates, and nonpolar lipids. Wall (1971) has indicated that these transitional compounds permit physical association and chemical bonding between the major components. Although most workers believe that changes in the starch are primarily responsible for bread staling, importance of physical association and chemical bonding among the various components cannot be disregarded.

#### Starch

Cornford et al (1964) studied the relationship between elastic modulus, time, and temperature in bread crumb, on the assumption that the increase in crumb modulus is proportional to the growth of starch crystallinity. These workers utilized the Avrami equation to describe quantitatively the rate of bread firming. They showed that the relative rate of increase in the limiting modulus became greater as storage temperatures were lowered towards the freezing point. This evidence emphasized the importance of the negative temperature coefficient of staling and the fact that crystallization, a physical process involving a more ordered arrangement of molecules, was the principal factor involved in crumb firmness. Later studies (Axford et al 1968, Colwell et al 1969, McIver et al 1968), using differential thermal analysis, confirmed the findings of Cornford et al (1964).

Table I shows that data for the Avrami exponent and the time constant for bread and starch gels are in good agreement. The time constant is the time for any given fraction of material to be converted to the stale form. These data thus indicate that bread staling is basically characterized by the retrogradation of the starch component of the crumb.

The extent of starch gelatinization in bread has been followed with amylograph studies of bread crumb slurries (Yasunaga et al 1968). The authors suggested the possibility of using an amylograph to measure the extent of staling. Banecki (1972) found that the peak viscosity of starches isolated from wheat bread decreased sharply in 24 hr and then showed lesser changes up to 96 hr. The course of the viscosity changes resembled firming curves and other measures that have been related to starch crystallization.

In a recent study conducted in our laboratory (Morad and

D'Appolonia 1980a), the effects on baking procedure and various commercial surfactants on the pasting properties of bread crumb measured with the amylograph were investigated.

Table II shows the values obtained for the pasting properties of control bread crumb and bread crumbs containing two surfactants after different storage periods. The two surfactants, Amidan B-250 and Panatex, were used at the 0.5% level based on flour weight.

Amidan B-250 is a powdered distilled monoglyceride composed of 82% distilled monoglyceride made from edible, refined hydrogenated fat and 18% of a mixture of food ingredients such as soya proteins and flour. The distilled monoglyceride had the following specification: monoester, 90% minimum; free fatty acids, 1.5% maximum; free glycerol, 1% maximum; and iodine value, 3. Amidan B-250 was obtained from Grinsted Products, Inc.

Panatex is a hydrate of hard distilled monoglycerides manufactured to produce a uniform plastic dispersion containing a minimum of 22.5%  $\alpha$ -monoglyceride (the active material). The surfactant was obtained from ITT Paniplus, Olathe, KS 66061. The bread was baked using a conventional straight dough procedure. Although pasting temperature did not change to any extent as the storage time was increased, incorporation of surfactant, in general, increased the temperature.

With the incorporation of a surfactant, the 15-min height of the viscosity curve obtained with the amylograph was greater than that of the control, although the two surfactants gave different results. With storage, the 15-min height values for the bread crumbs containing either surfactant also decreased. The decrease was greatest during the first few hours of storage. Height values at 50° C were likewise higher for the bread crumbs containing surfactants. The different response noted between the two surfactants was probably due to difference in composition.

Similar studies were conducted by Morad and D'Appolonia (1980a) on bread crumbs produced by the continuous mix baking procedure. The areas under the peak obtained during the cooling portion of the amylograph were also measured (Table III). A pronounced difference was noted in the area under the curve during the cooling cycle of the amylograph, with and without the incorporation of surfactant, and also as bread storage time increased. The importance of the peak and of its size during the cooling

TABLE I
Comparison of Avrami Exponent and Time Constant of Bread
and 50% Starch Gels Stored at 21° Ca

	Avrami Exponent	Time Constant (days)	Reference
Starch gel	1.02	3.76	McIver et al (1968)
	0.90	4.20	Colwell et al (1969)
	0.98	3.80	Kim and D'Appolonia (1977a)
Bread <sup>b</sup>	1.00	3.68	Cornford et al (1964)
Bread <sup>c</sup>	•••	3.28	Axford et al (1968)

<sup>&</sup>lt;sup>a</sup> From Kim and D'Appolonia (1977d).

