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W H E A T S T U D I E S

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THE STALE-BREAD PROBLEM

THE staling of bread is a serious burden to bakers. This WHEAT STUDY is devoted to the critical examination of existing information on the aging of bread. The crust is drier than the crumb and abstracts moisture from inside the loaf. In consequence, it becomes soft and tough. When bread is freshened by warming, the process is reversed, and the crust becomes crisp again. The crust effectively insulates the crumb which becomes stale before losing much moisture. The soluble-starch content of the crumb diminishes and the starch granules become opaque and harder. When bread is freshened, the change in the starch granules is reversed.

So far, all investigators are agreed. Some believe the change in the starch is a chemical one and make staling depend solely upon the change in the starch. They assume at the same time a transfer of moisture from the starch to the gluten. They regard both processes as reversed when the loaf is freshened by warming. However, there is no conclusive evidence of such a transfer of moisture. It is possible to explain many of the phenomena by merely assuming that, like other jellies, the starch hardens as it sets and softens as it is warmed up again without chemical change. Moreover, it has not been proven that change in the starch is the sole cause of staleness, for there is reason to believe that particularly well-made bread may seem fresh even though the starch has changed appreciably. The study further presents the methods that have been recommended to produce bread that keeps well and the conditions of storage that tend to keep it fresh.

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THE STALE-BREAD PROBLEM

ECONOMIC AND SOCIAL CONSIDERATIONS

When bread was baked at home or by the neighborhood or village baker, stale bread presented neither social nor economic problems, for it was possible to adjust production to demand with considerable exactness. There was little stale bread and what there was could be used for food purposes as such, or in the baking of cakes or of special types of bread like brown bread, or in cookery as bread crumbs. Under modern conditions, when bread is manufactured in rather large factories¹ and distributed over a wide territory round about each such bakery, the adjustment of production to demand is often quite imperfect. The serious losses, which have developed in the form of large daily accumulations of stale bread that cut into the baker's profits because unsalable at the standard price, constitute one of his most serious problems.²

Large stale-bread losses tend to raise the price of fresh bread to consumers, since the stale loaves are sold at a price about covering the cost of materials or are used in various ways in the form of crumbs. The baker must find compensation in the price of fresh bread. Where this practice prevails, no great economic waste is involved, and the mean price of bread to the consumer not much affected. The poor and others, for example charitable institutions, receive bread at a low price. Some bakers even give their stale bread

away. There are, however, not a few places where the volume of stale bread is so great it cannot be disposed of in this way but has to be sold for animal feed or even used for fuel. Where these practices occur, there is needless waste of food and, in the long run, the price of bread to the consumer tends to be raised.

Before the war, even among bakeries generally recognized as efficient, stale-bread losses of 6 to 10 per cent of production were common, and exceptional cases of much higher losses, running for brief periods as high as 25 per cent of the bread baked, admittedly occurred. In November 1917, the United States Food Administration estimated that loss from return of stale bread amounted to "upwards of 600,000 barrels" of flour a year,³ equivalent to about 2.7 million bushels of wheat.

During the war most European nations faced the danger of wheat shortage. Their problem was not so much to prevent waste as to curtail consumption of wheat products. One of the ways by which it was sought to limit bread consumption was to forbid the sale of fresh bread on the assumption that stale bread, being less palatable than fresh, would be consumed in smaller amounts. The British Ministry of Food, for example, forbade the sale of bread within 12 hours after baking. But neither bakers nor consumers would consent to have the regulations continued in times of peace. Without such restrictions, bakers are always at pains to increase the consumption of bakers' bread rather than to see it reduced; and, for this purpose, few methods are as successful as getting to consumers bread that will be regarded by everyone as fresh.

In the United States, the problem was different. No wheat shortage was impending. The policy of the Food Administration was to re-

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¹ C. L. Alsberg, *Combination in the American Bread-Baking Industry, with Some Observations on the Mergers of 1924-25* (Food Research Institute Miscellaneous Publication 3), January 1926.

² J. S. Davis and W. Eldred, *Stale Bread Loss as a Problem of the Baking Industry* (Food Research Institute Miscellaneous Publication 1), February 1923.

³ U.S. Food Administration, *Release 450* (mimeographed), Nov. 11, 1917, p. 2.

duce waste (and consumption) of wheat in order that the largest possible surplus above domestic requirements might be available for shipment to Europe. The Food Administration accordingly ruled against the return of unsold stale bread by retail distributors to bakers and supplemented the regulation by publicity campaigns designed to enlist the aid of bakers, dealers, and consumers in reducing the waste of bread. Although the regulations were not universally enforced, they led to a great reduction in the amount of stale bread returned. It has been claimed, however, that these wartime regulations were detrimental to the small independent bakers because allegedly they called into being numerous so-called "window" bakeries, exploiting the slogan "Hot from the oven to you."

The bakers generally had found this state of affairs so desirable that after the war, when sharpened postwar competition threatened to bring back prewar wastes, they endeavored to get laws passed in the several states—and succeeded in some—continuing or re-establishing the wartime prohibition of the return of stale loaves to the baker. In some localities food officials forbade the return of stale bread on the ground that it might be deleterious to health, since such returned bread is often handled carelessly, becomes moldy or contaminated with filth, or is moistened and warmed to "freshen" it so that it can be sold to the consumer as new-baked. Partly because of legislation, partly because wartime practices were adhered to voluntarily for a time, stale-bread losses were smaller than before the war. In 1923, Davis and Eldred¹ estimated the loss to the wholesale bakers of the United States as probably averaging at least 2.5 or 3 per cent of their sales.

¹ *Op. cit.*, p. 7.

² Holbrook Working, "The Decline in Per Capita Consumption of Flour in the United States," *WHEAT STUDIES*, July 1926, II, 265-92; J. S. Davis, "The World Wheat Situation, 1934-35. A Review of the Crop Year," *ibid.*, December 1935, XII, 176.

³ P. G. Pirrie, "House-to-House Stale Returns and Relations with Salesmen," *Bakers Weekly*, Oct. 10, 1931, LXXII, 47-48, 50.

⁴ C. Murray, "Manufacture and Distribution of Bread," *Journal of Accountancy*, March 1935, LIX, 190-200.

⁵ Alsberg, *op. cit.*

However, American bakers were not unanimous. Indeed, some of them have vigorously fought all attempts of states and municipalities to prohibit the return of stale bread to the baker. These bakers have felt that such measures would lead retailers to force stale bread upon purchasers, and that this would cause the demand for bread to fall and the volume of business done by the baking trade to diminish. This has seemed especially important to American bakers and millers because in the United States the per capita consumption of flour has been declining.²

These laws forbidding the return to the baker of stale bread have had varying fates and caused not a little litigation. In some states, they have been well enforced; in others, there has been more or less nullification. No recent study to determine the extent of the losses and waste resulting from the return of stale loaves to bakers in the United States seems to have been made. There is evidence, however, that they have become greater than at the time of the Davis and Eldred estimate. According to a survey made by *Bakers Weekly* in the spring of 1930, the country-wide average percentage of returns was 4.66. In individual states, the average was as high as 7.5 per cent. A year later, Pirrie expressed the opinion that they had increased still more.³ Murray has stated recently that losses from stale bread are often "as high as 5%, 6% or even 7%."⁴ There are a number of reasons for this, which it would be well now to pass in review.

In the days of the great baking mergers, say in 1924-25, the wholesale bakers acquired production capacity which was not merely ample for that time but not infrequently designed for an expansion which, taking the country as a whole, could not possibly come.⁵ On the contrary, the market of wholesale bakers tended to contract with the growth of chain grocery stores, which for the most part have gradually come to produce nearly all their own bakery products. Many of the big plants found themselves with overcapacity and, indeed, the industry as a whole was—and still is—in this condition. Competition became more severe not merely in the immedi-

ate vicinity of the large wholesalers, but these concerns, with improved bread-cooling and -wrapping machinery and faster trucks, and with better roads, also invaded the field of the rural retail and small wholesale baker. Naturally, their bread tended to be less fresh than that of the local baker and added its quota to the country's stale-bread loss. Furthermore, bakers could, and did, deliver a great deal more bread than could be sold, for excess capacity made this possible with no additional cost other than that for the ingredients, because neither men nor machines were working at capacity. Moreover, ingredients were cheap. Many a baker succumbed to his desire to get a big display in each grocery in the hope that customers might take his bread. Striking differences existed between bakers in the same region.

Then came the depression. Many more persons than before sought to buy day-old bakery goods, because they were cheap. Many "stale" or "day-old" stores were opened in cities; and relief agencies bought day-old bread at reduced prices. Some bakeries, in addition to their regular line, offered their day-old products as a second grade in lieu of producing a separate low-priced line. Eventually, it came to serious competition between day-old and fresh bread.

There were, of course, other factors in addition to the depression and intensified competition due to over-capacity. One of these was the now well-nigh universal practice of selling bread ready sliced as well as wrapped. It is less easy for the purchaser at retail to tell the condition of the loaf by the feel. Also bread in this form is said to grow stale faster than when unsliced.

These changes in the baking industry caused a realignment of the several classes of producers. It had always been recognized that consignment selling¹ was at the bottom of the stale-bread-loss difficulties of the trade; but it seemed hopeless to expect help from officials and legislatures in meeting the situation. The National Industrial Recovery Act created this possibility. It seemed feasible to enact a code for the trade which would deal effectively with the return of unsold bread and with consignment selling. At the hearings

held for the purpose of preparing a code, there was lively discussion of these proposed provisions. It was obvious that the trade regarded the situation with reference to stale-bread returns and consignment selling as serious. The outcome was a compromise. The return of stale bread was not prohibited, but the ways in which such bread could be disposed of were prescribed. These ways were designed primarily to prevent unfair competition between stale and fresh products and only incidentally to eliminate waste. "Consignment" was defined to "mean the delivering, shipping, and/or placing of bakery products by a member of the Industry to or with a retailer, wholesaler, restaurant or hotel keeper, or similar person, pursuant to an agreement or understanding that any products which are not sold will be taken back or credit given therefor or price if paid returned in whole or in part, or other allowance made." The national code did not prohibit these practices but made it permissible for any regional group of bakers to adopt a no-consignment provision if a truly representative group of the bakers concerned demanded it. Such a demand was forthcoming in only a few regions.

It is noteworthy that it did not seem to occur to anyone to define staleness. *Stale bread under the code was merely bread returned to the bakers unsold.* No time limit was established on the age of bread after which it was to be regarded as stale. This was probably because the trade as a whole is unacquainted with the existence of any objective test by which staleness may be established. It is clear that it is extremely difficult to enforce any law or regulation unless staleness is defined either in terms of the age of

¹ Wholesale bakers who sell to retailers rather than house-to-house do so through the drivers of their delivery wagons. These employees are both salesmen and drivers. They determine to a large extent how many loaves to leave in the shop of each retailer. Since they are usually paid in part on a commission basis, they are under the temptation to stock the retailer with too many rather than too few loaves. The retailer tends to be indifferent, for he does not pay for the fresh bread. On his next visit, the driver takes away the stale loaves and collects payment only for those that have been sold since his preceding visit. This is consignment selling.

bread or in terms of some objective chemical or physical test. To attempt to define staleness in terms of the age of the bread is not at present feasible, for the onset of staleness depends upon the character of the loaf, the methods of production, and the conditions to which it is subjected after it leaves the oven. If the industry desires to cope with its stale-bread problems through governmental processes which must stand the test of court review, it seems obvious that objective physical or chemical tests for the determination of staleness are essential. What progress has been made in meeting this problem is set forth in this study.

The hearings on the code showed that the position of bakers was in effect as follows:

Many retail bakers favored prohibition of consignment selling, because they believed many retail outlets in their own neighborhood would cease to carry the wholesalers' product, bread possibly excepted, if the owner had to gamble on the sale of bread and cakes. In cities, they tend to be more concerned about cake and pie than about bread on which the profit tends to be smaller.

Rural wholesalers also opposed consignment selling. They believed that the great wholesale bakeries in the cities would not then sell so readily to rural outlets far away, because rural grocers would not take the risk involved and would prefer to stock a small supply from the local wholesale baker and replenish it later in the day if necessary.

