Effect of Waxy Barley Starch and Reheating on Firmness of Bread Crumb[1]

K. GHIASI, R. C. HOSENEY, K. ZELEZNAK, and D. E. ROGERS[2]

ABSTRACT

Changing the ratio of amylose to amylopectin by adding waxy barley starch to a high-protein wheat flour resulted in loaves of bread that were softer at one day after baking. At days 3 and 5 the breads had firmness equal to the control loaves. Replacing all the wheat starch with waxy barley starch gave loaves that shrank excessively during cooling. Reheating bread in "browning bags" gave softer bread. The degree of softening was temperature dependent and appeared to be caused by at least two mechanisms. Differential scanning calorimetry was used to follow changes in crystallinity in bread crumb. The change in crystallinity did not correlate well with changes in staling (firmness).

Cereal Chem. 61(4): 281-285

The role of starch in bread is complex. Hoseney et al (1971) studied the baking performance of a range of cereal starches and found no correlation between granule size or gelatinization temperature and baking performance when the starches were reconstituted with a standard gluten and with water-solubles. They found that starches from rye and barley nearly equaled wheat starch in breadmaking, but that corn, sorghum, oat, rice, and potato starches were inferior. Greenwood (1976) reported that normal maize starch could replace wheat starch in a high-ratio yellow cake; however, when wheat starch was replaced by waxy maize starch the cake collapsed after leaving the oven. Similar results were observed when a waxy barley starch was substituted for wheat starch in a reconstituted bread dough (Hoseney et al 1978). Those results suggest that the amylose fraction of starch, perhaps as a result of rapid retrogradation, was responsible for setting the crumb structure.

Bread and similar baked products have a limited shelf life because they are subject to rapid deterioration in quality (both texture and flavor), commonly referred to as bread staling (Kulp and Ponte 1981, Maga 1975, Bechtel et al 1953). Bread staling is a complex phenomenon, the mechanism of which is not clearly understood. Katz (1928), using X-ray data, concluded that retrogradation of starch was the prominent factor bringing about staling. Schoch (1965) attributed the hardening of the crumb structure during staling to physical changes in the branched wheat starch molecules within the swollen granules, mainly because the amylose fraction retrogrades rapidly during initial cooling of bread loaves.

Axford and Colwell (1967) applied differential thermal analysis (DTA) to bread staling and found that the endothermic peak, which is absent in fresh bread, developed with storage time, and the rate of increase in peak area paralleled the increase in firmness (Cornford et al 1964).

The objectives of this study were to investigate the effect of varying the amylose-to-amylopectin ratio on bread staling and to study the effect of reheating bread on crumb firmness.

MATERIALS AND METHODS

Samples of barley (Campana) and waxy barley (Wapana), grown at Huntley, MT, were a gift from G. Fox. Wheat starch was supplied by Midwest Solvents, Atchison, KS. The high-protein flour (17.2% protein) was a blend of two hard wheats grown at Scott City, KS, and supplied by Seed Research Associates. The starches were dry-blended with the flour to produce a low-protein flour (12.5% N × 5.7).

Starch Isolation

Barley or waxy barley kernels were steeped at 50°C for 24 hr in an excess of 0.1% sodium meta bisulfite. After 24 hr, the kernels were ground in a Waring Blendor and the resulting slurry screened through a 16XX nylon bolting cloth. The starch slurry was wet-sieved twice through the bolting cloth, on which bran and endosperm cell-wall impurities were retained. Because of the strong starch-protein bonding, the residue was again ground in a Waring Blendor, and the above process repeated several times. The starch

[1]Contribution 83-101-J, Department of Grain Science and Industry, Kansas Agricultural Experiment Station, Kansas State University, Manhattan 66502.

[2]Graduate research assistant, professor, and research associates, respectively, Kansas State University.

Present address of K. Ghiasi: The Pillsbury Company, Minneapolis, MN 55414.

yield was still relatively low. Starch in the slurry was centrifuged in 250-ml polyethylene bottles at 1,500 × *g* for 10–15 min. The upper pigmented fraction, designated as tailings, was carefully removed by hand and discarded.