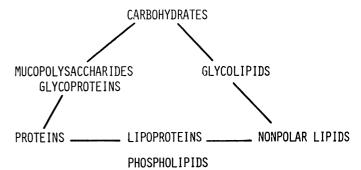


Fig. 1. Relationships between components of wheat flour (from Wall 1971).

TABLE II

Effect of Surfactants on the Pasting Properties of Bread Baked by the Straight Dough Procedure<sup>a</sup>

		Control		A	midan B-25	0		Panatex	
Storage Time (hr)	Pasting Temperature (° C)	15-min Height (BU)	Height at 50° C (BU)	Pasting Temperature (°C)	15-min Height (BU)	Height at 50° C (BU)	Pasting Temperature (°C)	15-min Height (BU)	Height at 50° C (BU)
0.16	83.5	390	700	83.5	615	835	85.0	455	825
1	80.5	395	715	85.0	590	775	85.0	440	775
5	80.5	380	690	83.5	570	780	86.0	410	730
12	80.5	390	700	85.0	510	700	83.5	410	740
24	82.0	380	685	83.5	555	745	83.5	420	770
48	82.5	375	690	84.0	540	740	82.5	385	725
72	82.0	390	705	83.0	520	715	82.5	380	725
96	82.0	320	615	82.5	550	755	83.5	390	735

<sup>&</sup>lt;sup>a</sup> From Morad and D'Appolonia (1980a).

<sup>&</sup>lt;sup>b</sup>Conventional baking process.

<sup>&</sup>lt;sup>c</sup>Chorleywood bread process.

portion of the curve in relation to bread staling has not been established. Figures 2 and 3 (Morad and D'Appolonia 1980a) illustrate the bread crumb amylograms with and without surfactants, after 0.16 and 96 hr of storage, respectively.

Kim and D'Appolonia (1977b) examined the effect of staling on the quantity and composition of soluble starch extracted from bread crumb during storage (Table IV). The amount of amylose in the soluble starch leached from the bread crumb after 0.16 hr of cooling was small, but a sharp decline in the amylose content occurred during the 5-hr cooling period after baking. These results support earlier observations of Schoch and French (1947) that most amylose retrogradation takes place during baking and subsequent cooling of the loaf.

Work was recently continued in our laboratory (Morad and D'Appolonia 1980b) to examine the effect of surfactants and baking procedure on water-solubles and soluble starch in bread crumb. Data on the amount of total water-solubles extracted are presented in Table V. The amount of extractable soluble material decreased at a faster rate during the first 12 hr of storage than thereafter in the presence or absence of surfactant. Lower amounts of water-solubles were obtained from the bread crumb containing surfactant than from the control during the early storage period. We also reported that the decrease in total solubles in the presence or absence of surfactant was not as great with the continuous-mix breads as with the straight-dough breads, which could be a result not only of the type of processing but also of the difference in formulation. Values for amylose content in the water-solubles of the bread crumbs are presented in Table VI. Amylose content decreased as the bread aged, with the greatest decrease occurring during the first 24 hr of storage. Significantly lower amylose content values were found for breads with surfactant than for the control. Soluble starch in bread crumb containing surfactant was less than that in the bread crumb without surfactant, although both decreased with storage.

TABLE III
Peak Area (cm²) During Cooling Portion of Amylograph Curves<sup>a</sup>

Storage	Straight Dough Procedure			Continuous Mix Baking Procedure		
Time (hr)	Control	Amidan B-250	Panatex	Control	Amidan B-250	Panatex
0.16	5.0	12.0	10.0	3.0	11.0	6.0
1	5.0	10.0	9.0	3.0	10.0	5.0
2	b	b	ь	2.0	8.0	4.0
5	4.0	9.0	8.0	1.5	8.0	4.0
12	5.0	8.0	8.0	1.0	8.0	3.0
24	4.0	9.0	8.0	1.0	8.0	3.0
48	4.0	8.0	9.0	1.0	8.0	3.0
72	5.0	9.0	9.0	0.7	8.0	3.5
96	5.0	9.0	10.0	0.5	8.0	3.0

<sup>&</sup>lt;sup>a</sup> From Morad and D'Appolonia (1980a).

<sup>&</sup>lt;sup>b</sup>Data unavailable.