The great wholesale bakers were divided. At heart few of them favored consignment selling, but they could not forecast what might happen. They knew they could not afford to take chances; even a small loss of business would be serious. Some thought that the grocer would tend to stock only one or two brands of bread, and they did not know whether it would be their bread or that of someone else. Others feared that if the grocer were forced to risk his own capital on his bread sales the various grocers' organizations might establish their own bread plants, on the theory that, if they must gamble individually, they might as well gamble in a group and spread the risk. Finally, as above pointed out, many wholesale bakers feared that, if con-

signment selling were abolished, retail grocers would force stale bread on customers as fresh. This, it was believed, would injure the reputation of the brand that happened to be sold in this way and cause demand for it to slacken.

It would seem that, despite the weakness of the Bakers' Code with respect to stale-bread returns and consignment selling, it had some effect in reducing wastes. After it became inoperative when the Supreme Court held the National Industrial Recovery Act to be unconstitutional, only regional codes promulgated under state acts remained in force. Certain it is, therefore, that the growing stale of baked products is still a question of importance, not merely to bakers but also to consumers, for undoubtedly the losses to bakers are passed on to consumers in the form of higher prices.

An important social question is also involved—night work by bakery employees to satisfy the insistent demand of the consuming public for very fresh bread. In some countries more advanced in social legislation than the United States, this is a serious question. In Holland, for example, night work by bakers is in violation of law and the sale of bread so fresh that it can be produced only by such work is prohibited. In consequence, as we shall see, special techniques to prolong the life of bread have been developed there. Unfortunately, they have not yet been put into general practice. It would undoubtedly be a social gain for the United States if ways and means, adapted to American circumstances, could be found to do away with night work.

Large-scale production of bread is growing. This tendency increases the importance of the stale-bread-loss problem in two ways. Directly, it enlarges the field within which considerable losses from stale bread are to be expected. Indirectly, a general reduction in the loss from this source, like other economies in production or distribution, will tend to permit the baker to sell on a narrower margin and thus to extend the market for his products into homes where household baking is practiced on grounds of economy.

The situation can be improved in three ways: by better adjustment of production to demand, by better distribution, and by pro-

longing the life of the loaf. With the first two of these, this study is not concerned. It deals primarily with the aging of bread. Prolonging the life of bread is one of the most important of the practical problems that confront scientists engaged upon the improvement of the technique of food manufacture. The shortness of the life of bread sets limits to the size of bread factories because their market is restricted to the territory in the vicinity which can be reached in not too long a time. Longer routes are attempted in the central part of the country than in the Atlantic or Pacific states. More speedy transportation or prolonged life of the loaf or both would make larger bread factories and more effective mass production possible with the economies of production and distribution therein involved.

As in medical research a specific for a disease is rarely found until the cause behind the disease—its etiology—is fully known, so other scientific problems are rarely solved until the phenomena involved are fully understood. We can hardly hope, except as the result of a lucky accident, to learn how to prevent or even appreciably to delay the growing stale of bread until we fully understand what this process of growing stale really is. Much progress has been made in recent years in its investigation. It is our purpose here to bring this material together, and to examine it critically in the hope that further research will be stimulated thereby and that the practical application of what is already known will be furthered.

STRUCTURE AND BEHAVIOR OF STARCH GRAINS¹

The aim of this section is to describe those properties of starch which are involved in the aging of bread, for, as we shall see, these properties are important factors—perhaps the most important ones—in the growing stale of bread. Acquaintance with the properties of starch should render it easier to grasp the phenomena concerned in the aging of bread. Unfortunately, the subject is complicated,

and, although the purpose of the writer is to treat it in a nontechnical manner, some readers may prefer to turn at once to later sections which have been written, it is hoped, so that they can be understood by themselves.

The starch granules of wheat are discrete particles of microscopic size and more or less of the shape of disks or bilaterally flattened spheres or saucer-shaped. They exhibit a series of rather faint concentric rings—probably because they are built up of a series of layers; in other words, they have a laminated structure. When a beam of light is passed through them, they change its direction and break it up into two components. This property is termed “double refraction” or “birefringence.” Starch grains are doubly refractive or birefringent. Birefringence can be made manifest to the eye if polarized light is passed through the granules, i.e., light consisting solely of waves which vibrate in the same plane. The polarizing microscope is an instrument which permits only such polarized light to pass through the object under examination. Starch grains viewed through such an instrument manifest their birefringence by showing a so-called black cross. The granules exhibit alternate luminous and dark quadrants so arranged that the dark areas appear like a more or less regular black cross.

Many crystals are birefringent, but non-crystalline materials may also exhibit this property when they are subjected to a mechanical stress or strain. A sheet of well-annealed glass, for example, may exhibit birefringence when it is put under stress by bending. Substances which are built up in such a way that their component parts are arranged in some orderly fashion, for example if the components are all placed parallel like corded firewood, may also exhibit birefringence.

Starch grains in their natural state are crystalline, at least in part. By crystalline, we mean that the molecules are arranged in some orderly fashion. This does not necessarily imply that the granule or its components possess a geometric form such as we are accustomed to find in an ordinary crystal, say rock candy. Many botanists have claimed that starch granules are of crystalline structure, but final

¹ Cf. C. L. Alsberg, “Studies upon Starch,” *Industrial and Engineering Chemistry*, February 1926, XVIII, 190; and “Starch and Flour Quality,” *WHEAT STUDIES*, February 1935, XI, 229–54.

proof became possible only in recent years through the use of the X-ray.

Parallel X-rays falling upon a photographic plate after passage through a crystalline substance produce a pattern which appears when the plate is developed. This pattern is known as an X-ray spectrum or X-ray diagram. It is characteristic of crystalline structures. The X-ray thus permits us to determine whether a substance which presents no evidence of crystallinity to the eye is in fact composed of crystals too minute to be visible or has an orderly arrangement of its molecules. It is unnecessary for present purposes to explain why this is so or what conditions must be observed in performing such experiments.¹ What concerns us here is that starch granules in their natural state behave in this way. They must therefore be crystalline. It is highly probable that they consist of tiny hair-like crystals which the older botanists called trichites, from the Greek *thrix*, a hair. These are probably arranged radially, i.e., one end is directed toward the interior of the starch granule, the other toward its periphery. The trichites thus lie more or less perfectly parallel.

¹ The reader who is interested in pursuing this subject further is referred to the standard texts, for example: G. L. Clark, *Applied X-Rays* (New York, McGraw-Hill, 1927).

² J. R. Katz, "X-Ray Investigation of Gelatinization and Retrogradation of Starch in Its Importance for Bread Research," *Bakers Weekly*, Mar. 24, 1934, LXXXI, 34-37, 46. The results of the X-ray studies of Katz and of his co-workers have been recorded in a series of papers in *Zeitschrift für physikalische Chemie*, Abteilung A.

³ J. R. Katz, *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers* (Dissertation, Amsterdam, 1917; 's-Gravenhage, van Langenhuisen, 1917), Part 1, p. 17. This dissertation has been published in German and somewhat modified in a series of articles appearing in *Zeitschrift für das gesamte Getreide- Mühlen- und Bäckereiwesen*.

⁴ Alsberg, "Studies upon Starch.

⁵ "X-Ray Investigation of Gelatinization and Retrogradation of Starch in Its Importance for Bread Research"; *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers*.

⁶ It may be that free water is required for the change. At low temperatures, the free water present in the granule, having been converted into ice, may no longer be able to play a rôle in the conversion.

When starch granules are heated with water, their X-ray diagram or pattern undergoes changes. In the case of wheat starch, the change in this pattern depends upon the amount of water present and the temperature. Katz has named the X-ray pattern of natural unaltered wheat starch its A-pattern.² If such starch showing the A-pattern be heated to 100° C. with but 50 per cent of its weight of water or if it is heated with an excess of water to only 60° to 70° C., its A-pattern is transformed into a new pattern, which Katz has termed the V-pattern. The starch apparently has been converted from one crystalline state to another. Katz³ has named this state of starch first-degree gelatinization.

A starch granule in the state of first-degree gelatinization is somewhat swelled, and in the larger ones this swelling may have caused the center of the granule to become converted into the beginnings of a cavity which is sometimes irregularly star shaped. The granules have become more permeable, for they stain with such dyes as Congo red and, when placed in water, they permit some of their substance to diffuse out. Natural, uninjured, unheated granules, on the contrary, neither stain with these dyes nor are they soluble. It is not to be inferred that the greater solubility of gelatinized starch is due necessarily to chemical change of the starch substance, for mere mechanical injury, such as cracking, renders starch soluble to an appreciable degree in cold water.⁴

If wheat starch in first-degree gelatinization is held at a temperature below 60° to 70° C. for some time, it changes. According to Katz,⁵ it becomes less translucent, there is less soluble starch in it, and its X-ray V-pattern changes to a new one, the B-pattern. Its crystalline form has again changed and this change proceeds more rapidly at lower temperatures. The rate of change becomes maximum at -2° to -3° C.⁶ At still lower temperatures, it is slowed up again, until at quite low temperatures, for example that of liquid air, it does not occur at all.

If wheat starch in the state exhibiting this B-pattern is warmed up to over 60° to 70° C., it is converted back again into starch exhibiting the V-pattern. Allowed to age at lower

temperatures, it turns back again into the B-pattern form, and it may thus be changed back and forth from one form to the other, provided care is taken to prevent too great a loss of moisture.

If, instead of heating with insufficient water or at a low temperature, the granules are heated to 100° C. with an excess of water, the method of making paste, the X-ray pattern disappears altogether; the starch has changed from the crystalline to the noncrystalline or amorphous state. This state Katz has termed second-degree gelatinization.

The starch granule in this state is greatly swelled. The individual granules have the appearance of hollow elastic bags filled with liquid. Some of the starch substance has diffused out into the surrounding water. The granules stain easily and there is, of course, no sign of birefringence. The black cross has disappeared.

Starch in second-degree gelatinization also changes with time. It returns again to the crystalline form and like first-degree gelatinized starch ultimately shows an X-ray B-pattern. This change is accelerated or retarded by lower temperatures, much as in first-degree gelatinization. The change in pattern is more rapid in the presence of much water than of little,¹ and different starches change at different rates, other things being equal. Potato starch changes more rapidly than starches from the seeds of cereals. Whether this is true of seed starches in general does not seem to have been investigated.²

Starch in second-degree gelatinization, as when it is in the form of paste or of a thin,

¹ Katz, "X-Ray Investigation of Gelatinization and Retrogradation of Starch in Its Importance for Bread Research."

² *Ibid.*

³ J. Field II, "Specific Rotation and Phosphate Content of Cold-Water-Soluble Fractions of Ground Corn and Wheat Starches," *Proceedings of the Society for Experimental Biology and Medicine*, May 1928, XXV, 711-12.

⁴ Alsberg, "Studies upon Starch."

⁵ C. L. Alsberg and E. E. Perry, "The Effect of Grinding upon Starch and Starch Pastes," *Proceedings of the Society for Experimental Biology and Medicine*, October 1924, XXII, 60-61.

⁶ K. H. Meyer, H. Hopff and H. Mark, "Ein Beitrag zur Konstitution der Stärke," *Berichte der Deutschen chemischen Gesellschaft*, May 1, 1929, LXII, 1103-12.

boiled, aqueous suspension, also undergoes gross changes visible to the naked eye. Paste, more or less translucent when newly made, gradually turns opaque and white. Thin suspensions gradually cloud up and ultimately separate a sediment. The supernatant liquid may become nearly clear and ultimately contains starch in accordance with its solubility in water.³ Paste, if not too concentrated, may also separate into a solid and a more or less liquid portion.

Wheat starch which has aged in this way seems to differ from natural wheat starch in that it is very difficult to disperse it again by heating in water. Gelatinized starches examined by the writer (potato, maize, wheat) did not again regenerate the paste when reheated. The reasons for this are probably in part merely mechanical. A starch paste owes its consistency to its structure visible with the ordinary powers of the microscope.⁴ In it, the swollen granules occupy nearly all the volume of the system, so that they touch and compress one another. Thus the system acquires firmness. Anything that breaks up this structure through breaking up the individual granules so that they collapse converts starch paste into a syrup, because the swollen granules no longer touch and support one another. This is the effect of grinding in a pebble mill,⁵ or of freezing. Such a syrup is very cloudy and still contains in suspension bits of paste and uncollapsed gelatinized granules that have escaped attrition. It cannot again be converted into paste by heating. Its starch, unless the syrup has aged, is still amorphous, but some of it becomes crystalline in time. As above stated, once it has taken this insoluble form, starch is very difficult to disperse in water again by merely boiling. It is no longer like the natural starch from which it was formed—why is not well understood.

