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STARCH AND FLOUR QUALITY

THE PART starch plays in determining the quality of flour is often overlooked because it is less conspicuous than that of gluten. In this WHEAT STUDY, existing information bearing on the influence of starch on baking value has been collected, some of the gaps in our knowledge are pointed out, and some of the problems awaiting solution are presented. With fuller knowledge, it may appear that variations in the properties of the starches of different flours influence baking quality materially. Already it is clear that starch absorbs about as much water as all other flour constituents combined. Variation in the absorption of flours might therefore depend to some extent upon the water capacity of their starches. The susceptibility of starch to diastase is one of the factors affecting the diastatic power of flour and in consequence panary fermentation. This susceptibility to attack depends not only upon the size of the starch granules and upon their intrinsic ability to resist conversion into sugar by diastase, but also upon their location—whether surrounded by a protecting envelope of gluten or freed from it. It is because fine grinding separates large numbers of granules from the gluten envelope that fine grinding increases the apparent diastatic power of flour. But it also injures starch granules so that they swell in cool water, thereby increasing the absorption of the flour; and at the same time some starch goes into solution. In consequence, diastatic power is increased because injured granules and dissolved starch are readily attacked by the enzyme. Finally, changes that the modified starch of bread undergoes in time seem to be the major factor in causing bread to grow stale.

STANFORD UNIVERSITY, CALIFORNIA

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WHEAT STUDIES
OF THE
FOOD RESEARCH INSTITUTE

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STARCH AND FLOUR QUALITY

The leavening of bread, as everyone knows, is the consequence of the formation of carbonic-acid gas in dough by the yeast plant. Bubbles of this gas, trapped in the dough, make it porous, and this porosity becomes more pronounced when the oven's heat first expands the bubbles and then sets their walls, as the white of egg in an omelet soufflé is coagulated and solidified in the oven. Thus dough acquires the solidity and texture characteristic of bread. Wheat and rye are the only crop plants from which bread leavened in this way can be baked, for only wheat flours, and to a lesser extent those from rye, form tough and elastic doughs. If mixtures of flour and water did not form doughs but merely batters in which bubbles would grow, expand, rise to the surface, and burst, a porous loaf would not be formed, but rather a batter cake or a cracker.

The primary rôle that the toughness and elasticity of wheat-flour doughs play in bread making has centered the attention of students upon them. Because these properties depend upon the constituent of flour known as gluten, and only indirectly upon other factors, an enormous amount of scientific study has been devoted to gluten, while the other constituents of flour have received far less attention. Although over 70 per cent by weight of flour is starch, its rôle as a factor determining the quality of flour and the properties of bread has been regarded by cereal chemists as minor. They usually treat starch as if it were merely a filler and a food for the yeast, though an important contributor to the food value of bread. Their attitude is to be explained not merely by the preponderant rôle played by gluten in determining the character of bread, but also by the widespread but erroneous belief that all starches are alike, and that therefore the variability of flours does not depend in an important degree upon variability in the properties of their starches. Yet starches do vary, and starch, in addition to serving as a filler, has

other functions, though less important ones than gluten. These functions are clearer now than formerly because more is known regarding the physical and chemical nature of the starch granule. The time would seem to be ripe for the reappraisal of the rôle of starch in flour, dough, and bread.¹ It is to such an appraisal that this study is devoted.

THE RÔLE OF STARCH IN GENERAL

The structure of starch and flour.—Viewed through a suitable microscope, wheat starch is seen to consist of small discrete granules which range from about two microns² to a little over 40 microns in diameter. The larger ones are lenticular, the small ones spherical or, less often, polygonal. Com-

pound granules, i.e., aggregates of two to 25 granules, also occur. The granules do not appear clear and homogeneous but consist of more or less concentric layers or rings of alternating more or less diffracting material so that they have a laminated appearance.

Starch is the only constituent of wheat that consists of discrete particles or granules. Gluten, the other principal constituent, is present as a more or less continuous matrix in which the starch granules are imbedded like raisins in a cake.³ However, unlike raisins, the starch granules are generally imbedded in the matrix not singly but in groups. In different kinds of wheat the starch bears different relations to the gluten and this, in a measure, determines the gross appearance of the kernels. With a sufficiently high ratio of gluten to starch, the starch and the gluten are ce-

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¹ Cf. C. H. Bailey, *The Chemistry of Wheat Flour* (New York, Chemical Catalog Company, 1925), p. 287; M. P. Neumann, *Brotgetreide und Brot* (Berlin, Parey, 1923), p. 210.

² One micron (the symbol is μ) = 1/1000 millimeter; 25.4 millimeters = 1 inch.

³ E. Verschaffelt and E. van Teutem, "Die Änderung der mikroskopischen Struktur des Brotes beim Altbackenwerden," *Zeitschrift für physiologische Chemie*, October 1915, XCV, 130-35.

mented together solidly as the grain dries out in ripening and the kernels appear vitreous or flinty; while in the absence of sufficient gluten, air spaces appear rendering the grain soft and also serving as light-refracting surfaces that make the grain appear opaque. A grain of hard wheat may be made to lose its vitreous appearance by soaking it in water till it begins to swell and then drying it.¹ This causes air spaces to appear within the berry. A true soft wheat naturally has air spaces diffusely scattered through the interior of the berry, i.e., through the endosperm.² When grown under unfavorable conditions, normally vitreous wheat varieties may assume the appearance of soft wheat in variable degree. The opaque soft part may be localized in a part of the berry or in spots. The air spaces to which this appearance is due are then localized in these areas; they are not diffusely distributed throughout the endosperm as in a genuine soft wheat.

It is obvious that a wheat with such air spaces, a soft wheat, is more friable and must break up into smaller particles in the milling process than a hard vitreous wheat with few or no air spaces. In consequence, the starch is distributed differently in strong and in weak flours. In a hard-wheat flour, the gluten is present in relatively large clumps in which the greater part of the starch is imbedded. Relatively few starch granules lie free. In soft-wheat flour, the gluten clumps are smaller and carry imbedded in them correspondingly less starch; relatively more of the granules are free. It is obvious that the two types of flour contain

different proportions of gluten particles of different sizes and that, if separated into fractions by sifting, soft flours will yield larger fractions passing through the finer-meshed sieves than hard-wheat flours.

It is obvious, furthermore, that the proportion of free unimbedded starch granules must depend upon the granulation or "dress" of the flour. Flours from hard vitreous wheat tend to be coarsely granular because of the nature of their gluten unless the miller deliberately grinds them fine. Flours from soft wheats tend to be finely granular without special grinding. By grinding flour fine, gluten clumps are broken up, the starch set free, and some of the starch granules injured and even shattered. The significance of the state of the starch in flour will appear as the rôle of starch in bread making is unfolded.

The distribution of starch and diastase in wheat and flour.—Starch is found in greatest proportion in the interior of the wheat berry and this proportion decreases from within outward. There is also a tendency for the starch to be more abundant in the immediate neighborhood of the germ or embryo.³ It follows that the interior of the berry is poorer in gluten and richer in starch than those portions of the berry that lie closer to the bran coat.

Diastase⁴ is a chemical agent occurring naturally in the wheat berry. Under favorable conditions it attacks starch and converts it into gum-like substances known as dextrines or into fermentable sugar which is known as maltose or malt sugar. It is formed only by living things and belongs to the class of agents known as enzymes. Its chemical nature is not as yet at all well known. It can be recognized only by its effects, of which the one already mentioned, the formation of sugar from starch, is the most striking. It diffuses very slowly through solutions and cannot pass through such biological membranes as surround cells. Its commonest commercial source is barley malt.

Diastase is present in the several organs of barley in different amounts. It is most abundant in the scutellum of the germ or embryo, and in the aleurone layer lying directly under the bran coat, and also occurs in minimal amounts in the endosperm which forms the

¹ Cf. W. Johannsen, "Développement et constitution de l'endosperme de l'orge," *Résumé du compte-rendu des travaux du laboratoire de Carlsberg*, 1883, II, 60-77.

² The endosperm is the main part of the wheat berry from which flour is formed by separating it from the seed coats, aleurone layer, and the germ.

³ The germ or embryo is that part of the berry from which in germination the wheat plant develops. The rest of the seed furnishes the food upon which the embryo is nourished until the young plantlet develops functioning roots. The embryo is a small body composing about 1.5 to 2.0 per cent of the wheat seed located at the end of the berry opposite to the end which is armed with the tuft of hairs. In making white flour by the roller-milling process, most of the germ is removed and appears in the offal, to the feed value of which it contributes markedly.

⁴ Some modern investigators use the word "amylase" instead of "diastase."

bulk of the interior of the seed and contains most of the starch.¹ While information concerning the localization of diastase in the wheat berry is far less complete, what there is of it is in full accord with the observations on barley, so that it may safely be assumed, pending evidence to the contrary, that in this respect wheat is like barley. Martin² found that in the wheat berry diastatic activity increases progressively from the interior to the exterior of the berry. In the inner endosperm, that is the endosperm without any traces of the aleurone layer, the amount of diastase is too small for any appreciable conversion of the starch. Moreover, the diastase of the inner endosperm, unlike that of the embryo and of the aleurone layer, does not form appreciable amounts of fermentable sugar.³

¹ F. Stoward, "A Research into the Amyloclastic Secretory Capacities of the Embryo and Aleurone Layer of *Hordeum* with Special Reference to the Question of the Vitality and Auto-depletion of the Endosperm," *Annals of Botany*, July 1911, XXV, 799-841.

² F. J. Martin, "The Distribution of Enzymes and Proteins in the Endosperm of the Wheat Berry," *Journal of the Society of Chemical Industry* (London), December 15, 1920, XXXIX, 327-28T.

³ H. P. Wijsman, Jr., "La diastase considérée comme un mélange de maltase et de dextrinase," *Recueil des travaux chimiques des Pays-Bas*, 1890, IX, 1-13; Stoward, *op. cit.*

⁴ Bailey, *op. cit.*; H. Kalning and A. Schleimer, "Die chemische Zusammensetzung des Weizens und seiner Mahlprodukte," *Zeitschrift für das gesamte Getreidewesen*, 1913, V, 199, cited in C. Oppenheimer, *Die Fermente und Ihre Wirkungen* (Leipzig, Thieme, fifth edition, 1929), Vol. IV, Part 2, p. 304; M. P. Neuman, "Brot," in *Ergänzungswerk zu Muspratt's Enzyklopädischem Handbuch der Technischen Chemie*, edited by B. Neuman, A. Binz, and F. Hayduck (Braunschweig, Vieweg, 1915), Vol. IV, Part 1, pp. 343-96.