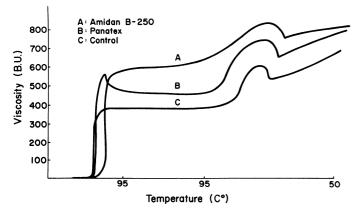


Fig. 2. Amylograms for bread crumbs with and without surfactants and baked by the straight dough procedure, after 0.16 hr of storage (from Morad and D'Appolonia 1980a).

#### Proteins

Several studies have been concerned with the influence of flour protein levels on bread staling; opinions differed. Willhoft (1973a) suggested that two factors had to be considered in rationalizing the antifirming effect of increased protein content. They were 1) a direct starch dilution effect, and 2) the effect of gluten enrichment on loaf volume and the concomitant effect on loaf softness.

Recent studies in our laboratory (Kim and D'Appolonia 1977a) have concerned the effect of flour protein content on bread staling rate (Table VII).

The time constants of breads made from flours of different protein content demonstrate that the staling rate of bread is inversely related to the protein content of the flour. However, the values for the Avrami exponent indicate that the basic mechanism of bread staling was not affected by the protein content.

Although the actual rate of staling depends on the specific loaf volume, the time constant should be independent of the specific loaf volume. Therefore, the time constants shown in Table VII were not the function of specific volume, although the specific volume of the bread varied.

The bread was made from flours designated A, A-1, B, and C, having different protein contents. Although flour A-1 showed greater strength than did flour A, the time constants for the breads produced from the A-1 and A flours were identical. This suggests that the staling rate of bread is independent of protein quality and supports Erlander and Erlander (1969), who emphasize the importance of the ratio of starch to protein in the dough in determining the rate of bread staling.

#### Pentosans

Pentosans, which are polysaccharide materials, are a minor component of wheat flour present at the 2-3% level. Of the total pentosans, about one half are extractable with water, and the remaining portion, the "water-insoluble pentosans," are extracted

TABLE IV

Effect of Staling on the Quantity and Composition of Soluble Starch

Extracted from Bread Crumb<sup>a</sup> During 12 hr of Storage<sup>b</sup>

.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Storage	Soluble	Composition of Soluble Starch		
Time (hr)	Temperature (°C)	Starch (%)	Amylose (%)	Amylopectin <sup>c</sup> (%)	
0.16	Room temperature	2.51	0.60	1.91	
2	Room temperature	2.34	0.39	1.95	
5 <sup>d</sup>	21	1.86	0.22	1.64	
12 <sup>d</sup>	21	1.74	0.18	1.56	

<sup>&</sup>lt;sup>a</sup> 13.9% flour protein on a 14% mb.

<sup>&</sup>lt;sup>d</sup> Breads were cooled for first 2 hr at room temperature and then stored at 21° for 3 and 10 hr, respectively.

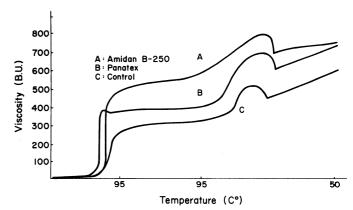


Fig. 3. Amylograms for bread crumbs with and without surfactants and baked by the straight dough procedure, after 96 hr of storage (from Morad and D'Appolonia 1980a).

<sup>&</sup>lt;sup>b</sup> All results reported on a dry basis (from Kim and D'Appolonia 1977b). <sup>c</sup> By difference.

TABLE V

Effect of Surfactants on Total Water-Solubles from Bread Crumb

Baked by the Straight Dough Procedure<sup>a</sup>

Storage Time	Control	Amidan B-250	Panatex	
(hr)	(%)	(%)	(%)	
0.16	9.66	8.84	8.56	
1	9.22	8.49	8.60	
2	9.13	8.04	8.45	
5	7.68	7.53	7.99	
12	7.58	7.04	7.60	
24	6.86	6.96	7.12	
48	6.85	6.90	7.08	
72	6.78	6.79	7.03	
96	6.70	6.52	6.78	

<sup>&</sup>lt;sup>a</sup> From Morad and D'Appolonia (1980e).