Breadmaking

A straight-dough pup loaf procedure was used. Doughs contained 100 g of flour (14% mb), 1.5 g of NaCl, 6.0 g of sucrose, 3.0 g of shortening (except where shortening was a variable), 4.0 g of nonfat dry milk, 2% compressed yeast, optimum $KBrO_3$, and optimum water. Doughs were mixed to optimum and fermented at 30°C (85% rh) for 180 min with punches at 105 and 155 min. After 55 min of proof, proof height was determined, and loaves were baked at 218°C for 24 min. Loaf weights and volumes were taken immediately after depanning.

TABLE I
Specific Loaf Volume and Amylose-Amylopectin Ratio

Sample	Specific Loaf Volume (cc/g)	Amylose-Amylopectin Ratio
Flour[a] + wheat starch	6.4	25:75
Flour[a] + barley starch	6.4	25:75
Flour[a] + waxy barley starch	6.2	16.6:83.4

[a] High-protein flour (17.2%) diluted with sufficient starch to give a flour of 12.5% protein.

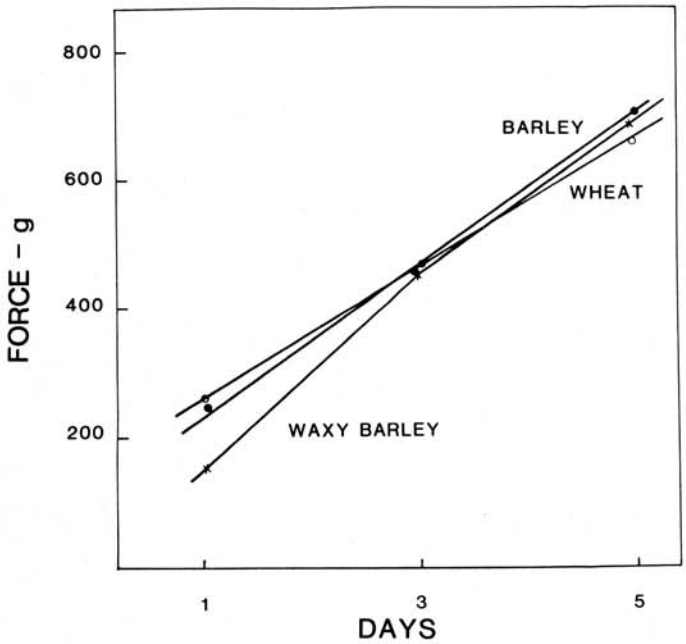

Fig. 1. Effect of diluting high-protein wheat flour with various starches on firmness of breads during storage.

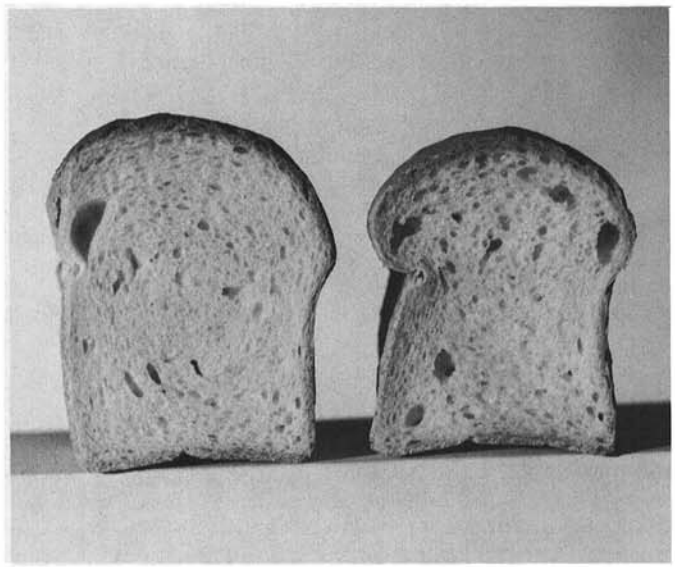

Fig. 2. Reconstituted bread containing wheat starch (**left**) and waxy barley starch (**right**).