Starch granules consist of at least two substances, α -amylose, which is very insoluble, and β -amylose, which is somewhat soluble in water. How these two carbohydrates are laid down in the natural granule with respect to one another is not known. It is not even known whether they are both crystalline or only one of them. According to Meyer, Hopff and Mark,⁶ α -amylose (amylopectin) is crys-

talline, but β -amylose is amorphous. But, according to van Itallie,¹ both have a V-pattern if prepared from fresh wheat-starch paste, but a B-pattern if prepared from aged paste.

Raw starch granules, if ground up and mechanically injured, give up β -amylose to cold water, and if enough of it be used practically all the β -amylose may be extracted from raw, finely ground starch. However, the solutions so obtained are opalescent; in time most of the β -amylose flocculates out, and ultimately a clear liquid may be obtained by filtration which hardly shows the Tyndall effect and which contains from 0.1 to 0.5 per cent of β -amylose.² In other words, one obtains the colloid equivalent of a supersaturated solution which ultimately separates out a merely saturated solution.

Indeed, from boiled starch, all the β -amylose may easily be extracted, and this has been proposed by Biedermann³ as a method for its preparation. This is what happens in the analysis of bread crumb and the amount of soluble starch obtained depends upon the conditions of extraction. As time goes on, the change in swollen granules above described makes it more and more difficult to extract β -amylose.

Katz, in his earlier publications before he had discovered the changes in X-ray patterns that occur in gelatinization, expressed the view that the aging of gelatinized starch in-

involved a simple physico-chemical equilibrium reaction.⁴ In 1917, he even went so far as to suggest that probably this reaction involved the taking up of water, the break-up of the starch molecule, and the opening up of a union of two hydroxyl groups, one of which is presumably an aldehyde and the other a hydroxyl group. To the freeing of hydroxyl groups in this manner, he attributed the greater water-binding power of gelatinized starch. Gelatinization he believed to be a chemical reaction which involves the taking up of water. This view is not tenable, because, as has long been known, merely injuring a starch granule causes it to swell in water at the site of injury and permits some of its substance to disperse into the surrounding solution.⁵ It is therefore indubitable that the swelling power of starch granules may be modified by procedures which cannot possibly involve a chemical reaction within the common meaning of that term.

After Katz had made his X-ray studies, he modified his position in that he then assumed that aging involves a heterogeneous reaction. He insists, however, that we have to deal with a physico-chemical equilibrium, as he maintained in his earlier publication. His evidence is that the transition of starch from one form to the other, as determined by swelling power and amount of soluble amylose, depends upon the temperature and yields a continuous curve with a narrow temperature interval.⁶ It may well turn out that this view is correct, but in the present state of our knowledge it really means very little. As Bayliss puts it: "... the temperature coefficient of a process cannot be used to decide whether it is chemical or physical. That of some physical processes is practically identical with that of certain other chemical reactions." And again when discussing enzyme reactions: "When a simple heterogeneous reaction, such as that of dissolving a piece of zinc in sulphuric acid, takes place, its rate depends on how fast the acid molecules diffuse to the zinc, and how fast the zinc sulphate diffuses away. But when the solid phase is in the form of colloidal particles in constant Brownian movement, as in enzymes, diffusion plays a negligible part, because the agent is uniformly present, and the distance which the

¹ T. B. van Itallie, *Bijdrage tot de Kennis der Verstijfeling en Retrogradatie van Zetmeel door Middel van de Röntgenspectrographie* (Dissertation, Amsterdam, 1930; Amsterdam, D. B. Centen's Uitgeversmij. [N.V.], 1930).

² Field, *op. cit.*

³ W. Biedermann, "Stärke, Stärkekörner und Stärkelösungen," *Pflüger's Archiv für die gesamte Physiologie des Menschen und der Tiere*, 1920, CLXXXIII, 168-96.

⁴ J. R. Katz, "Die Ursachen des Altbackenwerdens des Brotes vom physikalisch-chemischen Standpunkt betrachtet," *Zeitschrift für Elektrochemie*, Feb. 15, 1913, XIX, 202-06.

⁵ Alsberg, "Studies upon Starch."

⁶ J. R. Katz and L. M. Rientsma, "Abhandlungen zur physikalischen Chemie der Stärke und der Brotherzeugung. II. Die Stärke-Modifikation mit V-Spektrum (Verkleisterungsspektrum) ist bei höherer Temperatur die Gleichgewichtsform, bei niedriger Temperatur ist es die Modifikation mit B-Spektrum (Retrogradationspektrum)," *Zeitschrift für physikalische Chemie, Abteilung A*, September 1930, CL, 60-66.

substrate molecules have to travel is very short. Here the rate of reaction is controlled by that of the chemical reaction itself. The fact that an enzyme reaction may follow a unimolecular law, or that it has the temperature coefficient of a chemical reaction, throws no light of significance in the mechanism of the process as a whole."¹ The setting and melting of a gelatin or agar gel is, so far as chemical behavior is concerned, no different from that of gelatinized starch. For a given set of conditions, each melts and sets at the same temperature, and a solid gelatin gel in time may even separate out dense bodies suggestive of spheruliths—indeed, Bradford considers them crystalline.

More recently, Katz and Derksen have modified the views of Katz still further to explain why it is that granules of different size gelatinize at different temperatures. They assume a structural factor in the granule (*gewachsene Struktur*). They suggest that the behavior of the individual granule is determined by one variable more than by the ordinary physicochemical phase.² This structural factor may merely be the expression of differences in internal pressure developed as a result of differences in granule size.³

Moreover, as above indicated, there are other possible explanations for the X-ray spectrum changes described by Katz besides the one he adopted, to say nothing of one considered and rejected by him, namely, deformation of the lattice structure which is respon-

sible for the pattern. Katz and Rientsma put it thus: The assumption, for example, that the V-spectrum is merely the consequence of the development of irregularity in the crystal lattice is adequately disproved by the fact that higher temperatures would maintain just this disorder of the lattice. The facts would only then be understandable by means of an auxiliary hypothesis to the effect that this irregularity of the lattice is the consequence of conversion into another modification.⁴

However, treatments which cannot conceivably cause chemical changes in the starch substance do affect the X-ray pattern. Thus mere mechanical injury deprives starch of its power to exhibit an X-ray spectrum.⁵ Furthermore the X-ray pattern of natural starch seems to depend upon the presence of some moisture. Anhydrous starch does not give an X-ray spectrum.⁶ It again shows such a spectrum when moistened. Therefore the change of starch during gelatinization from one form giving a certain X-ray pattern to another giving a different pattern need not necessarily be the result of such a chemical change, as Katz suggests. We may have to do merely with changes in water of hydration or water of crystallization. The different forms of wheat starch conceivably may be merely the same starch associated with different amounts of water.

Another interpretation also suggests itself. We know that starch consists of more than one substance. We know that these have different solubilities. They must therefore disperse at different rates when warmed with water. It is conceivable that in natural native starch granules we get a composite X-ray spectrum of more than one substance, and that at higher temperatures the spectrum is simpler since one starch component has disappeared because dispersed. Certainly Katz's photographs and diagrams of the A- and V-patterns of wheat starch are not inconsistent with these possibilities. There is, in short, as yet not enough experimental basis for a final judgment regarding the changes starch undergoes when it is heated with water and when it ages after it has been heated, or gelatinized in this way. The preponderance of evidence is in favor of the views of Katz, but there is

¹ W. M. Bayliss, *The Colloidal State in Its Medical and Physiological Aspects* (London, Frowde and Hodder & Stoughton, 1923), pp. 58, 79.

² J. R. Katz and J. C. Derksen, "Abhandlungen zur physikalischen Chemie der Stärke und der Brotbereitung. XVI. Wiederverkleisterung des retrogradierten Stärkekleisters (im Zusammenhang mit der Frage der gewachsenen Struktur des Stärkekorns)," *Zeitschrift für physikalische Chemie, Abteilung A*, June 1934, CLXVIII, 334-38.

³ Alsberg, "Studies upon Starch."

⁴ *Op. cit.*, p. 65.

⁵ O. L. Sponsler, "The Structure of the Starch Grain," *American Journal of Botany*, November 1922, IX, 471-92; K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe auf Grund molekular-morphologischer Betrachtungen" (Leipzig, Akademische Verlagsgesellschaft M.B.H., 1930), p. 215.

⁶ Meyer, Hopff and Mark, *op. cit.*; Meyer and Mark, *op. cit.*

enough evidence inconsistent with it to give one pause.

Maquenne applied the term "retrogradation" to the behavior of gelatinized starch whereby it becomes less translucent and may separate under suitable circumstances into a precipitate and a liquid. He, Roux, and other French investigators regarded this phenomenon as peculiar to starch and published many papers upon it. Their observations, however, were by no means new. Many of them had been made as long ago as 1840 by Jacquelin.¹ Maquenne believed that the solid material separated in retrogradation was identical chemically with natural starch, and he described "artificial" starch granules in it, i.e., bodies that looked like very small natural starch grains. He termed the process "retrogradation" because he thought the starch had stepped back, retrograded, from the form in which it is found in solution or in paste into its original condition in the native granule before it was dispersed in water or converted into paste. In the case of wheat starch, at least, Maquenne was wrong, for, as above pointed out, Katz has shown that the X-ray pattern of retrograded wheat starch is not the same as that of natural starch.² As we have seen, there are other differences also between retrograded and natural starch. Retrograded starch is not so easy to disperse as natural starch, and it is more resistant to attack by diastase, the enzyme of malt.

Today the idea of retrogradation seems quite unnecessary;³ all its phenomena may be explained in harmony with the behavior either of supersaturated solutions or of gels. Indeed,

¹ Cf. M. Schoen, "La constitution de l'amidon (Revue critique)," *Bulletin de la Société de chimie biologique*, September-October 1930, XII, 1056.

² According to Katz, potato and some other starches in their natural state possess a B-pattern. Since the X-ray pattern of retrograded starch of all the kinds thus far examined is always a B-pattern, it may well be that there is justification for Maquenne's view in the case of potato starch as well as other starches that in the natural, raw state exhibit the B-pattern.

³ Cf. A. Hesse, "Fermente in der Nahrungsmittel-industrie," in C. Oppenheimer, *Die Fermente und Ihre Wirkungen* (Leipzig, Thieme, 5th edition, 1929), Vol. IV, Part 2, p. 326; Schoen, *op. cit.*

⁴ These are sometimes termed micellae. Cf. Meyer and Mark, *op. cit.*, p. 216.

the introduction of the idea that starch as a colloid behaves differently from other colloids was unfortunate and has caused confusion that is only now being cleared away.

The separation of liquid in the process of retrogradation is probably a special case of syneresis. Syneresis is the well-known phenomenon that many gels or jellies in time "weep" or sweat out fluid, as for example the separation of serum from a blood clot, the separation of whey from milk clotted by rennet, or the formation of "condensation water," so-called, in a gelatin or agar bacterial culture. This elimination of solution from the jelly is probably secondary to changes that take place in the finer physical structure of starch gel. We now turn to consideration of this structure.

The coarser structure of starch paste which is visible with the ordinary powers of the microscope has been described above. But there is also a finer submicroscopic structure which is not thus visible and is not at all well understood. The natural granule consists, as we have seen, of fine crystalline trichites and these in turn consist of bundles of long chains of atoms.⁴ In gelatinization, these chains are probably disarranged, so that they lie every which way instead of parallel as they do in the unaltered granule. Perhaps, too, they become more or less broken into shorter pieces. A "brush-heap" structure is what one would expect to result. This structure might be likened to cordwood piled haphazard. In this form, it occupies a larger volume and the aggregate volume of the spaces between the sticks is far greater than when the same wood is neatly stacked with all sticks tightly packed parallel.

Now a gel with brush-heap structure must strive to undergo that change which tends to reduce the area of the surface which the long chains expose to the surrounding liquid. To explain the reasons therefor would take us too far into the realms of colloid and physical chemistry. They are to be found in any standard text on the phase rule. One of the ways to accomplish this reduction of surface—by no means the only way but the only one we shall consider here—is for the aggregates of chains to come together in larger aggregates

and pack themselves in some orderly fashion. One of the ways for them to do this is to crystallize, for in a crystal the packing of the atoms is the closest possible. In the process, the submicroscopic interstices of the brush-heap structure must, of course, become fewer and larger.