⁵ H. Nuret and A. v. Ugrimoff, "Einige Versuche über die Körnung oder Grösze der Mehlpartikelchen der Weizenmehle," *Zeitschrift für das gesamte Getreide-Mühlen- und Bäckereiwesen*, April 1933, XX, 95-98; J. H. Shollenberger and D. A. Coleman, *Influence of Granulation on Chemical Composition and Baking Quality of Flour* (U.S. Department of Agriculture, Department Bulletin 1463), December 1926.

⁶ R. Newton and W. H. Cook, "The Bound Water of Wheat-Flour Suspensions," *Canadian Journal of Research*, December 1930, III, 560-78.

⁷ H. Rodewald, *Untersuchungen über die Quellung der Stärke* (Kiel and Leipzig, Lipsius und Tischer, 1896), p. 69.

⁸ L. Maquenne, "Sur la dessiccation absolue des matières végétales," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, October 16, 1905, CXLI, 609-12.

Since modern roller milling is a process of gradual reduction of the wheat berry to flour and offal, the flour separated at different stages of the roller process is derived preponderantly from different portions of the berry. That obtained from the interior of the berry in the earlier stages of reduction would naturally tend to contain somewhat more starch and less diastase than that obtained at later stages, and indeed this is what analyses of the different mill streams indicate.⁴ The different streams are of different quality. Moreover, flours of different fineness obtained by separation through sieves with different size meshes differ in quality.⁵ To what extent varying starch and diastase content is responsible for varying quality will be discussed below.

Absorption of moisture by starch.—Starch is very hygroscopic, that is to say, it absorbs moisture with the greatest avidity. Starch as it comes on the market, although dry to the touch, nevertheless contains appreciable amounts of moisture—how much depends upon the species of plant from which the starch is derived, upon the temperature, and upon the humidity of the atmosphere. Newton and Cook⁶ have shown by direct measurement that wheat starch suspended in cool water binds about 30 per cent of it. Rodewald,⁷ using a different method, found that wheat starch placed in an atmosphere saturated with water vapor at 21.5° C. binds about 36 per cent of water. This water is in some manner loosely held by the starch. It can be removed again by exposure to an atmosphere free from water vapor. The last traces can be expelled only with extreme difficulty. To dry the starch completely, it must be heated in hot *dry* air, for in hot *undried* air it retains some moisture most tenaciously.⁸

The absorption of water by starch at ordinary temperatures is not accompanied by any visible change in structure except a moderate degree of swelling (see below). None of the starch placed in cool water dissolves. It is otherwise when the granules are caused to swell or gelatinize by heating them in water. They then swell till ultimately they take on the appearance of tiny translucent globular sacks filled with liquid. For the most part, the

swollen granules of wheat starch do not disintegrate and burst. In the process of swelling, a considerable portion of the starch substance diffuses out of the granule and dissolves in the surrounding water. In swelling, when heated in water, starch absorbs more water than it does in water without heating. Wheat starch behaves in this way at a temperature well below that of boiling water.

If the quantity of water in which the starch is heated is not too great, the heated suspension sets to a more or less stiff jelly or gel on cooling. It is a solid, starch paste; the water has disappeared as such. But it does not necessarily follow that the gel contains more water of hydration than ungelatinized starch, for, if such a gel be ground in a pebble mill or otherwise disintegrated, it becomes much less stiff, may indeed be converted into a sirup.¹ Examination with the microscope shows that the tiny swollen starch sacks have been ruptured and their more fluid contents released. Obviously starch paste does not contain all of its water as water of hydration; some of it is held mechanically by the peculiar structure of the paste. It contains water in at least two forms, namely, water of hydration closely associated with or bound to the starch molecules, and water merely mechanically held. Whether in the process of gelatinization the starch molecules acquire a greater capacity to bind water is not known. It is not improbable, for Dumanski² has reported that boiled potatoes have a water-binding capacity of about 1.5 grams per gram of dry material. Since boiled potatoes are predominantly starch, this is suggestive of increase in hydration capacity resulting from boiling. In any event in the process of gelatini-

zation starch is capable of absorbing large quantities of water—whether as water of hydration or as water less firmly held.

Absorption of water a criterion of flour quality.—The amount of water that can be incorporated in flour without producing “slackness” of the dough, i.e., too great softness, is one of the criteria the commercial baker uses to evaluate flour. Plainly the more water he can use, the greater the number of loaves he obtains per barrel and the greater his profits, for the amount of water remaining in the loaf as it leaves the oven depends in part upon the amount of water in the dough. Therefore, other things being equal, the baker prefers that flour which absorbs the greatest amount of water. Indeed, flour strength has sometimes been defined as capacity to absorb water.³

This important trait of flour, absorption, is commonly thought to be related to the gluten alone without consideration of the rôle of starch. Yet, as we have seen, starch absorbs about one-third of its weight of water. Since starch constitutes nearly four-fifths by weight of flour, it is obvious that in doughing flour the starch plays a major rôle in absorbing and holding the water added. How does it compare with the other constituents of flour?

The distribution of moisture in dough.—The only other flour constituent present in large enough amount to be a factor in absorption is gluten, a mixture of proteins, which, as we have seen, gives to wheat-flour doughs their main characteristics of elasticity and toughness. Skovholt⁴ has based estimates of the distribution of water in dough upon his own determinations of the total bound water in dough and upon the hydration determinations upon starch of Newton and Cook,⁵ assuming that their figure of 30 per cent may be applied without serious error to all the nonprotein substances of dough. The average of his results obtained with three different flours was as follows: Of the water present in the doughs, 43.5 per cent on average was bound by the dough substances. Of this bound moisture or water of hydration, the fraction held by the nonprotein substances, predominantly starch, was 23.3 per cent of all the water present. The fraction held by the proteins was 20.2 per cent

¹ 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.

² A. Dumanski, “Die Bestimmung der Menge des gebundenen Wassers in dispersen Systemen. I Methode der Refraktometrie und Polarimetrie,” *Kolloid-Zeitschrift*, November 1933, LXV, 178–84.

³ F. B. Guthrie, “The Absorption of Water by the Gluten of Different Wheats,” *Agricultural Gazette of New South Wales*, September 1896, VII, 583–89.

⁴ O. Skovholt, *Effect of Plasticity and Related Physical Properties of the Substratum on Enzyme Activity* (Dissertation, Minnesota, 1934).

⁵ *Op. cit.*

of all the water in the dough. In other words the starch and other nonprotein substances held somewhat more water bound as water of hydration than the proteins. Starch is therefore at least as important in determining hydration as gluten. According to the calculations of Skovholt the average hydration of the proteins in the three flours studied was 196 per cent. Though gluten has far greater avidity for water than starch—close to 200 per cent as against 30 per cent—the proportion of starch in flour is so much greater than that of gluten that the starch holds about as much water as the gluten or even a little more.

The determinations by Newton and Cook¹ upon suspensions of flour in water and by Skovholt upon doughs of the amounts of water bound by gluten are in fact inferences. These investigators actually determined the amounts of water that were made incapable of serving as solvent for other substances, and this water, removed as it were from the scene, they termed bound moisture or water of hydration. After subtraction of this amount there remains over 50 per cent which is still available as solvent. But this water is not free as is the water in the pores of a coarse sponge. Skovholt² was unable to express it by means of a hydraulic press under a pressure of 45 kilograms per square centimeter. Yet when dough is dried, a great part of the water evaporates with ease. Gradually, however, it evaporates less and less easily as the moisture content of the drying dough becomes less, until the final fractions are removed only with the greatest difficulty. In short, over half the water in doughs behaves like ordinary liquid water so far as its solvent power and ability to form steam or vapor are involved. Yet this fraction cannot readily be separated from dough by mechanical means. How is it held?

¹ *Ibid.*

² *Op. cit.*

³ J. Loeb, *Proteins and the Theory of Colloidal Behavior* (New York, McGraw-Hill, first edition, 1922).

⁴ J. W. McBain, "The Apparent Viscosity of Colloidal Solutions and a Theory of Neutral Colloids as Solvated Micelles Capable of Aggregation," *Journal of Physical Chemistry*, February 1926, XXX, 239-47.

⁵ C. L. Alsberg and E. P. Griffing, "The Effect of Dry Grinding upon Gels," *Proceedings of the Society for Experimental Biology and Medicine*, November 1925, XXIII, 142-43.

A positive answer to this question cannot as yet be given, but a number of facts are known which point to an answer consistent with present knowledge.

Gluten is a solid tough jelly or gel. Loeb³ has suggested that such substances have a definite structure and that water is "entrapped" in the interslices of this structure. The structure itself has been likened to a "brush heap" made of interwoven aggregates of molecules between which water is held entrapped. This hypothesis of the nature of gels is consistent with the behavior of such jellies when subjected to mechanical manipulation. McBain⁴ has shown that shearing jellies of this character reduces their viscosity, a phenomenon that is best explained by the breaking up of the aggregates and the resulting freeing of "entrapped" water.

Moreover, Alsberg and Griffing⁵ have shown that severely overgrinding a flour changes the character of its gluten. The gluten washed from such a flour swells less in dilute acid than the control gluten prepared from the same flour before it was subjected to overgrinding. The difference was so definite that it was possible by mere inspection to distinguish the two kinds of swollen gluten. The control gluten, as it swelled in dilute acid, became translucent, shiny, and runny; while gluten from the same flour overground remained more opaque, swelled less, and was much firmer to the touch. This phenomenon is best explained on the assumption that severe and long-continued grinding breaks down the structure of gluten so that it is less capable of holding water "entrapped" in its interstices.

The manner in which gluten is laid down during growth in the endosperm of the wheat berry and the manner in which dough is made, kneading and mixing, presumably produce interstices of variable dimensions; in other words, dough contains pores of variable size. In these, what we have termed the "entrapped" water is contained. This, as we have seen, amounts to over 50 per cent of all the water in dough and, unlike water of hydration, is available as a solvent for all those elements of flour which, unlike gluten and starch, are soluble in water. Though the total proportion of these is small, their number is large, for flour is es-

entially crushed modified vegetable cells and therefore contains small amounts of a host of substances usually found in the tissues of plants. Sugars, organic and inorganic salts, diastase, and non-gluten proteins are among those significant in the present connection.