Measurement of Bread Firming

After baking, the bread was allowed to cool 1 hr before being placed in polyethylene bags and stored at room temperature. Bread

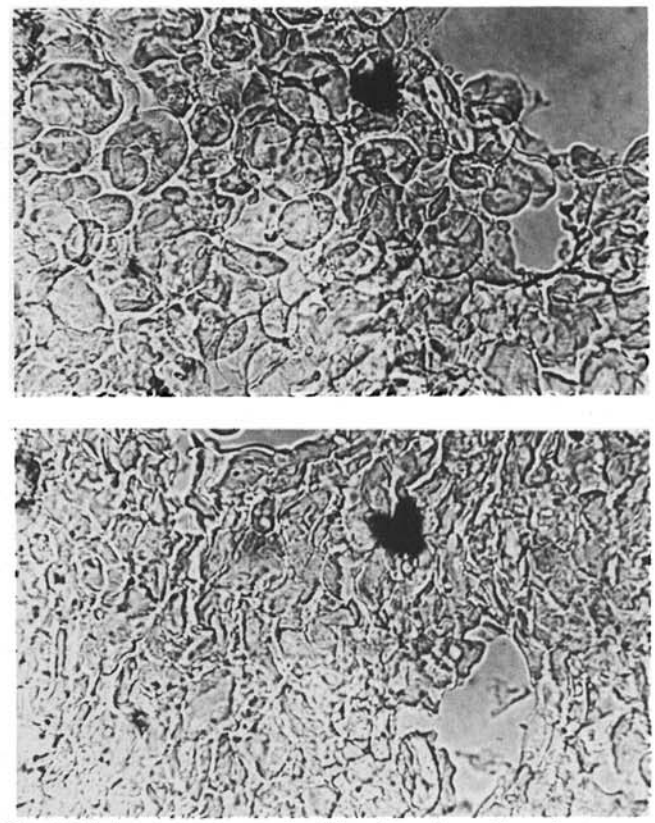

Fig. 3. Light photomicrograph of bread sections. **Top**, gluten, water-soluble, and wheat starch; **bottom**, gluten, water-soluble, and waxy barley starch.

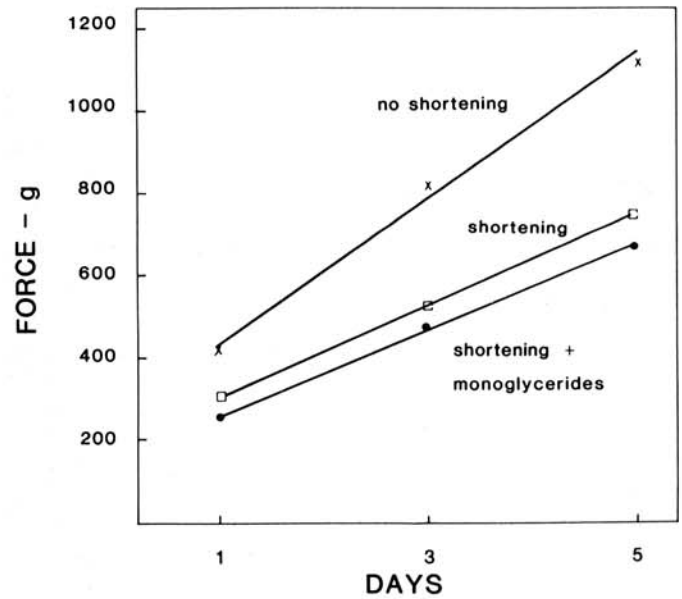

Fig. 4. Influence of shortening and emulsifier on the rate of bread-crumb firmness.

firmness was measured after one, three, and five days of storage.

An Instron testing device was used to determine changes in bread firmness during storage. Bread was sliced 1 in. thick. Compressions were taken in the center of the slice, and measurements of three slices from the same loaf were averaged. A 2,000-g load cell was used for the measurement; the Instron chart speed was 25 cm/min, and the crosshead speed was 5 cm/min. The compression was approximately 0.6 cm into the slice of bread. The standard deviation for measuring firmness was about 8% of the mean.

Method of Refreshening Bread

To refreshen bread, each loaf was placed inside a Reynold's Brown-in-Bag (14 × 20 in.). A thermocouple was inserted into the center of the loaf through the top crust at the opening of the bag. The bag was sealed securely around the thermocouple, placed in a preheated air oven, and connected to a digital thermometer. The oven temperature was set 25–30°C higher than the desired loaf temperature. The bread was left in the oven until the desired temperature was reached. It was then removed from the oven and cooled for 1 hr. When cool, it was removed from the bag, sliced, and the compression of each of three 1-in. slices was measured on the Instron. Moisture of the bread crumb was determined using the two-stage method (AACC 1983, method 44-15A).