If there is a relatively great amount of liquid as compared with the mass of the crystallizing substance, the interstices become too large to retain the liquid mechanically; it leaks or sweats out and the mass of the gel may shrink: the gel synerizes. If the mass of crystallizing substance is relatively great and the volume of liquid relatively small, all the liquid may still be retained—at least for a very long time, and syneresis does not occur.¹ Hence dilute gels, other things being equal, synerize soon, while very concentrated gels may synerize very slowly or not at all within finite time.² Indeed the structure of dilute gels is ordinarily fundamentally different from that of concentrated gels.³

It follows that in the aging of such a gel as starch paste two phenomena occur which investigators who have written of retrogradation have not always distinguished. One is the primary phenomenon, recrystallization or its equivalent; the other is the secondary phenomenon, syneresis, which, as we have seen, may or may not occur within finite time. The two phenomena need not proceed at the same rate and conditions which accelerate

one need not accelerate the other. Thus Katz states that starch in first-degree gelatinization changes from its X-ray V-pattern to its retrogradation B-pattern in much less time than it takes second-degree gelatinized starch, which has no characteristic X-ray pattern because it is not crystalline, to acquire the B-pattern of retrograded starch.⁴ Indeed, there is no evidence that first-degree gelatinized starch separates out liquid, that is to say, synerizes. The experiments of Meyer⁵ indicate that liquid is not extruded. He found that a gel made by heating 5 per cent of arrowroot starch in water to 138° C. and held at +2° C. for 12 days was white, brittle, comparatively firm, and had not extruded fluid (*Kondenswasser*). More concentrated gels reach this condition in a shorter time. They are transparent at first and then become opaque, and if they have been heated only to the temperature of bread in the oven, viz., 100° C. or less, instead of to 138° C., the temperature Meyer used, their tendency to synerize is less the more concentrated they are.

Though anticipating some of what is to follow, we may now in this summarizing paragraph review those starch properties which appear to play a part in the aging of bread: Starch gelatinized with little water swells somewhat by imbibing water and changes its crystalline nature in a manner demonstrable with the X-ray. This state Katz has named first-degree gelatinization. Starch in this state changes its crystalline form as it ages, again demonstrable with the X-ray. So far as its X-ray pattern is concerned, wheat starch retrograded in this way may be converted again to its condition before retrogradation by heating. Again aged, it retrogrades again and can be rejuvenated again. So long as loss of moisture is prevented, the process may be repeated back and forth many times. There is no evidence that water is set free in retrogradation of first-degree gelatinized starch. It is otherwise with second-degree gelatinized starch, which is starch heated with excess of water. Such starch, if in the form of not too concentrated a paste, separates water irreversibly as it retrogrades. Many kinds of reasonably dilute gels exhibit this phenomenon, which may or may not be irreversible.

¹ The writer does not mean to be understood as taking the position that all gels have a long-chain structure or that all syneresis is due to crystallization. On the contrary, some gels show quite different conditions and also synerize. Indeed, fundamentally, the separation of an emulsion into its component liquids seems to the writer, in essence, the analogue of syneresis.

² W. B. Hardy, "Über den Mechanismus der Erstarrung in umkehrbaren Kolloidsystemen," *Zeitschrift für physikalische Chemie*, May 2, 1900, XXXIII, 326-43; S. Woodruff and L. R. Webber, "A Photomicrographic Study of Gelatinized Wheat Starch," *Journal of Agricultural Research*, June 15, 1933, XLVI, 1099-1108.

³ Hardy, *op. cit.*

⁴ "X-Ray Investigation of Gelatinization and Retrogradation of Starch in Its Importance for Bread Research."

⁵ A. Meyer, "Beiträge zur Kenntnis der Gallerten, besonders der Stärkergallerten," *Kolloidchemische Beihfte*, Aug. 23, 1913, V, 1-48.

It is known as syneresis. It is secondary to retrogradation, i.e., it is the consequence of change in the state of the starch, but not a necessary one, for very concentrated gels do not synerize, at least they do so extremely slowly. Hence, a very concentrated starch gel, as in first-degree gelatinization, synerizes very slowly, if at all, though it may retrograde very rapidly. Its behavior is quite different from that of second-degree retrograded starch investigated by Maquenne, Roux, and others. Retrogradation is affected by temperature. Wheat starch in first-degree gelatinization does not retrograde at a temperature above 60° to 70° C., but retrogrades with increasing velocity as the temperature is lowered below this range. The velocity passes through a maximum at -2° to -3° C. As the temperature is lowered further the rate of retrogradation slows up until at quite low temperature retrogradation ceases altogether.

MANIFESTATIONS OF STALENESS

The word "stale" was probably derived from the root of the Teutonic word meaning "to stand," and was applied to fermented beverages that had stood till they had ac-

quired their full strength and become old and clear. It was rather a term of quality and came to be applied to something altered by keeping, "but when said of bread it is the ordinary opposite of *new*, without necessarily implying inferiority."¹

Staleness in bread is the change in flavor and texture that develops in time. What is called flavor is really the resultant of a number of factors. It is not simply a matter of the reaction of the taste buds, on the back and sides of the tongue and in the throat, to a specific stimulus. Flavor involves not merely the sense of taste but the sense of smell as well. Closing the nose by pinching the nostrils eliminates smell and only taste remains. Under such circumstances or when one has a cold in the head, one is reduced to a state in which food seems to be without flavor, for only sour, saline, sweet, and bitter tastes can be sensed, and onions produce the same sweetish taste that apples do.² The sense of smell is incredibly delicate; the sense of taste, comparatively crude. Since bread is not markedly sour, salty, sweet, or bitter, no doubt a considerable part of its flavor is due to its effect upon smell. Upon just what substances the odor of fresh bread depends and what changes they undergo as staleness develops is quite unknown. Possibly alcohol and other volatile substances³ produced by the yeast fermentation are involved, for fresh bread, despite the heating to which it was subjected in the oven, still contains small amounts of alcohol. If, indeed, flavor is dependent upon volatile substances of this sort, one would expect that, when stale bread is freshened by warming in the oven, the flavor would be improved through the vaporization of the flavoring substances—as indeed it is.

In this connection, it is significant that many bakers believe bread prepared from dough that has been subjected to fermentation for a long time tends to grow stale more slowly than bread made from rapidly fermented dough. Whether this view is justifiable does not seem to have been determined by exact measurements. If it is, it may be that one of the factors involved is flavor. One would expect bread made from a long-fermented dough to contain more alcohol, more volatile acids,

¹ *A New English Dictionary . . .*, edited by J. A. H. Murray, et al. (Oxford, Clarendon Press, 1919), Vol. IX, Part 1, p. 782.

² G. H. Parker, *Smell, Taste, and Allied Senses in the Vertebrates* (Philadelphia, Lippincott, 1922), pp. 173-74.

³ Recently Visser t'Hooft and de Leuw have found acetylmethylcarbinol, $\text{CH}_3 \cdot \text{CO} \cdot \text{HCOH} \cdot \text{CH}_3$ (synonyms: methylacetol, dimethylketol, and dimethylglycolose), in ripe dough and bread. This substance was first identified by C. A. Brown in abnormal cider vinegar and by Pastureau in abnormal wine vinegar. It was identified as a constituent of all cider vinegar by R. W. Balcom ("The Volatile Reducing Substance in Cider Vinegar," *Journal of the American Chemical Society*, February 1917, XXXIX, 309-15). C. B. van Niel, A. J. Kluyver and H. G. Derx ("Über das Butteraroma," *Biochemische Zeitschrift*, 1929, CCX, 234-51) found it and its oxydation product, diacetyl, $\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_3$, in butter and attributed to it a rôle in butter flavor. Acetylmethylcarbinol itself has no aroma, but diacetyl has. The rôle the former plays in bread is as yet uncertain. According to K. Farnsteiner (*Z. Nahr.-Genussm.*, II, 198-209 [1899]; cited by Balcom, *op. cit.*), it is not present in cider or wine but develops in them as they undergo acetous fermentation. It is possible, therefore, that it is not formed in dough by yeast, but by accompanying micro-organisms, as it is, according to van Niel, Kluyver and Derx, in the souring of cream.

and more of the other volatile products of fermentation than short-fermentation bread. These substances would therefore tend to disappear from such bread more slowly than if less of them were present and, in so far as bread flavor depends upon them, one would expect long-fermentation-time bread to retain the flavor of freshness for a longer period than short-fermentation-time bread. However, this is at present a mere speculation; experiments to test its validity still remain to be made.

Sourness is also a factor in the flavor of bread. A long fermentation time tends to produce more acid bread. Perhaps a considerable degree of acidity masks the characteristic flavor of bread to some extent and thereby renders change of flavor with time less noticeable; possibly, acidity in bread directly affects its flavor. Tryller,¹ in his study of adsorption by starch granules, has reported that the potassium and sodium compounds of potato starch possess a flavor reminding one of wheaten flour. The calcium compound has a slightly chalky flavor. It is conceivable, therefore, that if there is much acid in bread this acid may gradually remove some of the potassium and sodium from its combination with the starch of bread and so in time in some degree affect the bread's flavor. It is not impossible also, if Tryller's observations are correct, that the hardness of the water used in doughing may be a factor in flavor. Certainly it is well known that the character of water is important in determining the flavor of malt beverages.

Texture may also affect flavor indirectly. Everyone knows, as bread grows old, that the crumb becomes harder and tougher, more crumbly, and in the course of time hard and brittle. Old and fresh bread chew differently. Ordinarily dry foods are chewed longer and through their dryness stimulate the flow of saliva. Dry bread causes an abundant flow. In saliva, there is a chemical agent, the enzyme ptyalin or salivary amylase, which converts the starch to maltose or malt sugar. This sugar is sweet and so the flavor of a foodstuff

containing starch, if it has to be chewed long, tends to become sweetish.

In short, one may speculate about the nature of the processes that cause the flavor of bread to change as it grows stale, but there is as yet no adequate body of facts on which to build even a hypothesis regarding the processes involved. The changes themselves are known to everyone. They are quite different in the crust and the crumb.

The crust, if it is slightly bitterish, due to caramelization of starch in the oven's heat, remains so. The dry, crisp texture of the crust of fresh bread contributes to the judgment that the bread is fresh, just as the pliable, soft, and leathery crust of stale bread contributes to the opposite judgment. But texture or feel in the mouth is a sensation which many persons do not distinguish from flavor. Moreover, as above suggested, a crisp crust tends to be chewed longer, to cause a more copious flow of saliva, and this in turn tends to give a sweetish taste. The change in flavor of the crumb is more marked than that of the crust, but, as we have seen, the reasons are not understood at all. No doubt, the hardness and toughness of the crumb demand longer and more thorough mastication, but the change in flavor is pronounced before this factor would seem to be of much importance.

The change in texture of the crust is an easily understood phenomenon. In the oven, the crust is desiccated much more than the crumb and thereby acquires greater power to attract moisture. Therefore, as the loaf grows old, the crust attracts moisture from the interior until it is in equilibrium with the crumb. As it approaches this state, it becomes softer, less brittle, and more or less leathery.

The changes in texture of the crumb are more complex. They are not due to drying out. With advancing age, the crumb of course dries out ultimately, but bread becomes stale long before it has lost an appreciable part of its water. The change in texture of crumb really takes place in three stages: first it becomes tougher and harder, next it becomes crumbly, and finally after a much longer time it dries out.

In addition to these changes, the crumb loses some of its power to swell when im-

¹H. Tryller, "Beiträge zur Chemie der Kartoffelstärkefabrikation," *Chemiker-Zeitung*, Nov. 6, 1920, XLIV, 833-34; Nov. 11, 1920, 845-47.

mersed in water; it swells less than when fresh.¹ At the same time, its soluble-starch content decreases.² These changes occur in rye as well as in wheaten bread. They do not, according to Katz,³ occur in baked products of low-moisture content, like zwieback, Swedish bread, and mazoth. To the change in texture of crumb, its toughening and hardening and their causes, the remainder of this study is devoted.

HISTORY OF BREAD-STALING THEORIES

Until 1852, it was generally believed that the growing stale of bread was due to drying out. In that year Boussingault⁴ demonstrated by chemical analysis that bread turns stale long before it has lost any appreciable amount of moisture. He showed that it turns stale in

¹ K. B. Lehmann, "Hygienische Studien über Mehl- und Brot. Theil V: Beiträge zur physikalischen Beschaffenheit des Brotes," *Archiv für Hygiene*, 1894, XXI, 213-67.