In so far as these substances occur in molecules or aggregates of molecules of small size—for example, salts and sugars—they are able to dissolve in all the “entrapped” water and diffuse into the smallest pores, for it is well known that such substances diffuse through jellies and gels like gelatin almost as fast as through water. On the contrary, those flour constituents that exist in large molecules or large aggregates of molecules—for example, the non-gluten proteins and diastase—though they are water soluble, probably cannot diffuse into the gluten, for it is well known that such substances do not diffuse readily into gels. In consequence, there must be a very uneven distribution of the water-soluble substances in dough. Those with small molecules—salts, sugars, etc.—are fairly evenly distributed throughout the dough mass. Those with large molecules—proteins, diastase, etc.—are probably limited to the coarser interstices, namely, the surfaces of the gluten masses and the fissures and grosser spaces of the dough. They must be in fairly concentrated solution, and one of the effects of kneading is to distribute their solution more widely through the dough mass.¹

The relation of kneading to absorption by flour.—The hypothesis that gluten has a “brush-heap” structure may explain the effects of kneading and overkneading. It is a well-known fact that a certain amount of time must elapse before a dough achieves its maximum of toughness and elasticity; the phenomenon is known as the “development” of the gluten. Kneading facilitates, and tends to hasten, development. Many suggestions in explanation of why and how gluten “develops” have been offered; but the phenomenon is probably quite simple. It takes time for water to diffuse into the particles of gluten and give to it the dough characters of toughness, elasticity, and adhesiveness. Kneading, by bringing the gluten particles, as well as free starch granules, into more intimate contact with

water, would naturally tend to hasten absorption and therefore development of the gluten.

Large gluten particles would take more time to develop than small ones. We should therefore expect flours of fine granulation to absorb water more quickly than coarser ones,² and such is in fact the case. Since hard-wheat flours as a rule are more coarsely granulated than soft-wheat flours, and since hard-wheat flours contain more gluten than those made from soft wheat, we should expect hard-wheat-flour doughs to take more time to develop than doughs from soft-wheat flours, and this indeed is what is observed.

It is obvious, therefore, that kneading speeds up gluten development by mixing so as to bring the gluten particles more rapidly into contact with water. If gluten has a “brush-heap” structure, then perhaps kneading has another function, namely, to facilitate the drawing of water into the interstices of the “brush heap.” Water enters these interstices by capillarity; but the forces of capillarity are surface forces. Under the stress of these forces, the interstices of the “brush heap” endeavor to assume that shape which reduces the stresses arising from surface forces to a minimum. This shape is the sphere. Knead-

¹ It may be that the distribution of diastase in dough is to some extent independent of the water available for its solution. Diastase is adsorbed by starch, i.e., it combines loosely with it (cf. H. C. Sherman, M. L. Caldwell and M. Adams, “Enzyme Purification by Adsorption: An Investigation of Pancreatic Amylase,” *Journal of the American Chemical Society*, November 1926, XLVIII, 2947–56; and “Further Experiments upon the Purification of Pancreatic Amylase,” *Proceedings of the Society for Experimental Biology and Medicine*, March 1926, XXIII, 413–15). It would therefore tend to be removed from the “free” water in which it is dissolved by adsorption on starch granules. This would occur more in the case of a flour with many free starch granules than in a flour with few of them. Starch granules apparently have considerable adsorbing power, for they adsorb salts readily (H. Lloyd, “The Adsorption of Some Substances by Starches,” *Journal of the American Chemical Society*, July 1911, XXXIII, 1213–26). J. G. Malloch (“Studies on the Resistance of Wheat Starch to Diastatic Action,” *Canadian Journal of Research*, July 1929, I, 110–47) found that starch prepared from flour by washing still retains some diastase.

² J. H. Shollenberger, W. K. Marshall, and J. F. Hayes, “Influence of the Size of Flour Particles on Baking Quality,” *National Miller*, December 1921, pp. 29–31 and 66; cited in Shollenberger and Coleman, *op. cit.*, p. 2.

ing distorts this structure, the interstices are flattened and pulled out, and their surfaces are increased. Thereby the surface energy on the internal surfaces of the interstices is increased. Therefore, when they endeavor to approach again the spherical shape, force is exerted with which water is drawn into the fine meshes of the dough. The gluten is not merely hydrated, but water is also "entrapped."

Further support is given to the "brush-heap" structure hypothesis by the fact that excessive kneading tends in the end to reduce the toughness and elasticity of dough. It may be assumed that overkneading tends to break up the "brush-heap" structure of gluten, just as grinding breaks up the structure of starch pastes,¹ and shearing breaks up the structure of soap jellies.² Consistent with this hypothesis is the well-known loss of viscosity which flour-water suspensions undergo in time. Blair, Watts, and Denham³ have attributed this time effect to syneresis. Syneresis is the sweating-out of liquid by a jelly after a time, for example, the separation of whey from milk coagulated with rennet or of serum from a blood clot. Probably the effect of mechanical treatment (kneading, shearing, shaking, grinding) and syneresis go back to the same phenomenon. In the case of the separation of fluid from a gel by mechanical treatment, we have release of "entrapped" liquid by mechanical rupture of the structure. In the case of syneresis, we have the release of "entrapped" liquid because the particles aggregate into coarser clumps, so that the structure becomes less fine-meshed and in consequence not capable of holding so much water.

In doughs made from normal flours, there is practically no starch dissolved in the "entrapped" water; for whole, intact, unheated starch granules are quite insoluble. This is

¹ Alsberg and Perry, "The Effect of Grinding upon Starch and Starch Pastes."

² McBain, *op. cit.*

³ G. W. S. Blair, G. Watts, and H. J. Denham, "Effect of Concentration on Viscosity of Flour Suspensions," *Cereal Chemistry*, January 1927, IV, 63-67.

⁴ Neumann, *Brotgetreide und Brot*, p. 432.

⁵ K. Mohs, *Neue Erkenntnisse auf dem Gebiete der Müllerei und Bäckerei* (Dresden and Leipzig, 1922); cited in Bailey, *op. cit.*

not the case when bakers scald a part of the flour before working it into the dough, as they do, for example, in making barm for the Scotch bread process. There is, then, an appreciable amount of starch dissolved in the "free" water, the water-binding power of the dough is increased, and the bread keeps fresh longer.⁴ The addition of boiled potato to dough serves similar ends.

The considerations above presented are based on the assumption that both the gluten and the starch become fully hydrated and "entrap" the maximum of water. There is no experimental evidence that this assumption is warranted. It may be that neither starch nor gluten is fully saturated when kneading ceases or that only one of them is. Indeed, Mohs has suggested that added water does not penetrate the gluten particles of excessively strong flours, but is absorbed on their surface. In ordinary flours, on the contrary, part of the water, Mohs assumes, penetrates the particles of gluten causing them to swell, while when all the water penetrates the particles and none remains on their surface the gluten is characterized by being weak.⁵

Since it takes time to develop gluten, it may well be that those starch granules which are imbedded within gluten masses are unable to become completely saturated—at least not until after development is ended. Water must diffuse through a layer of gluten before it can reach such granules. It is therefore quite possible that in the ordinary process of kneading many of the starch granules of a strong flour never become fully saturated with water or else become so only gradually as fermentation progresses, whereas in weak-flour doughs most of the starch grains become fully saturated almost immediately. Possibly one of the modes of action of the high-speed mixer is to hasten the saturation of the starch granules and thus to contribute to the more rapid absorption effected by these machines. At the same time friction during kneading produces heat and warms up the dough. Raising the temperature of gluten up to a certain point increases its absorption power (see below).

Possibly it is in imperfect hydration and development that the explanation of lack of direct proportionality between gluten content

and absorption is to be sought. With rising gluten content of flour, one would expect absorption to rise faster than gluten content, because each unit of gluten replacing a unit of starch has greater water-absorption capacity than the starch. The question does not seem to have been tested directly by exact measurements relating gluten percentage to absorption, but experiments on fermentation rates and baking tests (see below) indicate that absorption rises less rapidly than gluten percentage.

It has generally and tacitly been assumed that, so far as absorption is concerned, the only variable is gluten, and lack of proportionality between gluten content and absorption has been attributed to some as yet unknown change of the character of the gluten as its proportion in flour increases. This is possible, but it is here suggested that the starch may also play a rôle. As above pointed out, in high-gluten flours, fewer starch granules are free than in low-gluten flours. More of their starch is but slowly accessible to hydrating water than in a soft low-gluten flour. Moreover, free starch granules may conceivably serve as centers for the formation of tiny pockets in the dough in which water is enclosed mechanically. Perhaps in hard flours with few free granules but little water is incorporated mechanically in this way.

The only estimations of the degree of hydration of the gluten in doughs of different kinds of flours are those of Skovholt¹ above discussed. Two of the flours he studied were hard-wheat bread flours and therefore, presumably, coarsely granular; one of them was a soft-wheat cake flour and therefore, presumably, finely granular. The cake-flour gluten when doughed was hydrated 277 per cent, whereas the bread flour glutes were hydrated 179 and 183 per cent, respectively. It may be that these differences are merely incidental, for the methods used involve an appreciable and undetermined margin of error. If it should turn out on further study that such a difference between the two types of flour in fact is normal, it would suggest that

the much greater hydration of soft-wheat flour is due to finer granulation and consequent more perfect hydration, for Newton and Cook² found the same hydration capacity for the gluten of strong and of weak flours. They experimented under conditions favorable to perfect hydration. They concluded that the greater water-absorption capacity of strong flours depends not on greater hydration of the gluten but rather upon the nature of its "brush-heap" structure which causes it to "entrap" more water than the gluten of a weak flour.

We see, then, that physical conditions are of great importance in determining absorption; and it is not unreasonable to surmise that the location of the starch granules, whether free or imbedded, may well be an important factor in determining absorption. When a starch granule is imbedded in a gluten particle, it will compete with the gluten of that particle for the water, as the water passes into the interior of the gluten particle where the starch granule lies. The tendency would be for the hydration and consequent development of the gluten to be slowed up, and in fact, as we have seen, strong flours tend to develop more slowly than weak ones. In any event, it is obvious that the quantity of starch in a flour, and probably its location, whether free or imbedded, play a large rôle in determining absorption.