Differential Scanning Calorimetry

A Perkin-Elmer DSC-2 with an Intracooler II system was used. Freeze-dried bread crumb (about 25 mg) was weighed in stainless

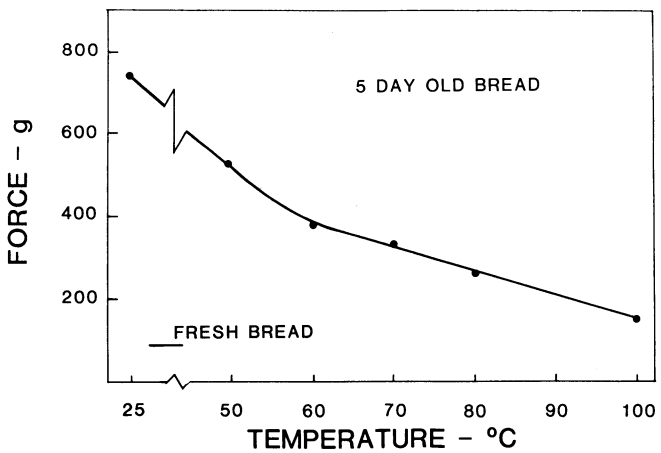

Fig. 5. Effect of reheating temperature on freshness of a five-day-old bread sample.

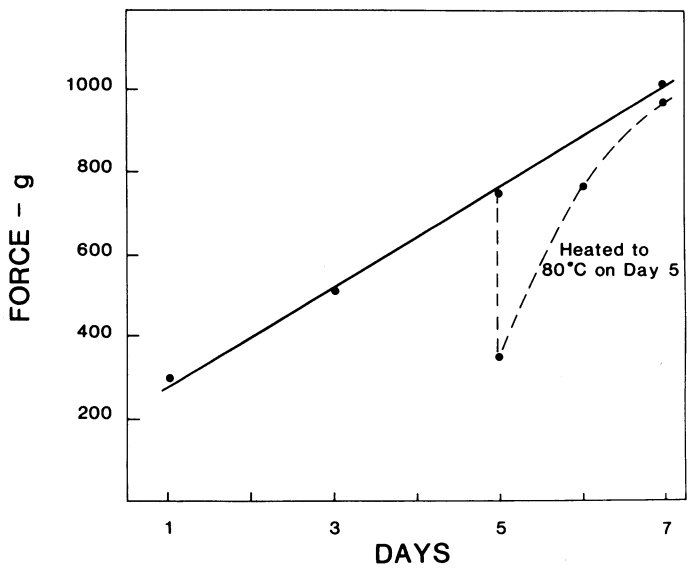

Fig. 6. Firming of bread as a function of time (——) and the effect of reheating bread after five days of storage to 80°C before holding it for one or two additional days (----).

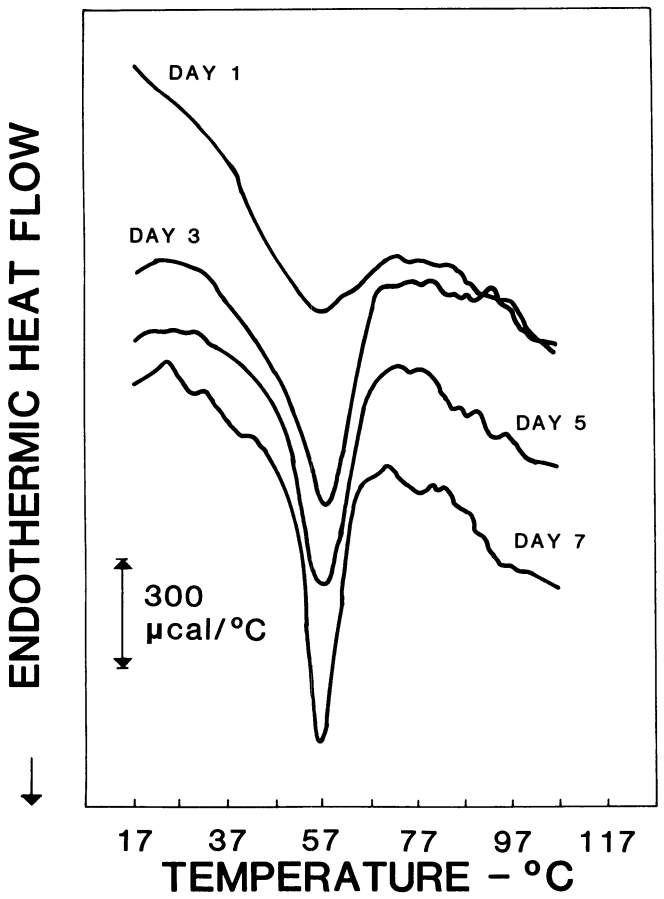

Fig. 7. Differential scanning calorimeter thermograms of bread samples stored for one, three, five, and seven days.