² L. Lindet, "Sur les états que présente l'amidon dans le pain tendre et dans le pain rassis," *Bulletin de la Société chimique de Paris*, May 23, 1902, Série III, XXVII, 634-39.

³ J. R. Katz, "Gelatinization and Retrogradation of Starch in the Bread Staling Process," in *A Comprehensive Survey of Starch Chemistry*, compiled and edited by R. P. Walton (New York, Chemical Catalog Company, 1928), Vol. I, Part 1, p. 103.

⁴ Boussingault, "De la transformation du pain tendre en pain rassis," in his *Agronomie, Chimie agricole, et Physiologie* (Paris, Gauthier-Villars, 2d edition, 1874), V, 416-17.

⁵ E. von Bibra, *Getreidearten und das Brot* (Nürnberg, 1861), p. 490.

⁶ In this connection, it is perhaps significant that native wheat-starch granules when fully hydrated contain about 30 per cent (according to Rodewald, 36 per cent) of water of hydration. Such water is of course less easily set free by warming than water not thus combined. Bread may range in water content from about 34 per cent for fine wheaten rolls to about 42 per cent for graham bread and 49 per cent for whole coarse rye bread. Cf. Alsberg, "Starch and Flour Quality."

⁷ Cf. also A. Maurizio, *Getreidenahrung im Wandel der Zeiten* (Zurich, Orell Füssli, 1916), p. 215; cited in A. Maurizio, *Die Nahrungsmittel aus Getreide* (Berlin, Parey, 2d edition, 1924), I, 368.

⁸ Cited by von Bibra, *op. cit.*, p. 411.

⁹ *Op. cit.*

¹⁰ *Op. cit.*

¹¹ E. N. Horsford, "Report on Vienna Bread," in *Reports of the Commissioners of the United States to the International Exhibition Held at Vienna, 1873*, edited by R. H. Thurston (Washington, Government Printing Office, 1876), Vol. II, B, pp. 1-122, especially pp. 92, 96.

an atmosphere saturated with water vapor in which, obviously, it cannot lose moisture. Housewives, of course, had known from time immemorial that stale bread could be freshened by warming. Boussingault showed that this took place at 50° to 60° C. and could be repeated indefinitely. He heated stale bread in a tight vessel till fresh, then allowed it to cool and grow stale again, and found that under these conditions, which prevented drying out, the cycle could be repeated many times. He advanced the hypothesis that stale bread is not different from fresh because it contains less water, but rather because of a change in the peculiar molecular state of its substance that begins when it cools and continues to develop more and more with time so long as the temperature does not rise above a certain level.

Von Bibra reached a similar view and extended his observations to rye bread.⁵ Others later did the same for barley bread. In addition, von Bibra showed that bread can no longer be freshened by warming if its moisture content has dropped to 30 per cent or less,⁶ but that bread as dry as this could be freshened if it was moistened before it was warmed up.⁷

It is an old belief of practical bakers that a long dough-fermentation period leads to bread that keeps fresh well. Graeger⁸ tested this notion and reached the conclusion that extension of the fermentation time beyond three hours at 25° C. did not lead to bread of better keeping quality even though longer fermentation increases the acidity of the dough. Perhaps, as pointed out above, a long fermentation has favorable effects on the keeping quality of bread, because of its effects upon flavor rather than texture.

Neither Boussingault⁹ nor von Bibra¹⁰ endeavored to analyze the process in detail. Von Bibra contented himself with the view that in warm bread the starch, nitrogenous substance, and water are combined in a peculiar molecular condition which is gradually changed on cooling and can be restored by warming.

Horsford¹¹ was apparently the first to suggest that the growing stale of bread is due to a change in distribution of water between

starch and gluten and that the change of texture is the result of change in the condition of the starch. Most hypotheses advanced since his time have been based upon such assumptions. "The gluten, which is mixed with it [the starch] in the crumb of bread, and which may be conceived to be continuous, however thin throughout the wall of the cell, has been, by the process of baking, dehydrated; that is, the heat to which it has been subjected has driven out a certain amount of water, which chemically sustains something like the same relation to the gluten from which it has been expelled that the water expelled by heat from alum-crystals sustains to the original body of alum. This is the condition of the gluten from the crumb in the interior of the loaf at the instant of its removal from the oven. On drying, it abstracts water from the starch with which it is coated, or intimately mixed, as the roasted alum absorbs the water that is sprinkled upon it. The starch by this process being dried and stiffened, gives its support to the wall of the cell, and renders the texture of the stale loaf more firm than that of the fresh loaf. . . . The gluten of the crumb-walls of stale bread which are stiff and brittle is dehydrated by the heat in freshening, and the water of hydration driven out softens the glacial, horny starch which coats and penetrates the gluten. Thus softened, the crumb is more palatable, because it is in condition to be dissolved by the saliva, and tasted. On cooling, the water is withdrawn from the starch, which is thereby rendered stiff, and restored to the gluten, and the bread becomes stale."

Lehmann¹ compared the imbibing power of fresh and of stale bread. He found that pieces of crumb shrink in drying, the shrinkage stopping in four days—much earlier than the water loss. Shrinkage and water loss are most rapid the first day. In shrinking, the pores contract but the pore space increases somewhat nevertheless because new pores, previ-

ously filled with water, are formed. If liquid is filtered through a slice of crumb, it flows through fresh bread more rapidly than through stale. However, stale bread sucks up liquid by capillarity more readily than fresh bread. Pieces of stale crumb placed in water imbibe it about as rapidly during the first few minutes as fresh bread. After ten minutes, stale bread drops behind fresh and reaches its maximum in half an hour, whereas fresh bread continues to imbibe for some time. In one of his experiments, fresh wheat bread imbibed 289 per cent, whereas stale imbibed only 153 per cent. Pieces of stale crumb keep their shape for weeks when stored under water, whereas fresh bread disintegrates. Pieces of fresh crumb may swell by imbibition as much as 16 per cent, but stale bread only 6 per cent. Crumb merely stale and crumb air-dry with only 12 per cent of moisture behave in the same way. When the imbibition experiments were made in water heated to 40° to 60° C., the stale crumb imbibed almost as much as fresh. Warming up stale bread restores its imbibition capacity. Lehmann did not offer a new hypothesis. He was content with the hypothesis of Boussingault and von Bibra, that water is held in different ways in fresh and stale bread. He believed that a substance is formed in stale bread, by unknown molecular processes, which swells with difficulty in cold water, but may be transformed by heat into the form in which it swells in water and occurs in fresh bread.

Boutroux² distinguished two stages in the process. During the first, the bread cools off to the temperature of the environment; during the second, it continues to grow stale if the temperature is not changed. Although the loss of water is at first but slight, this loss has nevertheless great significance. Boutroux assumed that during baking the crust reaches a temperature of about 300° C. The air of the oven is hotter than the crumb; therefore some of the water of the crust is driven into the interior of the bread and the crumb does not give off water to the air through the crust. If baking lasts some time, then the loss of water from the inside of the loaf is only attributable to the increase in thickness of the crust. This is the reason why, Boutroux asserts, Balland³

¹ *Op. cit.*

² L. Boutroux, *Le pain et la panification* (Paris, Baillière, 1897).

³ Cited by Boutroux, *op. cit.* Katz. (*Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers*, Part 1, p. 9) takes the same position. He was unable with certainty to establish a loss of water from the crumb during baking. The crust protects it.

and others found just as much water in fully baked crumb as in dough ready for the oven.

After removal of the loaf from the oven, the crust cools off first and soon is warmer than the air, but cooler than the crumb, a condition which is the opposite of that which obtains in the oven. The crust then gives off a little moisture to the surrounding air while surplus water of the crumb is condensed in the crust and held there. This redistribution of the water of the loaf may take place without much loss of moisture and yet profoundly affect the texture of the crumb. The crust is softened by the water that wanders to it from the crumb. The crumb becomes harder because of loss of water to the crust. When stale bread is returned to the oven, the process is reversed and the crust returns again to the crumb most of the water it had absorbed from the crumb.

Boutroux made one other assumption: it is that bread contains a supersaturated solution of amyloextrin formed from starch. Amyloextrin is a substance separated by Lintner and Düll¹ from among the products of the digestion of starch by malt diastase. It is freely soluble in hot but not in cold water and readily forms supersaturated solutions. Boutroux assumed, without experimental evidence, that such a supersaturated solution exists in bread, that on cooling amyloextrin separates as a solid, and that it is this separation that gives stale bread its texture. However, no one has actually found amyloextrin in bread crumb. Nevertheless, Boutroux seems to have been the first to assume that staleness is due to the separation in insoluble form of a derivative of starch, even though he was mistaken in the character of this derivative. This assumption in one form or another has constituted the center of most hypotheses since.

¹ C. J. Lintner and G. Düll, "Ueber den Abbau der Stärke unter dem Einflusse der Diastasewirkung," *Berichte der Deutschen chemischen Gesellschaft*, October 1893, XXVI, 2533-47.

² *Op. cit.*

³ The soluble starch found in fresh bread is β -amylose (see above)—not the soluble starch so-called obtained by partial decomposition of natural starch with acid or other powerful reagent.

⁴ E. Roux, "Sur l'état de l'amidon dans le pain rassis," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, May 30, 1904, CXXXVIII, 1356-58.

Lindet² confirmed some of the observations of Boutroux and introduced the idea that the growing stale of bread is due to retrogradation of the starch, i.e., its conversion into a less soluble form with the setting free of moisture. He found, however, that it was soluble starch³ rather than amyloextrin, as Boutroux assumed, that is formed under the influence of the heat of the oven. He noted that with time the amount of soluble starch in crumb decreases and it is this that he termed "retrogradation." He published data on only three experiments and among these there was only one adequate control, the determination of soluble starch in bread an hour old. It is only in this single analysis (whether done in duplicate is not stated) that a large difference in soluble starch content between fresh and stale bread is shown. In another experiment, the difference between 8-hour-old and 48-hour-old bread was 2.5 per cent; and in the third, there was no significant difference at all. The methods used were not given.

But, according to Lindet, this is not the whole story: change in the gelatinized starch is also involved. By a method which is obviously only roughly quantitative, he estimated the water absorbed by a gram of starch in bread of different ages. From his results, he drew the conclusion that with age the gelatinized starch granule imbibes less and less water. It retains six times its volume of water when the bread is warm; when it becomes stale, it imbibes two times less. He assumed that the starch contracts and becomes horny (*raccorni*) with time because it becomes less permeable.

Roux⁴ believed that in retrogradation some starch is converted into starch cellulose (amylocellulose), which is insoluble and therefore alters the texture of starch pastes. Roux examined bread to learn whether the starch of bread retrogrades in this way with age. He found it retrogrades but slightly. In fresh bread, there is no so-called amylocellulose, whereas it can be detected qualitatively after a few hours and it increases in time. Roux reached no positive conclusions and his approach is no longer significant, for views regarding retrogradation and amylocellulose have changed. It is doubtful that there is any

such substance as amylocellulose in wheat starch at all.

In 1912, J. R. Katz¹ and also E. Verschaffelt² made reports to the Dutch Foodstuff Congress meeting in Rotterdam on the stale-bread problem, for this had become a critical question in Holland in connection with the night work of bakers. In 1913, Katz³ presented evidence that there is a physico-chemical equilibrium in crumb such that at higher temperatures (50° to 100° C.) fresh bread is the stable form, whereas at room temperature (0° to 25° C.) stale bread is the labile, unstable form. Crumb stored without moisture loss at room temperature becomes stale within 24 hours, whereas, if stored at 60° to 70° C., it remains entirely fresh and does not change in taste or odor. The equilibrium is shifted with the

¹ "Rapport voor de Voedingsmiddelconferentie te Rotterdam in 1912," published in *Chemisch Weekblad* and *Pharmaceutisch Weekblad*, June 4, 1912; cited in Katz, *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers*, Part 2, p. 3.

² "Rapport uitgebracht op de Voedingsmiddelconferentie te Rotterdam Juli 1912," published in *Chemisch Weekblad* and *Pharmaceutisch Weekblad*, December 1912; cited in Katz, *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers*, Part 2, p. 15.

³ J. R. Katz, "Über die Analogie zwischen Quellen und Mischen, eine Experimentaluntersuchung über die Gesetz der Quellung im Wasser," *Zeitschrift für Elektrochemie*, Sept. 15, 1911, XVII, 800-805; "Die Ursachen des Altbackenwerdens des Brotes vom physikalisch-chemischen Standpunkte betrachtet"; "Die Ursache des Altbackenwerdens der Brotkruste und die Möglichkeit, diese Veränderung zu verhüten," *ibid.*, Sept. 1, 1913, XIX 663-67.