Fermentation.—Normal flour contains very little fermentable sugar, but sugar must be present in dough if it is to ferment, because yeast is only able to ferment certain sugars, i.e., to form carbonic-acid gas from them. Yeast is quite incapable of fermenting starch. As soon as yeast is incorporated in dough, it begins to ferment the small amount of preformed sugar present, and fermentation would cease as soon as this small amount of sugar had been consumed, if fresh sugar were not supplied. Leavening would remain incomplete, unless in some way fresh supplies of fermentable sugar were offered to the yeast. In most flours, such fresh supplies are offered through the action of diastase on starch. Hence the action of diastase upon the starch in flour is very important; indeed, it is one of the factors determining the baking quality

¹ *Op. cit.*, Table XVI.

² *Op. cit.*

of flour. The ability of a flour to form sugar in this way is known as its diastatic power.

In order that diastase may form sugar from starch, it must be able to get at the granules. As we have seen, diastase diffuses slowly through a solution and probably enters the gluten masses slowly if at all.¹ Such starch granules as are imbedded in gluten matrix presumably are still surrounded by the protoplasmic layer within which they were formed, and diastase from without passes through this layer with difficulty if at all.² Such granules are therefore inaccessible to diastase from without or accessible only with difficulty. Starch grains which have been freed from the matrix, it is to be expected, will have had these protoplasmic layers ruptured or removed. One would therefore expect flour with many free granules to show greater diastatic action than flour with few. Such evidence as there is points in this direction. Thus Malloch³ found that any treatment which made a flour finer (fine grinding, extraction with ether) without injuring (see below) many of the granules increased diastatic power.

Furthermore, very thorough mixing tends to increase the rate of sugar formation at the beginning of doughing. Thus Skovholt⁴ found a considerable increase of sugar formation in doughs mixed for ten minutes over the same dough mixed but one minute. One is tempted to infer that this is because the mixing has brought more starch granules in contact with diastase, for, as we have seen, diastase having molecules of large dimension does not diffuse readily into the interior of gluten masses. It needs to be brought in contact with gluten-

¹ Some investigators have suggested that diastase occurs in flour in a form that is not freely soluble, perhaps loosely combined with protein. J. S. Ford and J. T. Guthrie ("The Amylolytic and Proteolytic Ferments of Wheat Flour, and Their Relation to 'Baking Value,'" *Journal of the Society of Chemical Industry* [London], April 30, 1908, XXVII, 389-93; cf. also Bailey, *op. cit.*, pp. 233-34) found it difficult to extract all the diastase from flour unless they first partially digested the protein with the enzyme, papain. If in fact the diastase of flour is combined in some manner so it is not freely soluble, the starch imbedded in gluten matrix may well be quite inaccessible to attack.

² H. Ziegenspeck, "Ueber Sparstärke," *Botanisches Archiv*, August 1924, VII, 251-73.

³ *Op. cit.*

⁴ *Op. cit.*, Table XVII.

enmeshed starch granules by mechanical means, if it is to attack them. While, therefore, there is some evidence that the location of the starch in flour and dough is a factor in sugar formation, so many other factors are involved, as we shall see, that it is not justifiable, for the present, to say more than that the degree to which the starch is separated from the gluten is one of the factors determining the diastatic power of flours.

With the formation of gas in the dough by fermentation, the dough mass is puffed up, its volume increases, the dough "rises." This "rise" depends in part upon the rate of fermentation, which in turn depends upon the diastatic power of the flour and upon the activity and quantity of yeast. How the diastatic power is related to the "freedom" of the starch has been pointed out. But the rise depends also upon the elasticity and tenacity of the gluten which keep gas bubbles "entrapped" and do not permit them to escape. As we have seen, absorption of flours increases with their gluten content but less than proportionately. This seems also to be true of the rise of the dough and consequently of the volume of the baked loaf. As the gluten content becomes greater, each increment of gluten causes a smaller increment in loaf volume than the increment preceding. Each increment is progressively less effective in increasing the size of the loaf. Why this should be has not as yet been explained satisfactorily. This lack of direct proportionality between gluten content and absorption has been attributed to some as yet unknown modification of the character of the gluten as its proportion increases.

This is entirely probable; but it is also possible that the starch may play a rôle as well just as it may play a rôle in absorption. The greater the gluten content, the less the tendency of the flour to be very finely granulated, for, as has been pointed out, the endosperm of a high-protein wheat is less friable than that of a low-protein wheat. In consequence, the flour from high-protein wheat, as also pointed out, contains more of its starch locked up in a gluten matrix and less of it free. More of its starch is therefore inaccessible to diastase as well as slower to hydrate. The con-

sequences are probably less rapid sugar formation, slower initial rate of fermentation, and less rapid rise of the dough.

Some investigators have studied the relation of gluten percentage in flour to flour strength by diluting flour with starch and noting the effect.¹ The extensibility of the dough is reduced, its gas-retaining capacity is diminished, and the quality of the loaf is impaired. Most students of these questions have assumed that starch served merely as a diluent. They have not considered that different wheat starches, in all probability, resist diastase to variable degrees (see below). They have not taken into their calculations the fact that added starch is not present in the flour-starch mixture in the same state as the natural starch of flour. Much of the latter, especially in the stronger, high-gluten flours, is locked up in the gluten matrix and therefore but slowly accessible to water of hydration and accessible with great difficulty, if at all, to the diastase. Merely for mechanical reasons the effect of the added starch would be different from that of starch naturally present in the flour. Since the added starch is all free, it would become saturated with water at once and it would interfere with the tendency of the gluten particles to stick together. Mechanically, it must act quite differently from the natural starch of flour, because this is in great measure already surrounded and protected by gluten. "When patent or high grade flours containing an unusually low percentage of gluten are mixed into a paste or dough and washed with water, it proves impossible at times to recover an appreciable quantity of wet crude gluten. The

dilution of the gluten by starch is so great in such instances that the gluten particles are not afforded an opportunity to agglutinate into a coherent mass in the washing process."² Here we see occurring naturally what may be brought about artificially by the addition of starch to a stronger flour.

One would expect the dough from the starch-flour mixtures to be less strong mechanically, and perhaps this is one of the reasons why Johnson and Bailey³ found that doughs made from strong flours to which starch had been added exhibited a decrease in gas-retaining capacity.

But the results of Johnson and Bailey also show that the addition of starch increased the total volume of carbon-dioxide gas formed and that the rate of gas formation was more rapid at the beginning of fermentation than in doughs to which no starch had been added. This is what one would expect from the fact that the starch added is free starch accessible to immediate hydration and exposed to immediate attack by diastase.

Furthermore, since starch absorbs as much as 30+ per cent of moisture, it follows that if the starch-flour mixtures were doughed by the same formula, using the same amount of water as for the unmixed flours, the two sets of doughs would have different distributions of the water. Since the water capacity of gluten is greater than that of starch, in the starch-flour mixtures there would tend to be more water bound neither by gluten nor by starch. Such doughs would tend to be "slacker," and they would therefore tend to bake out somewhat differently.

Behavior of doughs in the oven.—In the oven, water vapor⁴ is formed in the dough which evaporates into the carbonic-acid gas bubbles, thereby aiding materially in the expansion of the loaf. At the same time both gluten and starch alter their water-absorption capacity. When gluten, as it occurs in flour, is moistened, it swells, becomes hydrated, and in addition takes up water into its finer interstices. When it is warmed in water, it absorbs slightly more of it⁵ up to a temperature of 50° C. or slightly higher. Above 50° C., its behavior is reversed and its swelling power becomes progressively less. Heat-coagulated

¹ The literature has been reviewed by Bailey, *op. cit.*, p. 261.

² Bailey, *op. cit.*, p. 257.

³ A. H. Johnson and C. H. Bailey, "Gluten of Flour and Gas Retention of Wheat Flour Doughs," *Cereal Chemistry*, March 1925, II, 95-106.

⁴ Dough contains small amounts of alcohol which is vaporized at a lower temperature than water. Its vapor no doubt contributes slightly to the expansion of the loaf in the oven. According to Neumann (*Brotgetreide und Brot*, p. 385) fresh bread still contains 0.25-0.4 per cent of alcohol.

⁵ F. W. Upson and J. W. Calvin, "On the Colloidal Swelling of Wheat Gluten," *Journal of the American Chemical Society*, May 1915, XXXVII, 1295-1304.

gluten¹ and gluten coagulated by treatment with alcohol-ether followed by drying² have greatly reduced swelling power, are less hydrated,³ and hold water less firmly.

Starch also swells when moistened in cool water and as it is heated continues to swell at temperatures at which gluten is already losing swelling power. Nyman⁴ observed starch to begin to swell at a temperature as low as 50° C., while LaWall and Graves⁵ and

Alsberg and Griffing⁶ found that swelling begins to some extent at even lower temperatures.

It follows that, within the range of temperature over which gluten is losing water capacity, starch is gaining water capacity. Clearly the distribution of water in the baked loaf must be quite different from that in dough.

When the fermented and proofed dough is brought into the oven, diastatic action must continue for a time, at any rate until the temperature in the baking loaf reaches about 80° C. In a moderate oven a temperature of 80° C. is reached in five to eight minutes.⁷ However, the action of diastase cannot be very extensive during this period, for very little of the products of its action is found in bread. From bread crumb, Stone⁸ extracted comparatively little soluble material derived from starch, while Katz⁹ found somewhat more in Dutch bread. The starch granules cannot therefore be gelatinized by the oven's heat in the same way as when heated in an excess of water, for under the latter conditions an appreciable proportion of the starch granule becomes soluble in water. Certainly there is not enough water in dough to permit anything like complete gelatinization of the starch even if all the water, water of hydration included, were available for that purpose. This has been shown definitely by Jago and Jago,¹⁰ by Whympers,¹¹ and by others. Some change, nevertheless, takes place in the starch granules, even though there is not enough water available to form genuine starch paste. No unchanged granules remain in ordinary bread crumb.¹² They have an altered appearance under the microscope, and all the granules may be stained to varying degrees with Congo red, showing that some alteration has occurred.¹³ Normal intact granules do not take up this dye. In the presence of insufficient moisture to completely gelatinize, heating probably disorganizes the crystalline structure (see below) of the grains. They take up as much water as is available and only swell to that extent. It is likely that in this condition they have acquired greater water capacity than they had in the unaltered state.

In any event, the changes dough undergoes

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

² Newton and Cook, *op. cit.*

³ J. R. Katz, "Über das Altbackenwerden des Brotes und die Möglichkeit, diese Veränderung hintanzuhalten," *Zeitschrift für das gesamte Getreide-Mühlen- und Bäckereiwesen*, March 1934, XXI, 63-68.