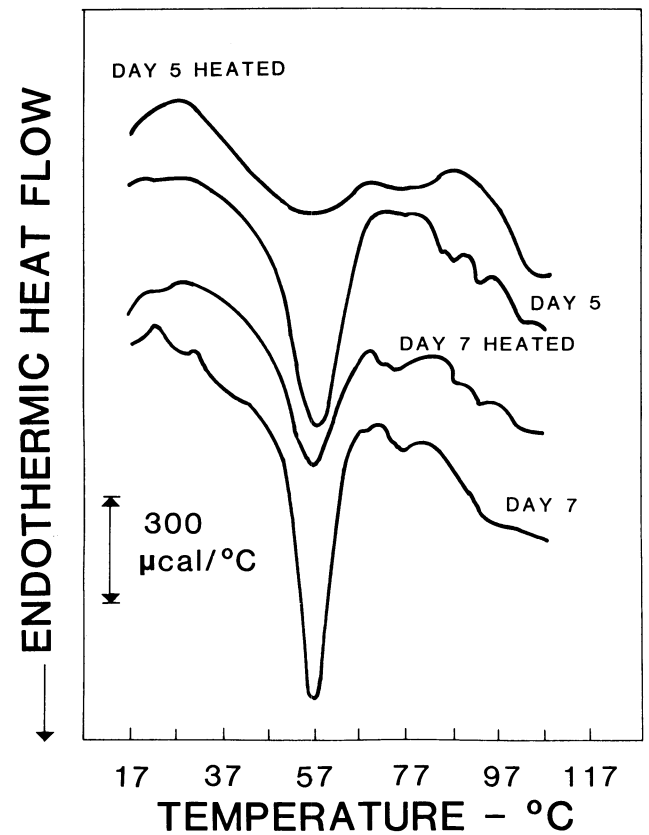

Fig. 8. Differential scanning calorimeter thermograms of five-day-old bread samples (day 5), after being heated to 80°C in browning bag (day 5, heated), after being stored at room temperature for two additional days (day 7, heated), and after being stored for seven days at room temperature (day 7).

steel pans and water added with a syringe in a 2.5:1 ratio of water to bread crumb. The pan was sealed and heated in the differential scanning calorimeter (DSC) at a rate of 10°C/min, a sensitivity of 1.0 m cal/sec. A pan containing water (approximately equal to water in sample plus half the weight of dry solids) was used as reference.

Light Microscopy

Sections of the crumb of the reconstituted breads containing wheat starch and waxy barley starch were cut on an American Optical Cryo-cut II cryostat rotary microtome by the following procedure. A portion of the crumb was trimmed to a 5–7 mm^3 size with a razor blade. This sample cube was bound to the specimen block with embedding medium and placed in the precooled (−10°C) microtome cabinet on a large copper quick-freeze shelf. When frozen, 20-μm sections were cut. The crumb sections were collected on a glass slide that had been coated with egg albumin and photographed with a Reichert Zitopan research microscope (NR 315 358).

RESULTS AND DISCUSSION

Effect of Amylose-Amylopectin Ratio on Crumb Firmness

The ratio of amylose to amylopectin in starch is under genetic control. However, with wheat starch, variation in the ratio appears to be small (Hoseney et al 1978). Because barley starch is functionally equal to wheat starch (Hoseney et al 1971) and because waxy barley starch was available, we had an opportunity to vary the amylose-to-amylopectin ratio in bread. A high-protein wheat flour (17.2%) was diluted to 12.5% protein with wheat, barley, or waxy barley starch. The specific loaf volume and estimated amylose-amylopectin ratios of those samples are shown in Table I.

Specific loaf volume did not differ among breads baked from flour diluted with the different starches. However, the amylose-to-amylopectin ratio of the sample diluted with waxy barley starch was significantly lower than that of the other samples. Assuming that normal starch has 75% amylopectin and 25% amylose, samples diluted with waxy barley starch (assumed 100% amylopectin) had an amylopectin content of 83.4% and an amylose content of only 16.6%.