TABLE VI
Effect of Surfactants on Amylose Content in Water-Solubles
of Bread Baked by the Straight Dough Procedure<sup>a</sup>

Storage Time (hr)	Control (%)	Amidan B-250 (%)	Panatex (%)
0.16	10.45	3.29	7.95
1	8.45	3.05	6.37
2	5.21	3.01	4.74
5	4.99	1.99	3.79
12	4.95	1.93	3.26
24	3.91	1.87	3.16
48	3.27	1.87	2.79
72	3.22	1.84	2.63
96	2.82	1.65	2.65

<sup>&</sup>lt;sup>a</sup> From Morad and D'Appolonia (1980b).

TABLE VII
Effect of Flour Protein Content on the Time Constant
of Bread Stored at 21°C\*

	of bicau Stored at 21 C				
	F	lour			
Bread from Flour	Protein <sup>b</sup> (%)	Farinograph Stability (min)	Bread Time Constant (days)		
A	11.0	5.5	3.74		
A-1	10.6	12.5	3.75		
В	13.9	16.0	5.44		
C	21.6	21.0	11.25		

<sup>&</sup>lt;sup>a</sup> From Kim and D'Appolonia (1977a).

by alkali; however, once extracted, they are water-soluble.

Figure 4 (Kim and D'Appolonia 1977d) shows the effect of pentosans on firming of starch gels. Pentosans had a definite effect on retarding starch retrogradation, with the effect exerted by the water-insoluble pentosans being more pronounced than that by the water-soluble pentosans.

Table VIII shows the effect of pentosans on the staling rate of bread at 21° C. Pentosans increased the time constant of the bread, with the effect exerted by the water-insoluble pentosans being more pronounced than that exerted by the water-soluble pentosans (Kim and D'Appolonia 1977c).

### Water

Several studies have considered the role of water in bread staling. They generally agree (Bechtel et al 1953, Clusky et al 1959, Wasserman and Dörfner 1972) that increasing absorption in bread dough enhances softness and retards firming. Moisture redistribution during bread storage, however, has been a controversial subject. Senti and Dimler (1960) reported that moisture transfer would occur from the starch to the gluten in the crumb during aging, whereas Willhoft (1973a) found a moisture transfer from gluten to the starch phase.

# Lipids

The studies conducted on flour lipids have been concerned primarily with their functional properties in bread baking. The

TABLE VIII

Effect of Pentosans on the Time Constant of Bread Stored at 21°Ca

	Time Constant (days)			
Bread	Overall	Over the First Day Storage		
Control <sup>b</sup>	5.44	4.80		
With 1.0% soluble pentosans	6.53	4.23		
With 1.0% insoluble pentosans	8.54	5.88		

<sup>&</sup>lt;sup>a</sup> From Kim and D'Appolonia (1977c).

<sup>&</sup>lt;sup>b</sup>Bread made from flour having 13.9% protein on a 14% mb.

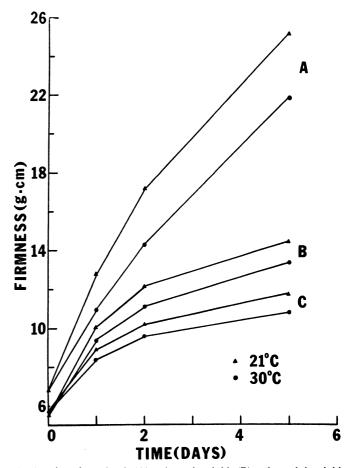


Fig. 4. Aging of starch gels (A) and starch-soluble (B) and starch-insoluble (C) pentosan gels at 21 and 30°C (from Kim and D'Appolonia 1977d).

improving effect of lipids, particularly of the polar lipids, on loaf volume are negatively related to bread staling. Pomeranz et al (1966) reported on compressibility of bread to which vegetable shortening and nonpolar, polar, and total lipid fractions from six wheat flours were added. Adding 0.5 g of nonpolar lipids per 100 g of wheat flour reduced crumb firmness only slightly. For significantly retarding crumb firmness during storage, 0.5 g of polar lipids were as effective as was 3 g of shortening. Wehrli and Pomeranz (1970) reported that a complex between glycolipids and starch was apparently significant and could be responsible for the improved freshness retention of bread baked with glycolipids. Areas such as these should be investigated further as additional studies are conducted in bread staling. What effects do the lipids in the starch granule, although present in only small amounts, have on bread staling? The possible importance of interactions among various components and their effects on bread staling should likewise be examined further.

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<sup>&</sup>lt;sup>b</sup>14.0% mb.

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