⁴ M. Nyman, "Untersuchungen über die Verkleisterungstemperatur bei Stärkekörnern," *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel*, December 1, 1912, XXIV, 673-76.

⁵ C. H. LaWall and S. S. Graves, "Studies in Carbohydrates. The Composition and Digestibility of Wheat Bread and Allied Foods. Gelatinization of Starches," *Transactions of the Wagner Free Institute of Science*, 1913, Vol. VII, Part 2, pp. 37-45; cited in *A Comprehensive Survey of Starch Chemistry*, compiled and edited by R. P. Walton (New York, Chemical Catalog Company, 1928), Vol. I, Part 2, p. 133.

⁶ "The Heat Coagulation of Gluten."

⁷ L. E. Stout and F. Drosten, "Heat Flow through Bakery Products. I. Time-Temperature Relationships Existing during the Baking of Bread," *Industrial and Engineering Chemistry*, April 1933, XXV, 428-30.

⁸ W. E. Stone, *The Carbohydrates of Wheat, Maize, Flour, and Bread and The Action of Enzymic Ferments upon Starches of Different Origin* (U.S. Department of Agriculture, Office of Experiment Stations Bulletin 34), 1896, p. 28.

⁹ J. R. Katz, *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers* ('s-Gravenhage, van Langenhuysen, 1917), Part 2, p. 23.

¹⁰ W. Jago and W. C. Jago, *The Technology of Bread-Making* (London, Simpkin, Marshall, Hamilton, Kent, 1911), pp. 81, 428.

¹¹ R. Whympers, "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.

¹² Verschaffelt and van Teutem, *op. cit.*; A. Maurizio (*Die Nahrungsmittel aus Getreide* [Berlin, Parey, second edition, 1924], I, 350) observed that large and small granules behave alike.

¹³ C. L. Alsberg, "Starch in Flour," *Cereal Chemistry*, November 1927, IV, 485-92.

in the oven while being converted into bread cause changes in the water capacities of the constituents and a fundamental change in water distribution. Gluten, because coagulated, loses water capacity; starch gains it. Presumably this is accompanied by some transfer of water from gluten to starch, and this transfer must depend to some extent upon the spatial relations of the starch granules to the gluten. Possibly an explanation is here to be found for the fact that some types of bread grow stale more rapidly than others (see below).

Probably the starch granules have been converted into an extremely concentrated jelly. But many dry jellies—for example, dry gelatin—have great avidity for water; they swell while absorbing it. A concentrated starch jelly, of which the granules after baking are probably composed, would be avid for water.

In summary, we may say that starch shares at least equally with gluten in determining the absorption of flours—possibly it may even hold more water. In different types of flour, the starch is in different relations to the gluten. In hard-wheat flour, nearly all of the starch is surrounded by gluten; very little of it is free. Therefore, most of the starch of such flours is more or less protected from the attack of such agents as diastase. In soft-wheat flours, contrary conditions obtain. The location of the starch is undoubtedly a factor in determining the rate of fermentable-sugar formation by diastase in dough and therefore the initial rate of panary fermentation, but it is not possible to say what is the importance of this factor relative to the numerous others involved in the diastatic powers of flour and the fermentation rates of doughs. Finally, in the oven, starch gains in water-absorbing power, while gluten loses, and a redistribution of water in the loaf different from that in dough follows.

¹ R. J. Katz, "Gelatinization and Retrogradation of Starch in the Bread Staling Process," in Walton, *op. cit.*, Part 1, pp. 100-117.

² For a fuller discussion of retrogradation the reader is referred to Oppenheimer, *op. cit.*, Vol. I, Part 9, pp. 661 and 681-82.

³ "Gelatinization and Retrogradation of Starch in the Bread Staling Process."

Behavior of starch in bread.—This redistribution, however, is probably not permanent, for starch jellies change their state. In time, they show the phenomenon of syneresis (see above), and Katz¹ has made this the basis of a hypothesis regarding the manner in which bread goes stale. It has long been known that drying out is not the reason why bread grows stale; it shows the characteristics of staleness long before it has lost appreciable amounts of water. Indeed, bread placed in a hermetically sealed container in which it cannot dry out becomes stale about as soon as in air.

The behavior of starch paste upon which Katz bases his hypothesis is sometimes known as "retrogradation." In time, the starch in pastes undergoes a change: the paste becomes harder and tougher and water separates from it. In a system consisting of starch gelatinized in so much water that it is merely a cloudy viscous liquid or a very thin jelly, much of the starch ultimately settles out leaving supernatant liquid which contains some starch substance in solution. French investigators interpret these phenomena as indicating that a part of the starch which has been changed by the gelatinizing process gradually returns to its original state in the unaltered granule. For reasons which it is unnecessary to detail here, a much more probable explanation is that the phenomenon is merely due to change of the state of aggregation of the starch whereby, as explained above, the molecules clump together in larger aggregates and thereby lose power to hold water.² If this occurs in bread, there must in time again be a redistribution of water in the loaf. There is as yet no way to demonstrate the occurrence of such a redistribution of water by experiment, but it is a fact that as bread goes stale the amount of soluble starch that can be extracted from it with water becomes less.

Furthermore, the change in gelatinized starch which is termed retrogradation takes place more rapidly at lower temperatures than at higher ones; and Katz³ has shown that the rate at which bread grows stale passes through a maximum at -2° to -3° C. At the temperature of liquid air (-185° C.) and also between $+60^{\circ}$ C. and $+90^{\circ}$ C., bread remains fresh for a long time. On this behavior of

bread, Katz¹ has based a commercial method for controlling the rate of growing stale of bread.

Katz has also proposed a method for determining the degree of staleness of bread based on the observation of Lehmann² that fresh bread imbibes more water and swells more than stale bread. The method is as follows: A weighed piece of bread crumb is disintegrated in water and the suspension forced through a sieve. The resulting finer suspension is made up to a known volume by adding water, poured into a graduated cylinder, and allowed to settle. The volume of the sediment is noted and compared with that of fresh bread crumb similarly treated. The staler the bread, the smaller the volume of the sediment as compared with that of fresh bread.

Whether or not the hypothesis of Katz proves to be the final explanation of why bread grows stale, it seems quite certain that in the process starch plays the major rôle.

Katz's hypothesis applies only to bread crumb and not to crust. In fresh bread, the crust is crisp and brittle; as bread begins to grow stale, the crust becomes soft and pliable. This is due to an increase in the moisture content of the crust. In the oven, the crust, being at the surface of the loaf, becomes drier

¹ *Het Oudbakken Worden van het Brood in Verband met het Vraagstuk van den Nachtarbeid der Bakkers.*

² K. B. Lehmann, "Hygienische Studien über Mehl- und Brot. Theil V: Beiträge zur physikalischen Beschaffenheit des Brotes," *Archiv für Hygiene*, 1894, XXI, 215-67, especially p. 238.

³ E. T. Reichert, *The Differentiation and Specificity of Starches in Relation to Genera, Species, etc.* (Carnegie Institution of Washington Publication 173), 1913.

⁴ There is much confusion in the nomenclature. Some authors term Meyer's α -amylose "amylopectin," a term that is objectionable because this substance has none of the characteristic chemical properties of pectins; nor does it serve similar functions. The β -amylose of Meyer is often termed simply "amylose." It has seemed best in this study to follow H. C. Sherman and his school in retaining the nomenclature originally introduced by A. Meyer in 1895, in his *Untersuchungen über die Stärkeköerner* (Jena, Fischer, 1895).

⁵ T. C. Taylor and J. M. Nelson, "Fat Associated with Starch," *Journal of the American Chemical Society*, August 1920, XLII, 1726-38; H. A. Iddles, *Separation of the Amyloses in Some Common Starches* (Dissertation, Columbia, 1925).

than the crumb, and some of the starch is changed to dextrines, quite hygroscopic substances. In consequence, after the loaf has cooled, the dry crust attracts moisture from the moister crumb beneath it, whereby the crust becomes softer and more pliable.

CONSEQUENCES OF VARIABILITY IN THE NATURE OF STARCH

Thus far we have assumed that starch is the same in all flours. Only differences in the spatial relation of the starch granules to the gluten matrix have hitherto been considered. We have next to determine whether the physical and chemical character of the starch itself is the same in all flours, and, if it is not, to what extent the variability of the starch may affect the behavior of flour in doughing, fermentation, and baking.

The properties with respect to which starch may be conceived to vary may be grouped into the following categories:

Variability with respect to chemical composition.

Variability with respect to size and size distribution of granules.

The state of the granules—whether intact or injured.

Variability with respect to water-holding capacity.

Variability with respect to resistance to diastase.

Variability of starch in chemical composition.—Until recent decades the belief prevailed that, chemically speaking, all starches are identical. In 1913 Reichert³ brought forward evidence that different starches reacted differently to various chemical reagents. In recent years it has been shown by a number of investigators that starch is not a single chemical individual but that the bulk of the granule consists of two substances which A. Meyer termed α -amylose and β -amylose.⁴ Besides these, small amounts of silica, of iron, and of hemicellulose have been reported. Other mineral substances occur accidentally because of the great adsorptive power of the granules.

Alpha-amylose contains an acid, either phosphoric acid or a fatty acid,⁵ as a constituent part of its molecule, whereas β -amy-

lose contains none.¹ The α -amylose of wheat starch is hardly, if at all, soluble in cool water and contains phosphoric acid; the β -amylose is soluble and is free from phosphoric acid.² Alpha-amylose is rather resistant to decom-

position by weak hydrochloric acid, whereas β -amylose breaks down readily into sugars.³ Furthermore, malt diastase attacks α -amylose more slowly than β -amylose.⁴

It has been established that the percentages of α -amylose and of β -amylose vary from species to species.⁵ It may therefore be regarded as definitely proved that the starches of different species have different chemical composition. Iddles⁶ has even found differences in the percentages of α -amylose and β -amylose in different samples of starch of the same species (corn, rice, potato).

¹ Compare, however, A. R. Ling and D. R. Nanji, "Studies on Starch. Part I. The Nature of Polymerised Amylose and Amylopectin," *Journal of the Chemical Society* (London), *Transactions*, 1923, CXXIII, 2666-88.

² 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.

Beta-amylose should not be confused with the "soluble starch," so-called, of chemical literature. This is starch that has acquired solubility by chemical treatment. It is altered starch that does not occur as such in the natural granules. Beta-amylose occurs as such in the granules, for it may be extracted from them by first shattering the granules and then dissolving in water. There is no reason to believe that merely cracking granules mechanically produces any chemical change.