Figure 1 shows the effect of various starches on firmness of bread during storage. Loaves containing the waxy barley starch were softer after one day of storage than were loaves diluted with wheat or barley starch. However, after storage for three or five days, the loaves had equal firmness. This suggests that amylose is involved in staling through day one but not for bread stored for longer periods. The starch fraction is generally considered to be primarily responsible for the staling phenomenon. Because the amylose fraction retrogrades rapidly during initial cooling of bread, slow changes in the amylopectin fraction, particularly after the first day, are implicated in further firming of bread (Kim and D'Appolonia 1977).

Amylose, because of its rapid retrogradation, is believed to be responsible for setting bread-crumb structure. Bread made with 100% waxy barley starch has been reported to collapse after baking (Hoseney et al 1978). To confirm those findings, flour was fractionated into starch, gluten, and water-solubles. The freeze-dried fractions were reconstituted in the ratio of 5% water-solubles, 17% gluten, and 78% wheat or waxy barley starch. Photographs of the resulting bread are shown in Fig. 2. The bread containing the waxy starch did not collapse after baking, but the loaf did shrink excessively (keyhole). The experiments described here were with 100-g pup loaves, and the previous reports were with 10-g microloaves.

The bread made with waxy barley starch had a softer crumb that was also sticky. Light photomicrographs of sections of bread crumb from both breads are shown in Fig. 3. The starch granules in bread made with wheat starch are swollen but still intact, whereas starch granules in the waxy barley starch bread are more highly disrupted.

Effect of Reheating on Crumb Firmness

Using DTA, Colwell et al (1969) investigated the progress of aging of concentrated wheat starch gels and found a close relationship between the aging gels as measured by DTA and staling of bread as measured by crumb firmness.

Shortening and emulsifiers are known to reduce bread-crumb firmness. The staling phenomenon is clearly shown in Fig. 4. The greatest increase in firmness was found for bread baked without shortening. The difference in crumb firmness between bread with shortening (control) and bread without shortening increased significantly as a function of storage time. That indicates that the staling rate was much greater for bread containing no shortening. Breads containing monoglycerides were slightly softer than the control after one day of storage and then maintained the difference during storage.

To reheat bread, samples were placed in "browning bags" and heated in the oven to the desired temperature. The effect of the reheating temperature on freshness of a five-day-old bread sample is shown in Fig. 5. As the reheating temperature increased, the loaves became softer. The curve is clearly biphasic, with a break at about 60°C.

We found no difference in firmness between samples heated to 50°C for 30 min or 2 hr, indicating that the partial heat-reversible aggregate is temperature dependent and not time dependent. Similar results on refreshening bread were obtained when bread was heated in a sealed steel chamber instead of in the browning bags.

The firming of bread as a function of storage time is shown in Fig. 6. Staling, as measured by an increase in firmness, is clearly evident and appears to be essentially linear over the seven days. When a loaf of five-day-old bread was heated to 80°C in a browning bag, the firmness value dropped from 750 to 333 g. After bread was refreshened, however, firmness increased rapidly when that sample was held for two days after reheating. Therefore, the rate of staling or firming was much faster for the reheated samples. The moisture content of the reheated loaf was essentially unchanged from that of the unheated loaves; the difference in moisture was less than 1%. At seven days, both bread samples had essentially equal firmness values.

Differential scanning calorimeter thermograms of bread crumb samples stored for one, three, five, and seven days are shown in Fig. 7. A single endotherm was observed between 40 and 60°C. This appears to be the endotherm reported by Von Eberstein et al (1980) for aged amylopectin gel. The enthalpy of the transition increases between the one- and the three-day-old samples; however, not much increase was found for bread crumb stored more than three days (Table II). However, the firmness data (Fig. 6) showed a rapid and continuous increase in firmness for bread crumb stored for up to seven days. When the five-day-old sample was heated to 80°C in browning bags, freeze-dried, and reheated in the DSC, the endotherm was much smaller (Fig. 8). The reheated sample was then held for one and two days and endotherms again determined. As shown in Table II, the reheated sample held for two days has a ΔH of 0.63 or is essentially equal to that of two-day-old bread (average of day one and three or 0.65). Thus, retrogradation, as shown by the DSC, progresses at the normal rate after reheating, whereas firmness goes at a much faster rate.