⁴ "Gelatinization and Retrogradation of Starch in the Bread Staling Process"; *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers*; "Über das Altbackenwerden des Brotes und die Möglichkeit, diese Veränderung hintanzuhalten," *Zeitschrift für das gesamte Getreide-Mühlen- und Bäckereiwesen*, March 1934, XXI, 63-68.

⁵ Katz, "Gelatinization and Retrogradation of Starch in the Bread Staling Process," p. 102. In an investigation as yet unpublished, M. Lopin found at the Food Research Institute that the method is improved if 25 per cent alcohol be used instead of water. Sedimentation occurs much more rapidly and readings are sharper. Whether the method in this modification is as delicate as in the form introduced by Katz was not studied. Incidentally, it may be stated that, whether water or weak alcohol be used, the uppermost layer of the sediment consists mainly of starch and differs in gross appearance with the age of the bread.

⁶ Katz, "Gelatinization and Retrogradation of Starch in the Bread Staling Process," p. 102.

temperature. The rate of growing stale is accelerated as the temperature drops and passes through a maximum at -2° to -3° C. As the temperature is lowered further, bread goes stale less and less rapidly, and at very low temperatures, as at the temperature of liquid air, it remains fresh indefinitely.

Katz⁴ followed the rate of growing stale by the following three methods:

1. By testing crumbliness and hardness with the finger.

2. By changes in the swelling power based on the observations of Balland, Lindet, Lehmann, and others that stale crumb swells less in water than fresh. "Ten grams of bread crumb together with an excess of water are passed through fine bolting cloth (80 mesh per cm.). The volume of the liquid (which is saturated with toluene in order to prevent fermentation) is raised to 250 c.cm. and the mixture allowed to settle in a graduated glass of 250 c.cm. capacity. After 24 hours the volume of the decantate or deposit is read off. Upon shaking again, another 24 hours is allowed for settling, a second reading made and the mean of the two readings taken. The volume of the decantate is shown to be considerably larger for fresh bread than for stale bread, for instance, 52 c.cm. compared with 34 c.cm. The volume of decantate is obviously a suitable criterion for determination of the swelling power."⁵

3. "The quantity of soluble amylose, which may be extracted from bread is larger for fresh bread than for stale bread . . . This quantity of soluble amylose, extractable from bread, is a function of the degree of comminution of the bread. Hence, it is necessary to work always under the same conditions and then readily comparable figures may be obtained. In practice the determination was so carried out that the clear liquid above the decantate, in the determination of swelling power, was poured off, filtered clear, evaporated to a small volume and precipitated with excess alcohol, the resulting precipitate being collected in a tared filter and dried and weighed."⁶

According to Katz, the second method is the most satisfactory for all-round purposes. Hardness, swelling, and quantity of soluble

starch may be measured with sufficient accuracy; crumbliness cannot. The rate at which staleness proceeds can be determined accurately.¹ In Dutch bread, hardness, swelling power, and quantity of soluble starch nearly reach the values found in fully stale bread within 9 to 10 hours, whereas crumbliness is definitely present only after 24 hours.

The microscopic appearance of fresh and stale bread, according to Katz, explains this lag in the onset of crumbliness, as is shown by the investigations of Verschaffelt and van Teutem² made at the instigation of Katz. In fresh-bread crumb, each starch granule is completely surrounded by gluten, and this gluten capsule fits the granule as closely as a glove. No soluble starch is found outside the granules. In stale bread, no precipitates are formed anywhere, but the outlines of the granules become sharper because of the development of fine air channels between the starch granules and the gluten matrix which surrounds them. For the larger granules, the width of the air spaces is from about one-twentieth to one-tenth the diameter of the granules; and this is true for bread that has not suffered loss of moisture. The appearance is such as one would expect if, by shrinkage of starch and gluten, these elements of the crumb had become separated from one another.

These observations are in entire harmony

¹ J. R. Katz, "De snelheid van het oudbakken worden van brood." (Akademie van Wetenschappen te Amsterdam, Verslag, 1914, deel 23, p. 652-655); cited by Walton, *op. cit.*, Part 2, p. 77; "Das Altbakkenwerden der Brotkrume vom physiologisch-chemischen Standpunkte betrachtet. I," Hoppe-Seyler's *Zeitschrift für physiologische Chemie*, Oct. 19, 1915, XCV, 104-29; II, *ibid.*, pp. 136-46; III, *ibid.*, pp. 147-51.

² E. Verschaffelt and E. van Teutem, "Die Änderung der mikroskopischen Struktur des Brotes beim Altbakkenwerden," *Zeitschrift für physiologische Chemie*, October 1915, XCV, 130-35.

³ K. Mohs, *Mehlchemie, Neue Erkenntnisse auf dem Gebiete der Müllerei und Bäckerei* (Dresden and Leipzig, Steinkopff, 3d edition, 1931).

⁴ *Op. cit.*

⁵ J. R. Katz, "Het oudbakken worden is een verandering die niet enkel bij tarwe- en roggenzetmeel voorkomt doch bij alle zetmeelsoorten, maar die toevallig alleen bij tarwe en rogge tot practisch belangrijke resultaten voert." (Akademie van Wetenschappen te Amsterdam, Verslag, 1914, deel 23, p. 655-658); cited by Walton, *op. cit.*, Part 2, p. 77.

with the well-known phenomenon that a loaf of bread shrinks as it ages,³ and with the observation of Lehmann⁴ that, though the pores of fresh bread shrink, new pores are formed by shrinkage of the bread mass, so that the sum total of the volume of the pores of stale bread is moderately increased.

Verschaffelt and van Teutem reported, moreover, that bread which is about nine hours old and therefore, according to Katz, no more crumbly than fresh bread, though in respect to its other properties stale, has the microscopic appearance of fresh bread. The development of the air spaces apparently parallels the development of crumbliness and not the development of the other characters of stale bread, viz., the development of hardness, loss of swelling power, and reduction of soluble amylose content. According to Katz, this disparity depends upon the time required for water to diffuse from the starch to the gluten.

Verschaffelt and van Teutem found that the outlines of the starch granules in stale bread had become not merely sharper, but also somewhat crenulated (*zackig*) and irregular. Moreover, they believe that in fresh bread the granules of starch are under strain. If a thin lamella of fresh-bread crumb be placed in a little water on a microscope slide, covered with a cover glass, and pressure immediately exerted on the cover glass, some granules near the thin edge of the lamella may be observed to free themselves with a jerk, provided examination be made at once after putting in the water. From stale bread, they are not freed with a jerk.

Katz found that an excess of water inhibits the aging of bread. Fresh bread suspended in water with a disinfectant to prevent fermentation and putrefaction retains the swelling power of fresh bread, and stale bread similarly stored does not change its swelling power.

Katz holds the view that the changes starch undergoes in bread with age are the same all starches undergo when they are gelatinized with the same amount of water as in bread.⁵ In bread, starch is in first-degree gelatinization (see above). He therefore concludes that the growing stale of bread is the expression of the change in the starch. This change he

identifies with retrogradation. It is accompanied by some redistribution of water. Retrograded starch holds water less firmly and in consequence moisture wanders from the retrograded starch to the crust and to the other components of the crumb, principally the gluten. This change in the starch is a physico-chemical reaction with an equilibrium characteristic of such reactions and obeying physico-chemical laws. In the process of retrogradation, the starch granules shrink away from the gluten so that microscopic fissures are produced between many of the starch granules and the gluten network. When bread is freshened by warming, the process of retrogradation is reversed and moisture wanders back into the starch granules whereby they are softened. Stale bread is hard and tough, because retrograded starch is harder and tougher than starch freshly gelatinized to the first degree.

Katz holds the opinion, moreover, that the changes in swelling power of gelatinized starch and the lessening of soluble starch in it are quite unrelated processes, for he has found that they proceed at quite unrelated rates in bread to which aldehyde had been added. He believes they are to be explained as retrogradation (see above).

Ostwald,¹ while agreeing with Katz that it is change in the starch that causes bread to grow stale, rejected Katz's hypothesis that this change is retrogradation. He interpreted the phenomenon as follows: The baking of bread depends upon the formation of starch gel of a definite structure; its growing stale

is an internal change of state of this starch gel which consists of a lessening of its degree of dispersion and dehydration, with resulting extrusion of liquid, or syneresis (see second section). The syneresis of aging bread is plainly to be observed when it is protected in a tin can from evaporation. According to Ostwald, after one or two days the bread feels damp, although no moisture from without has access to it. In fact, the dampness is derived from the interior of the bread; the aging starch gel is no longer able to hold as much water. Water is set free from it by syneresis and brought to the surface. By warming for a short time—exactly as with a synerizing gelatin jelly—water is again taken up by the starch gel, at least in part, and thereby the former state is again restored.

This view of the processes that go on in bread when it grows stale, viz., that they depend upon syneresis, is accepted, at least in part, by a number of other investigators, for example Whympster,² while some investigators hold some of the views of Katz combined with the idea of Ostwald.

Since the publication of his large monograph in 1917,³ Katz has modified his views to harmonize them with his own observations by means of the X-ray and those of others. These findings, in so far as they are pertinent to the present inquiry, have been described in the preceding section. His present view seems to be essentially identical with that he formerly held, except with regard to the nature of the change in the starch.⁴ Bread, he finds, shows the same changes in X-ray pattern as starch, and in bread these changes run parallel with the change in swelling power and amylose content of the crumb. His views on the shift of moisture within the crumb apparently remain unchanged, but he no longer regards the process of retrogradation as involving a simple homogeneous equilibrium reaction. He now tends to the view that the process is much more complex and involves a heterogeneous equilibrium. At the same time, he has introduced a new nonchemical factor, the structure of the starch granule itself. The significance of this interpretation of the known facts has been discussed in the preceding section.

¹ W. Ostwald, *Die Welt der vernachlässigten Dimensionen* (Dresden and Leipzig, Steinkopff, 1915).

² R. Whympster, *The Conditions That Govern Staleness in Bread* (reprinted from the *British Baker*), 1919; "Colloid Problems in Bread-Making," in "Colloid Chemistry and Its General and Industrial Applications, Third Report of the Committee . . .," *British Association for the Advancement of Science, Report of the Eighty-eighth Meeting, Cardiff—1920, August 24–28* (London, Murray, 1920), Appendix, pp. 61–74.

³ *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers*.

⁴ J. R. Katz, "Abhandlungen zur physikalischen Chemie der Stärke und der Brotbereitung. I. Über die Änderungen im Röntgenspektrum der Stärke beim Backen und beim Altbackenwerden des Brotes," *Zeitschrift für physikalische Chemie, Abteilung A*, September, 1930, CL, 37–59.

CRITIQUE OF COMPETING HYPOTHESES

We see then that all the hypotheses hitherto advanced in so far as they are more specific than that of Boussingault and von Bibra make staleness depend upon a shift in moisture from one element of the crumb to another. Horsford was the first to advance this idea. He assumed that as the loaf cooled the gluten gave off moisture to the starch, a process that was reversed when stale bread was freshened by warming. Apparently, according to his hypothesis, these two ingredients are assumed to share more or less equally in the process of growing stale. For Horsford, the whole question was apparently merely a matter of a shift in the relation of the vapor pressure of the gluten gel to that of the starch gel with the temperature, although he does not use the term vapor pressure. At higher temperatures, the vapor pressure of gluten gel was, he assumed, greater than that of starch gel and, therefore, water vapor shifted from the gluten to the starch, making the starch softer and more elastic, which expressed itself in the characteristics of fresh bread. At lower temperatures, the reverse obtains. Unfortunately, Horsford's experiments in support of his hypothesis were neither appropriate nor significant, for he took no account of the fact that during baking gluten is coagulated and loses much of its capacity to absorb water.

French investigators, notably Lindet and Roux, went a step further and assumed that it was the starch primarily that, by retrograding, set free water which wandered to the other components of the loaf. They reasoned by analogy from the behavior of starch pastes and solution which on aging in fact separate moisture. It is of course impossible to demonstrate this phenomenon in bread. But bread and the starch pastes or solutions with which French investigators studied retrogradations are not comparable. Their pastes were comparatively rich in water so that the starch in them was in a state of second-degree gelatinization and not in first-degree, as Katz has found it to be in bread. The solutions they studied were prepared by heating a suspension of starch in water under pressure at 138° C. or over, temperatures never approached in the

interior of loaves in the oven. Now, as we have seen, starch in first-degree gelatinization does not extrude water within a period so brief as that required for bread to grow stale, though it may retrograde in that it becomes more opaque and more firm, and changes its X-ray pattern (Katz). It seems reasonably certain, therefore, that if there is a shift of moisture from starch to gluten it cannot be due to extrusion of liquid water as in retrogradation of starch under the conditions employed by French investigators.