³ T. C. Taylor and H. A. Iddles, "Separation of the Amyloses in Some Common Starches," *Industrial and Engineering Chemistry*, July 1926, XVIII, 713-17.

⁴ H. C. Sherman and J. C. Baker, "Experiments upon Starch as Substrate for Enzyme Action," *Journal of the American Chemical Society*, September 1916, XXXVIII, 1885-1904.

⁵ Ling and Nanji (*op. cit.*), however, have stated that α -amylose and β -amylose practically always occur in the ratio 2 : 1. Taylor and Iddles found relatively much more β -amylose.

⁶ *Separation of the Amyloses in Some Common Starches* (Dissertation).

⁷ *Op. cit.*

⁸ C. E. Mangels, "Varietal and Regional Variations in Properties of Wheat Starches," *Cereal Chemistry*, October 1934, IX, 571-85.

⁹ However, there is some evidence that the α -amylose of different kinds of starch may vary in phosphoric-acid content, for Samec has reported that in different starches all the phosphoric acid is not bound with equal firmness (M. Samec and H. Haerdtl, "Studien über Pflanzenkolloide, IX. Zur Kenntnis verschiedener Stärkearten," *Kolloidchemische Beihefte*, Heft 12, 1919, XI, 281-300). Moreover, several investigators have found that extraction with dilute hydrochloric acid removes a variable fraction of the phosphoric acid from natural starch grains. Furthermore, there is some evidence that the β -amyloses from different starches are not identical (cf. J. J. Lynst Zwikker, "L'action des enzymes amylolytiques sur les grains d'amidon naturels et la structure colloïdale de l'amidon," *Recueil des travaux botaniques néerlandais*, 1921, XVIII, 1-102). These are questions that await a final solution.

¹⁰ A Fernbach, "Quelques observations sur la composition de l'amidon de pommes de terre," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, February 15, 1904, CXXXVIII, 428-30.

As yet no direct determinations of the proportions of α -amylose and of β -amylose in the starch from different samples of wheat seem to have been made. Reichert⁷ reached the conclusion that the starches of different wheats react very similarly to the reagents he employed but that the starch of emmer, *Triticum dicoccum*, is more sensitive to these reagents than that of common wheat, *T. vulgare*. Mangels⁸ has found that the starches from different kinds of wheat contain different percentages of phosphoric acid and that the same variety may vary in this regard in different seasons. Since the phosphoric acid is contained in the α -amylose and not in the β -amylose, it follows that percentage of phosphoric acid in wheat starch is an index to the percentage of α -amylose it contains.⁹ Mangels' observations therefore indicate that there is probably more α -amylose (and correspondingly less β -amylose) in a starch sample with a high phosphoric-acid percentage than in those with a low percentage. Wheat starches may therefore differ in their chemical composition.

This inference is supported by the observation of Fernbach¹⁰ upon potato starch. He washed potato starch with dilute hydrochloric acid and then separated it into large and small granules by fractional sedimentation. The small granules contained appreciably greater percentages of phosphoric acid than the larger ones. This would indicate that small potato-starch granules contain more α -amylose than large ones.

It remains to be determined whether wheat-starch granules of different sizes contain different proportions of phosphoric acid and,

therefore, different proportions of α -amylose. If it turns out that they do, then this fact may well explain some of the differences in the behavior of different wheat starches to be discussed below, for we know that they differ with respect to granule size and we also know that α -amylose and β -amylose possess different chemical and physical properties.

Variability of starch with respect to size and size distribution of granules.—Reichert¹ seems first to have claimed that the size, shape, and other properties of starch granules are characters differing from variety to variety of the same species and heritable. Darbishire² and Gregory³ found that smooth-seeded garden peas have simple starch grains, whereas wrinkled-seeded peas have compound ones, the component granules of which are smaller in size than the simple granules of smooth-seeded peas. Intermediate varieties that are pitted rather than wrinkled have simple grains. If the different horticultural varieties of a single species like the garden pea show

such great variability in the character of their starch grains, it is reasonable to expect other species, such as wheat, also to show analogous variations.

As we have seen, wheat-starch granules vary in size; while all sizes occur over the size range most of them are either large or small. Armstrong⁴ found that the small granules range in size from 3 to 5 μ and the largest from 30 to 35 μ . Naudain⁵ divides them into two classes: those less than 7 μ and those more than 7 μ in diameter. The size of the granules and the proportions of small and large granules are somewhat different in the several species of the wheat genus, *Triticum*, but the differences are not very great except in the case of *Triticum monococcum*, or Einkorn, which has appreciably smaller granules than the common wheats.⁶ Buchanan and Naudain⁷ found the size of the starch granules different in different varieties of the same species, and on the whole the strongest wheats tended to have the smallest granules. This is quite in accord with the observations of Holzner⁸ and of Thausing⁹ that vitreous barley kernels contain a relatively smaller number of large starch granules than soft ones, a fact definitely corroborated by Johannsen,¹⁰ who by comparing corresponding portions of the endosperm of hard and soft barley kernels from the same harvest established that hard kernels contain a much larger number of small granules than soft ones. One may encounter analogous differences in a batch with only vitreous kernels.

It has long been known that the larger granules of any given starch gelatinize at lower temperatures than the smaller ones,¹¹ though some starches exhibit the opposite behavior.¹² Nägeli long ago observed that the larger granules of potato starch begin to gelatinize at 55° C., whereas the smallest granules do not begin to gelatinize until a temperature of 65° C. is reached. Nyman¹³ made similar observations and suggested that this might be due to the fact reported by Lenz¹⁴ that the membranes of the larger grains are thinner than those of the smaller ones. The reason may, however, be merely that in swelling large grains necessarily develop greater internal pressures per unit of granule surface

¹ *Op. cit.*

² A. D. Darbishire, "On the Result of Crossing Round with Wrinkled Peas, with Especial Reference to Their Starch-Grains," *Proceedings of the Royal Society* (London), 1908, Series B, LXXX, 122-35.

³ R. P. Gregory, "The Seed Characters of *Pisum sativum*," *New Phytologist*, December 22, 1903, II, 226-28.

⁴ E. F. Armstrong, "The Chemical Properties of Wheaten Flours," *Journal of the Board of Agriculture*, 1910, XVII, Supplement 4, pp. 45-52.

⁵ G. G. Naudain, "Study of the Properties of Wheat Starch and the Baking Qualities of Flour," *American Food Journal*, May 1925, XX, 251.

⁶ L. Eynon and J. H. Lane, *Starch. Its Chemistry, Technology and Uses* (Cambridge, Heffer, 1928), p. 79.

⁷ J. H. Buchanan and G. G. Naudain, "Influence of Starch on Strength of Wheat Flour," *Industrial and Engineering Chemistry*, October 1923, XV, 1050-51.

⁸ Cited by Johannsen, *op. cit.*

⁹ *Ibid.*

¹⁰ *Op. cit.*

¹¹ R. Wymper, "Microscopical Study of Changes Occurring in Starch Granules during Germination of Wheat," in *Seventh International Congress of Applied Chemistry, London, May 27 to June 2, 1909* (London, Partridge and Cooper, 1910), Section VI A, pp. 7-13.

¹² Reichert, *op. cit.*

¹³ *Op. cit.*

¹⁴ W. Lenz, in *Arbeiten aus dem Pharmazeutischen Institut der Universität Berlin*, 1910, Vol. VII; cited by Nyman, *op. cit.*

than small ones.¹ Naudain² found that the larger granules of wheat starch swelled relatively much more than the small ones, which may indicate that internal pressure may have much to do with the different behavior of small and large granules. Naudain also found the small granules to resist swelling much more than large ones, but his findings were based on only two flours. They must therefore be regarded as merely suggestive until confirmed with more samples.

Very probably variability in size distribution accounts for the differences in gelatinization temperatures of granules and in the viscosity of pastes that have been observed in different varieties of starch from the same species. Dox and Roark³ found that the gelatinization temperatures of thirteen varieties of maize starch ranged from 64.1° to 71.1° C.⁴ Francis and Smith⁵ made analogous observations. Rask and Alsberg⁶ have shown that the viscosity of pastes made from the starches of different varieties of wheat varies greatly. One of the factors that determines the viscosity of pastes is the size to which the individual granules swell.⁷ If Naudain's statement that small and large wheat-starch granules swell to different sizes relatively is con-

firmed, it may well prove to be that differences in the size distribution of the granules account in part for the differences in the viscosities of the pastes of starches from different horticultural varieties of the same species.

Grewe and Bailey,⁸ contrary to Buchanan and Naudain⁹ and to Naudain,¹⁰ were unable to find any direct correlation between granule size and baking quality. They concluded that differences in the properties of starch that are related to baking strength of flour or to diastatic activity must be attributable to properties of the starch other than those involved in the size of the granule alone. These conclusions were based on the measurement of the granules from seventeen flour samples.

Naudain,¹¹ again using but two samples, found that small granules imbibe relatively less water than large ones, but Grewe and Bailey,¹² using seventeen samples, were unable to discover any correlation between granule size and heat of imbibition such as one might expect if granules of different sizes possessed different powers of combining with or imbibing water. However, the gelatinization of starch is a complex phenomenon,¹³ and the results of Naudain and of Grewe and Bailey are not necessarily contradictory.

In this connection, one further question needs consideration. As we have seen, small granules tend to swell at higher temperatures than large ones, and they also swell more slowly. It follows that in the oven large granules will begin to swell first. In doing so they must absorb water and thereby affect the plasticity of the baking dough. If the average granule size is small, this effect would come later than if the average size is large. The longer the dough remains plastic, the larger, presumably, the spring in the oven, other things being equal. And so it may be that in this way granule size is one of the numerous factors that determine the volume of the baked loaf.

Diastase attacks intact granules at the surface. It is obvious that small granules expose a proportionately greater surface than large ones. Therefore, other things being equal, diastase should form sugar more quickly in flours with small-grained starches than in those with large-grained ones. Such flours

¹ C. L. Alsberg, "Studies upon Starch," *Industrial and Engineering Chemistry*, February 1926, XVIII, 190.

² *Op. cit.*

³ A. W. Dox and G. W. Roark, Jr., "The Determination of Gelatinization Temperatures of Starches by Means of an Electrically Heated Chamber on the Microscope Stage," *Journal of the American Chemical Society*, April 1917, XXXIX, 742-45.