The DSC measures only the degree of retrogradation or crystallization of the starch molecules, and those processes do not appear to be closely related to the rate of staling or bread firming. The degree of crystallinity of the bread-crumb samples can also be determined by X-ray diffraction. Dragsdorf and Varriano-Marston (1980), using X-ray diffraction, concluded that starch

TABLE II
Enthalpy of Bread Crumb

Day	ΔH/ Bread	Heated on Day 5 to 80°C
1	0.42	···
3	0.88	···
5	0.82	0.33
7	0.94	0.63
9	1.09	···

crystallization and bread firming are not synonymous. Similar conclusions were reached by Zobel and Senti (1959), also from X-ray data.

The fact that Fig. 5 is biphasic implies that more than one phenomenon is responsible for refreshening and presumably for staling. If retrogradation of amylopectin was responsible for staling (firming), then heating to temperatures greater than 60°C should completely refreshen bread. This clearly does not happen, although the break in the refreshening curve occurs at 60°C, suggesting that retrogradation is responsible for part of the change in firmness. What is responsible for the additional firming is not clear, although the migration of water between gluten and starch, as suggested by Breaden and Wilhoft (1971), cannot be ruled out.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1983. Approved Methods of the AACC. Method 44-15A, approved October 1975, revised October 1981. The Association, St. Paul, MN.

AXFORD, D. W. E., and COLWELL, K. H. 1967. Thermal investigation of bread staling. Chem. Ind. London. 467 pp.

BECHTEL, W. G., MEISNER, D. F., and BRADLEY, W. B. 1953. The effect of the crust on the staling of bread. Cereal Chem. 30:160.

BREADEN, P. W., and WILHOFT, E. M. 1971. Bread staling. II. Measurement of the redistribution of moisture in bread by gravimetry. J. Sci. Food Agric. 22:647.

COLWELL, K. H., AXFORD, D. W. E., CHAMBERLAIN, N., and ELTON, G. A. H. 1969. Effect of storage temperature on the aging of concentrated wheat starch gels. J. Sci. Food Agric. 20:550.

CORNFORD, S. G., AXFORD, D. W. E., and ELTON, G. A. H. 1964. The elastic modulus of bread crumb in linear compression in relation to staling. Cereal Chem. 41:216.

DRAGSDORF, R. D., and VARRIANO-MARSTON, E. 1980. Bread staling: X-ray diffraction studies on bread supplemental with α-amylase from different sources. Cereal Chem. 57:310.

GREENWOOD, C. T. 1976. Starch. Page 119 in: Advances in Cereal Science and Technology. Vol. I. Y. Pomeranz, ed. St. Paul, MN.

HOSENEY, R. C., FINNEY, K. F., POMERANZ, Y., and SHOGREN, M. 1971. Functional (breadmaking) and biochemical properties of wheat flour components. VIII. Starch. Cereal Chem. 48:191.

HOSENEY, R. C., LINEBACK, D. R., and SEIB, P. A. 1978. Role of starch in baked foods. Bakers Dig. 52(4):11.

KATZ, J. R. 1928. Gelatinization and retrogradation of starch in relation to the problem of bread staling. Page 68 in: Comprehensive Survey of Starch Chemistry. Vol. I. R. P. Walton, ed. Chemical Catalog Co., New York.

KIM, S. K., and D'APPOLONIA, B. L. 1977. Role of wheat flour constituents in bread staling. Bakers Dig. 51(1):38.

KULP, K., and PONTE, J. G. 1981. Staling of white pan bread: Fundamental causes. Crit. Rev. Food Nutr. 15:1.

MAGA, J. A. 1975. Bread staling. Crit. Rev. Food Technol. 5:443.

SCHOCH, T. G. 1965. Starch in bakery products. Bakers Dig. 9(2):48.

Von EBERSTEIN, K., HOPCKE, R., KONIECZNY-JACDA, G., and STUTE, R. 1980. DSC-Untersuchungen und Starken. Teil I. Moglichkeiten theormalytischer Methoden zur Starchcharkerisierung. Staerke 32:397.

ZOBEL, H. F., and SENTI, F. R. 1959. The bread staling problem. X-ray diffraction studies on breads containing a cross-linked starch and a heat-stable amylase. Cereal Chem. 36:441.

[Received May 16, 1983. Accepted February 6, 1984]