However, there might nevertheless be a shift in moisture from starch to gluten as the loaf ages without the physical transfer of fluid water. This transfer might be in the form of water vapor. But in order that this may happen, the vapor pressure of the starch must change relative to that of the gluten. We are justified in assuming that the vapor pressure of the gluten remains constant and practically that of water, for the gluten, having been coagulated, has lost most of its great imbibing power for water. The vapor pressure of starch in first-degree gelatinization is not known, but it is probably not greater than that of water. If it were, the vapor pressure of bread would be greater than that of water, for starch composes over four-fifths of the solid matter of bread. As a matter of fact, Katz¹ and recently Platt² have shown that the vapor pressure of crumb is the same as that of water. A transfer of water vapor from starch to gluten is therefore improbable. There is no good basis for the assumption of French investigators that, in the aging of crumb, starch loses water to the gluten.

The French investigators, however, discovered one piece of evidence which is not analogy, the fact that the amount of soluble starch which can be extracted from crumb grows less as bread grows stale, a fact abundantly confirmed by Katz, Whympier, and others. The significance of this phenomenon has already been discussed, but merits some further consideration.

Field³ and the writer⁴ have found that

¹ "De snelheid van het oudbakken worden van brood."

² W. Platt, "Staling of Bread," *Cereal Chemistry*, January 1930, VII, 1-34.

³ *Op. cit.*

⁴ Unpublished observations.

starches thoroughly dry-ground in a pebble mill and then suspended in water and centrifuged, or filtered, yield quite concentrated solutions of β -amylose. On standing, these solutions flocculate till ultimately, after days, an equilibrium is reached such that the liquid contains a certain amount (0.5 to 0.9 per cent usually) of β -amylose in solution. When this point is reached, no further precipitation occurs. We have to deal in this case with complex colloid phenomena which are as yet little understood since they do not seem to obey the phase rule. Such a phenomenon has been studied in the writer's laboratory by Straup,¹ who found that, when isoelectric gelatin was dissolved in warm water, cooled, and allowed to stand for many days till an equilibrium was established, the amount of gelatin contained in the liquid was a function both of the temperature at which the equilibrium was reached and also of the total mass of gelatin present. Moreover, at different temperatures the gelatins remaining in solution had different solubilities. It is possible by holding at any desired number of temperatures to obtain an equal number of fractions with as many different solubilities. The writer has some unpublished evidence that starch behaves somewhat similarly. The observation of Katz² that the proportion of starch extracted from bread is about the same whether the amount of water is great or little points in the same direction. The indications therefore seem to be that the changes in extractable amylose in bread depend upon complex phenomena which it is premature to interpret.

¹ D. Straup, "The Flocculation of Gelatin at the Isoelectric Point," *Journal of General Physiology*, May 20, 1931, XIV, 643-60.

² J. R. Katz, "Abhandlungen zur physikalischen Chemie der Stärke und der Brotbereitung. XX. Über den Zusammenhang der Änderung der Stärke beim Altbackenwerden des Brotes und beim Retrogradieren von Stärkekleister," *Zeitschrift für physikalische Chemie*, Abteilung A, August 1934, CLXIX, 321-38.

³ J. R. Katz and J. C. Derksen, "Abhandlungen zur physikalischen Chemie der Stärke und der Brotbereitung. XIV. Ist die Stärke im Stärkekleister kristallinisch oder amorph?" *Zeitschrift für physikalische Chemie*, Abteilung A, November 1933, CLXVII, 129-36; J. C. Derksen and J. R. Katz, "Roentgenspektrographische Beobachtungen über das Gelatinieren von Stärkesolen," *Recueil des Travaux Chimiques des Pays-Bas*, 1932, LI, 523-26.

Ostwald's view that the change in the starch is not retrogradation but syneresis is open to the objection already stated, that a gel as concentrated as first-degree gelatinized starch does not extrude water. His view has, however, the merit that he does not regard starch as innately different from other gels. He seems to take the position that the starch gel hardens when it is cooled and extrudes moisture like most other gels. He does not hold that an ordinary chemical reaction is involved which obeys the mass law and in theory should be slowed or speeded up by a suitable catalyst. He seems to hold it to be a common colloid-chemical phenomenon. Ostwald apparently does not consider where the moisture goes that he alleges is synerized, and in his hypothesis this is not a matter of moment.

Katz's contributions to the subject—and they are of fundamental importance—are the proof that the changes of starch in bread as it ages closely parallel those in paste, and the proof that there is the same profound change in the starch as shown by the X-ray diagram in both cases. It can now be regarded as definitely established that the starch is principally responsible for the change in crumb which is commonly called staleness. Prior to his investigations, this was far from certain. The facts on which he bases this conclusion cannot be questioned. His interpretation of his facts is that the change involves a physico-chemical reaction with heterogeneous equilibrium. As pointed out in a preceding section, this interpretation may be correct but it has not been proved. Some of his more recent X-ray studies³ have led him to the conclusion that gelatinized starch (two parts water, one part starch) is amorphous when warm and partly crystallizes when cooled. He finds that a solution of commercial soluble starch gelatinizes because on cooling it crystallizes out into tiny crystals which are felted together (*verfilzt*). Certainly mere crystallization is not, in the ordinary meaning of the term, a chemical reaction. He further concludes that one of the consequences of the changes in the starch is that it gives off moisture to the gluten. This, as has been pointed out already, is at least unproved. Moisture might wander from the starch to the gluten either as liquid

extruded by the retrograding granules or as vapor. It is unlikely that it wanders in the form of liquid, since very concentrated gels extrude water either very slowly or not at all. If it wanders as vapor, it must be to some other crumb component with a lower vapor tension than that of first-degree gelatinized starch. Certainly gluten is not such a substance. Alsberg and Griffing¹ have shown that the swelling capacity of coagulated gluten, and hence its avidity for moisture, is slight. There remains the liquid held by neither starch nor gluten in which salts, sugar, etc., are dissolved, and it is indeed possible that this very concentrated solution may take up moisture from both the starch and the gluten as the bread ages. It is not likely, however, that the effect is great—otherwise bread would not have the same vapor tension as water.

But it is not at all necessary to assume that there is a shift in moisture. It is possible without in the least questioning the important findings of Katz to interpret them somewhat differently. We may then regard the growing stale of bread as taking the following course. In the oven, the gluten is coagulated and loses most of its power to hold water. The starch granules become incompletely gelatinized, taking up what water they can from their surroundings. A part of this water is derived from the coagulating gluten which is no longer able to hold all it held in the dough because it is coagulated. As the bread leaves the oven, the moisture is distributed through the loaf in the following manner: some is in the form of vapor filling the pores of the crumb; some is still in the gluten; some is serving as a solvent for salts, sugar, etc., in the crumb solution; some is imbibed in the partially gelatinized starch. In this state the starch is soft and the gluten tender. As the bread cools, the soft starch jelly sets and becomes a stiff but still elastic gel which contains less water than is necessary for complete gelatinization. In the process of setting and for some time afterward, the starch gel shrinks a little as it cools, a phenomenon very common in the setting and aging of warm gels whether or not they syne-

rize. Perhaps the gluten too shrinks and becomes harder, because it is losing moisture to either the starch or the crumb solution, or both. Thus strains are set up at the surfaces where the gluten and starch meet, which ultimately cause them to separate. The bread then becomes crumbly. Before this stage is reached, the starch begins to retrograde. The granules become opaquer, whiter, harder, and firmer, and the bread is stale.

While all this is going on, the loaf as a whole has been losing some moisture. The crust which is drier than the crumb competes with the starch of the crumb for the moisture of the loaf. It extracts some water from the crumb on its inner surface and loses some water to the atmosphere on its outer surface. And thus the loaf ultimately dries out in addition to growing stale. When the bread is freshened by warming, the starch gel becomes soft again and increases a little in volume—possibly takes up a little water from the gluten and the bread becomes fresh, for the starch is no longer hard and tough.

This interpretation of the facts thus far established has the advantages over others that have been suggested in the following respects. It makes no assumptions regarding the chemical nature of the change in the starch. It does not assume that starch gel has properties not found in many other colloid gels. It is not inconsistent with the known facts of retrogradation—a phenomenon that has its counterpart in gels other than those of starch.

Whether the starch of aging bread merely undergoes the colloid-chemical changes characteristic of many other gels that set when cooled and soften when warmed, or whether it undergoes some chemical change, as Katz supposes and as do those who write of retrogradation, is not an academic but a very practical question. If we have to deal with a chemical reaction involving an equilibrium, then it should be possible in theory to find a substance, a catalyst, that is able to shift this equilibrium in such a manner that the equilibrium is the same at room temperature as at 55° C. Then bread would not go stale under ordinary conditions of storage. On the contrary, if the change in the starch is a purely

¹ C. L. Alsberg and E. P. Griffing, "The Heat Coagulation of Gluten," *Cereal Chemistry*, November 1927, IV, 411-23.

colloidal phenomenon and therefore not involving any chemical reaction in the strict sense of the word, then it is idle to search for a catalyst to delay the onset of staleness. This process in that event could be slowed or inhibited only by means which inhibit colloidal changes, and the search for a method to produce stale-proof bread would have to follow quite different paths.

PROLONGING THE LIFE OF BREAD

While the analysis of the known phenomena presented in the foregoing sections clearly shows that there is still much to learn regarding the mechanism responsible for the changes in bread as it ages, the known facts indicate that the commercial life of bread may be prolonged either by special methods of handling and storing after the bread has left the oven, or by methods of manufacture which produce a loaf of inherently long life. Let us now consider each of these groups of methods separately, but before doing so let us first consider the methods by which the degree of staleness may be measured with some exactness.

These methods as developed and refined by Katz have been described in the section on the "Structure and Behavior of Starch Grains":

1. The estimation of crumbliness or compressibility of crumb by some sort of mechanical testing instrument.

2. The quantitative estimation of the soluble starch in crumb.

3. The observation under standard conditions of the sedimentation volume of crumb pulped in water.

For the estimation of compressibility, satisfactory devices have been invented by a number of students,¹ but they do not seem as yet to have been employed extensively.

The quantitative estimation of soluble starch in crumb is difficult and time consuming. The objections to it have already been discussed. The soluble-starch content does

not exactly run parallel with the changes in the starch granules.

The sedimentation test is the one most used. Undoubtedly the results obtained with it give a good index to the condition of the bread. Unfortunately, as Katz² reports, and as the writer has also found, it does not show that any of the procedures of manufacture, which the baking trade is fully agreed prolong the life of bread (see below), delay the aging of the starch granules of the crumb. Yet it cannot be doubted that some of these practical procedures do have the effect claimed for them. The explanation probably is that the sedimentation test tells the state of the starch correctly but that this is probably not the whole story.

If, for example, the quality of the gluten or the changes in the distribution of the moisture in the loaf are of importance in determining the texture of crumb, the sedimentation test might indicate the age of the bread with considerable exactness and yet not indicate with equal exactness the physical condition of the crumb. It is not impossible, as Katz points out, that the way the fermentation of the dough is conducted, the amount and quality of the yeast, the amount and quality of the gluten, the presence of gelatinized starch, of milk, and of shortening, etc., do not delay the changes in the starch but in some way mask their effects so that despite hardening of the starch granules the crumb as a whole still feels soft for a time. If this is the case, the sedimentation test would permit rather exact comparison between two loaves manufactured in the same way but might be less satisfactory in comparing two loaves of different types to learn which remains fresh the longer, if other factors in addition to starch changes are concerned in the aging of bread. The sedimentation test would not measure, for example, differences in moisture distribution or differences in gluten texture if such there be.

The next step in the developing of methods for testing stale bread would seem to be the comparison of the sedimentation test with the compressibility test using different types of bread; in other words, the checking of the indirect sedimentation method against the di-

¹ J. R. Katz, "What Is the Fundamental Change in the Staling of the Bread Crumb?" *Bakers Weekly*, Dec. 1, 1934, LXXXIV, 31-34; Platt, *op. cit.*; L. H. Bailey, "A Simple Apparatus for Measuring the Compressibility of Baked Products," *ibid.*, July 1930, pp. 340-41.