⁴ Eynon and Lane, *op. cit.*, p. 48.

⁵ C. K. Francis and O. C. Smith, "The Determination of the Gelatinizing Temperature of the Starches from the Grain Sorghums by Means of a Thermo-Slide," *Journal of Industrial and Engineering Chemistry*, June 1916, VIII, 509-11.

⁶ O. S. Rask and C. L. Alsberg, "A Viscosimetric Study of Wheat Starches," *Cereal Chemistry*, January 1924, I, 7-26.

⁷ Alsberg, "Studies upon Starch."

⁸ E. Grewe and C. H. Bailey, "The Concentration of Glutenin and Other Proteins in Various Types of Wheat Flour," *Cereal Chemistry*, May 1927, IV, 230-47.

⁹ *Op. cit.*

¹⁰ *Op. cit.*

¹¹ *Ibid.*

¹² *Op. cit.* Cf., however, Jago and Jago, *op. cit.*, p. 322.

¹³ Alsberg, "Studies upon Starch."

should exhibit greater diastatic power and doughs made from them should begin to ferment at a faster rate. Perhaps the size of the granules is the key to the observation of Collatz¹ that the starch of strong flours appears to be more easily hydrolyzed by diastatic ferments than that of weaker ones. However, Grewe and Bailey, as stated above, were not able to demonstrate any relationship between granule size and diastatic power (see also below).

But the area of surface exposed to diastase action may not be the only factor that determines susceptibility to diastatic attack. Johannsen² found that the smaller granules of barley have thicker walls and are firmer—observations in harmony with those of Lenz.³ Furthermore, it is probable, as we have seen, that the chemical composition of granules of different sizes is different and this, too, may be a factor in determining the variability in resistance to diastase, which has been established by Whymper,⁴ Collatz,⁵ and Rumsey.⁶ Obviously the resistance of starch granules is the resultant of a number of factors; to what extent susceptibility to diastatic attack is a function of granule size needs further investigation.

In barley the starch in the outer layers of the endosperm and toward the tip of the kernels consists of quite small granules, but there are small granules in the interior also. In

¹ F. A. Collatz, *Flour Strength as Influenced by the Addition of Diastatic Ferments* (American Institute of Baking Bulletin 9), 1922.

² *Op. cit.*

³ *Op. cit.*

⁴ "Microscopical Study of Changes Occurring in Starch Granules during Germination of Wheat."

⁵ *Op. cit.*

⁶ L. A. Rumsey, *The Diastatic Enzymes of Wheat Flour and Their Relation to Flour Strength* (American Institute of Baking Bulletin 8), 1922.

⁷ Johannsen, *op. cit.*

⁸ Gregory, *op. cit.*

⁹ Alsberg and Perry, "The Effect of Grinding upon Starch and Starch Pastes."

¹⁰ E. P. Griffing, cited in Alsberg, "Studies upon Starch."

¹¹ This phenomenon is not peculiar to starch. It is well known that grinding cellulose (wood pulp) very fine increases its affinity for water (cf. J. R. Katz, "Die Quellung," *Ergebnisse der Exakten Naturwissenschaften*, 1924, III, 347).

general they grow larger from the periphery inward,⁷ and this is true also for garden peas.⁸ While similar observations do not seem to have been put on record for wheat, it is to be assumed that the same condition obtains. As we have seen, in the modern process of milling, flour is produced separately from different parts of the berry; these fractions or "streams" are combined by the miller to produce the several grades of flour. As we have also seen, these streams differ in respect to the location of the starch and in respect to their diastase content. To these differences, we may now add differences in the size of the starch grains; those streams coming from the outer regions of the endosperm should tend to have larger proportions of small granules as compared with those from the interior. This may be a further factor contributing to differences in the quality of the different streams.

Effect of injury on starch granules.—As already pointed out, the starch granule in its natural state is wholly insoluble in cold water. If, however, it is injured mechanically—if, for example, a bit is chipped out of its circumference—it swells at the site of injury and some of its substance dissolves. The more completely the granule is shattered, the greater the amount dissolved.⁹ No very great force is necessary, although the microscopic size of the granules makes it technically difficult to apply what little force is required.

That the injured granule swells is shown by the fact that a 10 per cent suspension of ground-potato starch in cold water is at first merely sirupy and viscous. In time, it becomes much thicker and may ultimately form a mechanically fragile jelly.¹⁰ Therefore, a flour with many injured granules absorbs more than if it had few or none.¹¹ The dough of a severely overground flour has a somewhat modified consistency and tends to exhibit a shiny surface probably due to dissolved starch.

Very few dyestuffs stain intact unheated starch granules, but injured ones stain readily at the site of the injury and staining is confined to this area. Granules swollen by heating in water also stain, but the entire granule takes up the dye throughout. Hence, it is easy to detect injury to, or swelling of, granules by

staining them, for example, with Congo red. The presence of injured granules in flour may readily be detected in the following way: Place a tiny bit of the flour on a glass slide, add a drop or two of water containing a little of the dye, Congo red, and observe under the microscope. Most of the starch granules will remain unstained, but wherever a granule has been injured it takes up dye at the site of the injury and usually it can be seen to be swelling at this spot. With the swelling, some of its substance is going into solution. Another method is to stain with an iodine solution so dilute it tinges intact granules but faintly. Injured granules will be seen to be stained intensely at the site of injury.¹ Injury may also be detected by examining with a polarizing microscope. The injured granules have more or less lost their birefringence.²

Diastase acts but slowly upon ungelatinized starch; but it has long been known that sugar is formed with great rapidity by diastase acting upon mechanically injured raw starch grains.³ Indeed, there is little difference between the rate of sugar formation from shattered granules and from boiled ones.

Moreover, as already pointed out, injured

granules give off more or less starch to the surrounding watery medium. Wanklyn and Cooper,⁴ Alsberg and Griffing,⁵ and also Shollenberger and Coleman⁶ have shown that overgrinding increases the portion of flour soluble in cold water. A part of this is starch which in the dissolved state is more susceptible to attack by diastase than intact starch granules.

It follows that if a flour contains appreciable numbers of injured starch granules it must exhibit greater diastatic power than if it contained few of them, for the dissolved starch and the injured granules are very readily attacked by diastase. Such a flour would exhibit more rapid initial dough fermentation, for the diastase acting upon dissolved starch and injured granules would make sugar rapidly available to the yeast. It should be possible to remedy deficient diastatic power of some flours by overgrinding them slightly to increase the injured granules or by blending them with a small amount of heavily overground flour. Alsberg and Griffing⁷ found that heavily overground flour when doughed begins to ferment very much more vigorously than it did before it was overground, and this has been confirmed by Shollenberger, Marshall, and Hayes,⁸ and by Malloch.⁹

A number of investigators at the University of Minnesota¹⁰ have found that an appreciable amount of sugar is formed very early in dough. It may be that it originates from injured granules, for these must always be present though in ordinary flours probably in small numbers. Perhaps the augmentation of early sugar formation by severe mixing is to be attributed to the speedy bringing of diastase in contact with such granules. It is of course also conceivable, though it seems improbable, that severe mixing injures granules. In any event, in future comparisons of the diastatic power of different wheats, it will be necessary to make certain that in the grinding of flour from them no undue numbers of starch granules have been injured.

In interpreting the effects of overgrinding upon flour, one must take into consideration that all of its diastase does not readily dissolve. Ford and Guthrie¹¹ have shown that to get the maximum of diastase into solution it

¹ Scheffer, "Ueber den Nachweis von mechanischen Beschädigungen der Staerkekoerner," *Zeitschrift für das gesamte Getreidewesen*, May-June 1919, XI, 41-43.

² *Ibid.*

³ H. T. Brown and J. Heron, "Contributions to the History of Starch and Its Transformations," *Journal of the Chemical Society (London), Transactions*, 1879, XXXV, 596-654; L. Maquenne, A. Fernbach and J. Wolff, "Rétrogradation et coagulation de l'amidon," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, January 4, 1904, CXXXVIII, 49-51; L. Maquenne, "Sur la nature de la féculé crue," *ibid.*, February 8, 1904, CXXXVIII, 375-77; E. P. Griffing, unpublished work cited in C. L. Alsberg, *The Role of Starch in Bread Making*, in Walton, *op. cit.*, Part 1, p. 91.

⁴ J. A. Wanklyn and W. J. Cooper, *Bread Analysis. A Practical Treatise on the Examination of Flour and Bread* (London, Kegan, Paul, Trench, Trübner, 1881).

⁵ C. L. Alsberg and E. P. Griffing, "Effects of Fine Grinding upon Flour," *Cereal Chemistry*, November 1925, II, 325-44.

⁶ *Op. cit.*

⁷ "Effects of Fine Grinding upon Flour."

⁸ *Op. cit.*

⁹ *Op. cit.*

¹⁰ Reported by Skovholt, *op. cit.*, pp. 60 ff.

¹¹ *Op. cit.*

is necessary to digest the flour with proteolytic enzymes, for apparently the proteins of flour in some manner lock up a part of the diastase. If they do so by mechanically surrounding the diastase so it cannot be reached by water, then fine grinding should set more of the diastase free and thus increase the diastatic power of flours. The effects, then, of overgrinding are rather complex.

Shollenberger and Coleman¹ believe that in commercial practice overgrinding to an extent great enough to be of practical significance does not occur. However, ordinary commercial milling presumably injures at least some of the granules, for the cold-water-soluble carbohydrate material is greater in flour than in grain. This is probably due to some injurious effect upon starch grains during milling. It is well known to millers that heavy grinding, or handling in horizontal conveyors, tends to impair certain properties of the flour produced from middlings. This is probably due to a number of causes.² Perhaps injury to starch is among them. At any rate Miller attributes the "instability" and the poor keeping quality of flours milled from wheat stocks that are too dry to the formation of an excessive amount of soluble starch by the milling process.³ Of course no "soluble starch" is formed (see p. 245) but β -amylose is released. Such flours undoubtedly include unusually large numbers of injured starch granules which permit β -amylose to diffuse and disperse, i.e., to dissolve out at the points where the granule is injured, into the free water of the dough. Perhaps such flours are more hygroscopic than normal flours. If they are—and this remains to be determined—then their greater "instability" may be accounted for, since moist flours tend to spoil.

¹ *Op. cit.*

² Bailey, *op. cit.*, pp. 284–87.

³ E. S. Miller, "The Significance of Moisture," *Northwestern Miller*, September 30, 1925, CXLIII, 1428.