² *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers.*

rect measurement of one of the physical traits of the crumb. Some work has been done in this direction but its volume is not yet adequate.¹

Let us now turn to the prolonging of the life of bread by methods of handling and storing after the loaf has left the oven.

Bread may be kept fresh by freezing. A temperature of -6° C. delays the onset of staleness and a temperature of -10° to -20° C. prevents it altogether. It is not yet feasible under ordinary commercial conditions to freeze bread because of the expense and because of the difficulties that arise in thawing. This takes much time, and moisture condenses on the crust which makes it soft like that of stale bread. To avoid this the bread must be thawed out in dry air.

Bread may be held at a temperature above 55° C. The objections to this procedure are that the crust becomes hard and dry, and bacteria are likely to develop inside the bread. If drying out is prevented by holding in a sealed chamber, the crust becomes soft and leathery and the crumb may acquire a crusty flavor. No practical method seems as yet to have been devised to keep bread fresh by holding at an elevated temperature.

Since consumers judge bread when they purchase it in part by the condition of the crust, and since the crust becomes soft before the crumb is noticeably stale, Katz has proposed to disregard the change in the crumb but to keep the crust reasonably brittle by holding in an atmosphere with a humidity of about 75 per cent. He has constructed an apparatus to accomplish this.² It consists of a closed chamber in which the cooled fresh loaves are stored with a ventilating fan to circulate the air within the chamber and drive it over the surface of a pan containing a brine or calcium chloride solution. Its concentration is so chosen that it removes water vapor from the air, or adds it, so as to keep the circulating air at the desired humidity. The device was employed in an Amsterdam bakery with success. Bread ten hours old was sold with-

out complaint. With the great improvements in air-conditioning of recent years, there is no doubt that this apparatus can be improved upon; but in America the method would be of little service to wholesale bakers, who must deliver to the retailer. It might, however, be useful to retail bakers, but these need it less than wholesalers because they are in good position to adjust production to demand. It is possible that inexpensive foolproof devices of this sort might be placed in retail groceries to good advantage, but in the aggregate this would require a large investment on the part of the wholesaler. It would not relieve him of the necessity of baking a loaf with a long life, for the growing stale of the crumb is not delayed—the crispiness of the crust is merely retained for a few hours longer.

We must therefore examine manufacturing methods that have been suggested to prolong the life of the loaf. These may be grouped in two general categories: processes and ingredients. Among manufacturing processes that are said to prolong the life of bread are the following:

a) Use of high-speed mixer.

b) Fermentation at low temperature, say 22° to 26° C. The liquid used in doughing should not be warm, say not over 25° C. It should of course be cooler if a high-speed mixer is used.

c) Fermentation as long as is consistent with avoidance of breaking down of gluten.

d) Use of sponge method.

e) Use of not too much yeast.

f) Proper handling of dough so as to punch at optimum time. This favors a uniformly small-pored loaf in which hardness and crumbliness are less conspicuous when they develop.

g) Loaf should not be overbaked so as not to lose too much moisture in the oven.

h) Oven should not be too hot, and baking should be slow rather than fast.

i) Loaf must not lose too much moisture in cooling.

j) A thin crust when stale is less conspicuous than a thick one.

Other factors in the manufacturing process on which there seems to be less general agreement are:

¹ Cf. Platt, *op. cit.*

² Depicted in J. R. Katz, "Can We Retard or Prevent the Staling of Bread?" *Bakers Weekly*, Feb. 10, 1934, LXXXI, 35.

a) Very rapid cooling of loaf is advantageous, if at the same time the loaf is not permitted to lose too much moisture.

b) Slow baking is said by some to be advantageous, but denied by others. It is said to hasten staleness especially with slack doughs.

c) Sour-dough fermentation is said to produce a bread that grows stale slowly. On the other hand, acidity is said to hasten staleness,¹ although sour dough is liable to be more acid than yeast bread.

The following ingredients seem to affect the life of the loaf:

a) High-quality flour acts favorably, especially short extractions. The dress seems also of influence; very fine grinding is said to be unfavorable.

b) Yeast quality is important. The effects of different types of yeast have not yet been adequately investigated. Some English bakers believe beer yeast produces bread with longer life than distillers' yeast.

c) Milk is favorable.

d) Too little salt is said to be unfavorable.

e) Five to ten per cent of rye flour is said to be slightly favorable.

f) Gelatinized starch as in scalded flours or boiled potatoes is favorable. However, according to Katz, potato starch retrogrades much faster than wheat starch.

g) Shortening is favorable — why is unknown. The writer has suggested that it forms membranes impervious to moisture and carbonic acid which tend to hold back both in

fermentation, to reduce loss in weight during the first few hours after the baked product comes from the oven, and to affect the redistribution of moisture as the loaf cools.²

h) Malt extract added to dough is favorable.

i) Katz³ found that aldehydes and some alkaline bases prolong the life of the loaf indefinitely. However, their use has not been found practicable, partly because they are not without physiological effects, partly because they need to be used in appreciable amounts.

In some of the respects above listed the crust behaves in a manner quite opposite to crumb. To secure a crust that will remain crisp for a long time the following practices should be observed:

a) High fermentation temperature.

b) Much yeast.

c) As little water as possible in dough.

d) Small amount of salt.

It may again be pointed out that the several effects on crumb of the procedures or ingredients above listed have not been established by exact measurement. They are based on inspection. How unreliable such judgments may be has been pointed out by Platt.⁴ It is important that they be firmly established by such measurement, for which perhaps only mechanical methods to determine the structural strength of crumb by testing instruments such as are used by engineers will prove reliable. Until this will have been done, it is idle to speculate about the reasons why specific procedures or specific ingredients act as they do. For the present, about all one can say is that:

1. Anything that increases the water content seems to be favorable to long life (much high-quality gluten, gelatinized starch, milk, high-speed mixing, malt extract).

2. Anything that hampers the mobility of moisture in the cooled loaf perhaps prolongs life (shortening, small-pored texture).

3. Anything that conceals the effects of aging of starch prolongs the loaf's life in that the loaf remains acceptable to the consumer (thin crust, very brittle crust).

¹ Cf. L. Boutroux, "Sur la fermentation panaière," *Annales de chimie et de Physique*, June 1892, Série VI, XXVI, 145–201. According to E. Fouard, acid tends to coagulate starch solutions (*Thèses présentées à la Faculté des Sciences de Paris ... 1^{re} Thèse.—Recherches sur l'état colloïdal de l'Amidon, et sur sa constitution physico-chimique. 2^e Thèse.—Application des parois semi-perméables à la détermination des poids moléculaires* (Dissertation, Paris, 1911; Laval, Barnéoud, 1911), pp. 78 ff.

² G. M. Weber and C. L. Alsberg, *The American Vegetable-Shortening Industry, Its Origin and Development* (Food Research Institute Fats and Oils Studies 5), June 1934, p. 279.

³ *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers.*

⁴ *Op. cit.*

FOOD VALUE OF FRESH AND OF STALE BREAD

In former times, it was believed that stale bread had greater nutritive value than fresh, perhaps because it was believed, erroneously, to be drier and therefore a more concentrated food per unit of weight.¹ Indeed, the conviction existed, and in some quarters persists to the present day, that the consumption of fresh bread may be injurious. It has been claimed that it causes symptoms of gastric pressure and even vomiting. Cases are on record in which it is alleged that death resulted.² In view of the insistent demand of today for absolutely fresh bread, one wonders whether in such cases bread had to take the blame which really belonged to some other element of the diet or whether the breads of former times were so different from those of today that the consumption of considerable fresh bread did in fact produce feelings of malaise and even illness.

The bread of former times was undoubtedly different from that of the present. Flour contained more of the bran coat of the wheat berry, which is digested with difficulty. The nature of fermentation was not understood and pure yeasts were unobtainable. Bakers used brewers' yeast or saved a piece of dough from one batch with which to inoculate the next. The fermentation process was therefore less well under control. Furthermore, formerly—and in some countries today—it was the custom to bake quite large loaves. These require a longer period of baking to permit the heat to penetrate to the center of the

dough mass than small loaves. If for any reason the temperature of the oven is too low, or if the time of baking is too short, the interior may remain somewhat doughy and for this reason perhaps not very digestible. In such bread, some yeast might easily remain alive and lose vigor only after a time, so that such bread when fresh might cause gastric fermentation. Furthermore, when chewed, fresh bread of this character might easily form compact boluses which perhaps irritate the stomach. Hammond³ showed that recently baked yeast bread when pressed into a compact condition resisted the digestive power of the stomach much longer. It is therefore quite possible that in olden times fresh bread caused untoward effects, and the more so since per capita consumption was much greater then—at least in America—than now.

Jungmann,⁴ however, compared the behavior of fresh and of stale bread in the mouth and toward pepsin-hydrochloric acid without being able to discover any material difference. He suggested that, since fresh bread takes less chewing to prepare it for swallowing than stale, possibly it forms firmer lumps in the stomach and therefore calls forth sensations of pressure or even vomiting and gastric cramps in persons with a so-called delicate digestion. He was not, however, able to secure experimental evidence in support of his suggestion.

Lindet,⁵ on the contrary, states that stale bread is less digestible than fresh. This is an inference based on the fact that stale bread contains a somewhat lesser quantity of soluble starch than fresh, since Lindet presented no experimental data on the digestibility of bread. Lindet assumes that soluble starch is more digestible than insoluble and that therefore stale bread is less digestible. Roux,⁶ however, studied the changes starch undergoes in bread to determine whether they are the same as those that take place with time in starch paste and render it more resistant to such digestive ferments as diastase and therefore perhaps less digestible in the gastro-intestinal tract. He reached the conclusion that the starch in bread does not behave like starch paste and that stale bread is no less digestible than fresh. Katz,⁷ however, found the starch

¹ Boussingault, *op. cit.*

² Maurizio, *op. cit.*, p. 362.

³ W. A. Hammond, "Experimental Researches Relative to the Nutritive Value and Physiological Effects of Albumen, Starch, and Gum, When Singly and Exclusively Used as Food. Prize Essay," *Transactions of the American Medical Association*, 1857, X, 511-87.

⁴ E. Jungmann, "Studien über Mehl und Brot," *Archiv für Hygiene*, 1895, XXIV, 109-23.

⁵ L. Lindet, "Sur la transformation du pain tendre en pain rassis," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, Apr. 21, 1902, CXXXIV, 908-10.

⁶ *Op. cit.*

⁷ "Abhandlungen zur physikalischen Chemie der Stärke und der Brotbereitung. XX. Über den Zusammenhang der Änderung der Stärke beim Althackwerden des Brotes und beim Retrogradieren von Stärkekleister."

of stale bread less easily attacked by malt diastase than that of fresh bread.

Katz,¹ using the technique of Pawlow, found that there is no difference in the quantity of saliva, gastric juice, or pancreatic juice secreted by dogs when they are fed fresh and stale bread. However, after salivation and chewing, fresh and stale crumb have quite different consistencies. The stale bread was then crumbly, but the fresh bread formed a heavy lump from which small particles could be broken off only with difficulty. Katz suggests that herein may lie a basis for the commonly believed difference in the digestibility of fresh and of stale bread.

One is tempted to infer that the attitude in former times may really have been a rationalization in response to the generally low level of the standard of living. Fresh bread, because attractive in flavor and in texture to most persons, is consumed in greater amount than stale bread. Perhaps it seemed a good

way to keep consumption down not to serve bread until some time after it had left the oven when, because of the beginning onset of staleness, it was less attractive to the taste and therefore less largely eaten. It must be remembered that those were the days when servants, retainers, employees, and apprentices very often received but little in money wages and were lodged, clothed, and fed by their masters or employers. It was to the interest of the employer or lord of the manor to encourage the consumption of cheaper foods like the coarse grains.

At any rate, the belief that the serving of stale bread tends to reduce consumption was held during the World War. As has been pointed out above, in many countries threatened with a shortage of the wheat supply, regulations were passed prohibiting the sale of bread until a certain number of hours after leaving the oven. Under the conditions of the present, there seem to be no scientific data on record demonstrating any material difference in the food value or wholesomeness of fresh and of stale bread.

¹ "Gelatinization and Retrogradation of Starch in the Bread Staling Process."

This study is the work of Carl L. Alsberg

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