⁴ Alsberg and Griffing, "Effects of Fine Grinding upon Flour."

⁵ A. Hesse, "Fermente in der Nahrungsmittelindustrie," in Oppenheimer, *op. cit.*, Vol. IV, Part 2, pp. 306, 323.

⁶ W. Nossian, "Ueber das hygroskopische Verhalten mehrerer Stärkearten," *Journal für praktische Chemie*, 1861, LXXXIII, 41.

But flours with many injured starch granules have much material, β -amylose, dissolved out of the starch granules, as was explained above. This starch requires water for its solution and therefore enters into competition for water with the gluten, the starch, and the other water-soluble constituents of flour. It is therefore only to be expected that overground flours absorb more water than the same flour before it was overground, and this is actually the fact.⁴

Finally, overgrinding is not the only way in which starch granules may be injured. They are injured through diastatic attack when wheat sprouts, but the effects are best considered below in connection with water absorption and diastatic power.

Variability of starch in water-holding capacity.—As has been pointed out, starch is responsible for at least half the absorption of flour. We have also seen that freedom of the individual starch granules and mechanical injury influence absorption, and the possibility that starch-granule size does so has been discussed. We have next to consider whether granules injured otherwise than by fracture and intact granules exhibit differences in their capacity to absorb water.

When wheat sprouts, some of its granules are attacked by diastase and this injures them. According to Hesse,⁵ diastase in attacking the surface of ungelatinized starch granules increases their water-binding power. To this effect upon the starch granules Hesse attributes the fact that doughs made with the addition of commercial diastase preparations stiffen some time after the kneading is over and may therefore be made up thinner, that is, with more water. In such doughs, Hesse states, the water is more uniformly distributed, more firmly bound, and less is given off in baking. Bread yields are correspondingly larger.

Differences in absorptive power of different uninjured starches might be due to (a) differences in the hydration capacity of the starch substance itself, or (b) differences in the physical structure of the granules, rendering them capable of holding more "entrapped" water.

Nossian⁶ has reported that the starches of

different plants absorb different amounts of moisture from an atmosphere of the same humidity, but Grewe and Bailey¹ seem to be the only investigators who have made comparative studies on the hydration capacity of the starches of different wheats. Their method was indirect: the determination of heat of imbibition. They found differences between different samples; these were not correlated with granule size. In view of these findings and in view of the different behavior of different wheat starches in swelling, in gelatinization, and in the viscosity of the pastes they form, it is quite probable that direct measurements may uncover differences in the capacity of different starches to bind water of hydration. The significance of differences in gelatinization and viscosity will be considered below in connection with the analysis of conditions in the loaf. Here we shall consider other forms of swelling only.

Mangels and Bailey² have shown that aqueous suspensions of starches from different types of wheat will vary in viscosity when treated with agents that swell the granules without heat. Later, Mangels³ extended these observations and found further that not merely varietal but also seasonal and regional factors affect the properties of wheat starches, as indicated by the degree of their swelling in the cold under the influence of various swelling agents, such as sodium hydroxide and urea. He reached the conclusion that variation with regional environmental conditions is not due to a single chemical or morphological factor. Seasonal variation indicated "that in

¹ *Op. cit.*

² C. E. Mangels and C. H. Bailey, "Relative Viscosities of Wheat Starches," *Industrial and Engineering Chemistry*, April 1933, XXV, 456-60.

³ *Op. cit.*

⁴ Meyer, *op. cit.*, p. 127.

⁵ H. de Vries, "Leerboek der Plantenphysiologie," in C. A. J. A. Oudemans and H. de Vries, *Leerboek der Plantenkunde* (Nijmegen, Alfen, Noman, 1895), I, 147.

⁶ On the crystalline structure of wheat starch see R. O. Herzog and W. Jancke, "Über den physikalischen Aufbau einiger hochmolekularer organischer Verbindungen," *Berichte der Deutschen Chemischen Gesellschaft*, November 13, 1920, LIII, 2162-64.

⁷ A. F. W. Schimper, "Ueber die Krystallisation der eiweissartigen Substanzen," *Zeitschrift für Kristallographie und Mineralogie*, November 16, 1880, V, 130-68.

⁸ E. P. Griffing, unpublished work cited in Alsberg, "Studies upon Starch."

hot, dry seasons the wheat plant produces wheat starches less susceptible to action of swelling agents than when the starches are produced in seasons of lower temperature and more abundant rainfall." Hot, dry weather tends to favor the production of hard vitreous kernels, and such kernels, as we have seen, tend to have more numerous small granules. Perhaps, small granules are less susceptible to swelling, for, as we have seen, they tend to require a higher temperature for gelatinization.

It has long been known that dry granules swell when brought into water, and the increase in the length of their axes may be as much as 15 per cent or more.⁴ Such shrinking and swelling, unlike swelling in hot water, is not accompanied by any change in structure visible under the polarizing microscope, except that in drying rifts may develop which when granules are swelled again in water do not again close completely. Moreover, drying deprives granules of their power to reassume their former volume when wetted.⁵

This shrinking and swelling without heat of starch granules may seem astonishing in view of the fact that X-ray analysis has shown starch granules to possess crystalline structure,⁶ if by this is meant an orderly arrangement of the atoms and molecules. The bodies we have been accustomed to regard as crystalline have geometrical shapes, do not swell, and could only do so with the sacrifice of their geometric characteristics. However, types of crystals are known that do swell, for example, protein crystals,⁷ and in doing so they change their shape. Moreover, many vegetable fibers, now known through X-ray analysis to possess an orderly arrangement of their molecules, behave very much like starch in that they also swell in cold water.

But drying also affects the power of granules to swell when heated in water. Potato starch dried to a moisture content of 8 per cent and then heated in water was found⁸ to swell to such a size that the area of its largest optical cross section was only 57 per cent of that of the undried starch when it was gelatinized. After allowing the dried starch to remain in contact with the atmosphere and to absorb moisture from it for two days, swelling

increased 10 per cent. This observation is in accord with that of Mangels and Bailey,¹ who found that a wheat starch prepared without drying at a temperature higher than that of the laboratory changed its capacity to swell when it was wetted and redried at 80° C.

These observations of Griffing, moreover, are consistent with those of Mangels, above cited, to the effect that hot, dry weather renders starch less susceptible to swelling than cool, moist weather. In the light of these facts, the statement of Whympers² that the temperature of gelatinization varies with the state of maturity of the starch granules, and the observations of Fernbach and Wolff³ that starch from immature peas is different from that of a mature sample of the same variety, gain significance.

In this connection, it is perhaps worth while to bring to the reader's attention that but little gluten is formed in the development of the wheat berry before its moisture content has dropped to 40 per cent or less.⁴ With further reduction of the water content, the point is approached at which starch in the berry would have to give up water of hydration (36 per cent, according to Rodewald; 30 per cent, according to Newton and Cook; see above). It is to be presumed that as this point is reached the nature of the starch formed must be affected, if indeed starch is still formed so late in the life of the berry. Very possibly the rate at which the berry dries out and ripens determines some of the characteristics of its starch. Certainly we know that

hot, dry weather after flowering tends to raise the protein content of the berry and make it vitreous;⁵ and Johannsen⁶ has found that vitreous barley kernels have more small starch granules than soft kernels. It is stated by certain investigators⁷ that small granules exhibit a higher temperature of gelatinization than large ones, that is, they resist swelling in hot water more. All these observations hang together, so that one is tempted to assume some sort of causal relationship between growing conditions and starch properties.

Further evidence that cultural conditions affect the properties of starch is furnished by the findings of van de Sande-Bakhuyzen,⁸ who found that wheat grown with continuous illumination and under uniform conditions of temperature and humidity produced wheat berries with starch grains that did not show the lamellation or rings that can be seen with the microscope in the starch of ordinary wheat seeds.

The effect of growing conditions which seems to be correlated with granule size and ability to swell may in the last analysis prove to be the expression of chemical composition. As we have seen, starch granules are composed of α -amylose and β -amylose, of which α -amylose alone contains phosphoric acid. As we have also seen, there is reason to believe that small granules contain more phosphoric acid than large ones. One is therefore justified in surmising that small granules contain relatively more α -amylose than large ones. Alpha-amylose when dispersed in water is thick and viscous, whereas β -amylose yields rather thin and mobile solutions. This may well indicate that α -amylose binds more water than β -amylose. If this be true, one would expect small-granule starches with a high phosphoric-acid content and therefore a high α -amylose content to bind more water than those with low content. That this is likely ultimately to be proved to be the case is indicated by the conclusion of Mangels:⁹ "An inverse relationship between phosphorus content and swelling capacity or viscosity is indicated." However, the experiments of Grewe and Bailey,¹⁰ above discussed, point in the opposite direction.

¹ *Op. cit.*

² "Microscopical Study of Changes Occurring in Starch Granules during Germination of Wheat."

³ A. Fernbach and J. Wolff, "Analogie entre l'amidon coagulé par l'amylocoagulase et l'amidon de pois," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, June 5, 1905, CXL, 1547-49.

⁴ For a fuller discussion, see C. L. Alsberg, "Environment, Heredity, and Wheat Quality," *WHEAT STUDIES*, March 1934, X, 229-49.

⁵ *Ibid.*

⁶ *Op. cit.*

⁷ Nyman, *op. cit.*

⁸ H. L. van de Sande-Bakhuyzen, "The Structure of Starch Grains from Wheat Grown under Constant Conditions," *Proceedings of the Society for Experimental Biology and Medicine*, January 1926, XXIII, 302-05.

⁹ *Op. cit.*

¹⁰ *Op. cit.*

In short, while there is as yet little direct evidence on record that different starches bind or absorb different percentages of water, there is much indirect evidence that investigation of this question is likely to show that this is indeed the fact. The few measurements of hydration of wheat starch made by Newton and Cook¹ are suggestive, for their values range from 18 to 30 per cent.

The conclusion seems justifiable that much evidence points to the variability in the properties of starch being a factor in determining the variability in respect to absorption of different flours.

Perhaps such a causal relationship explains the very high absorption and relatively poor baking qualities of flours from certain wheats grown in very hot, very dry localities and harvested very dry (5-8 per cent moisture), for example, some Indian and Persian wheats. Their great absorption is not an indication of great flour strength; it is probably due in the main to the dryness of the starch which gives it very great moisture capacity. But it is possible also that a change in the physical character of the starch is involved, for, as pointed out elsewhere, sharply dried starch does not swell to its original volume when moistened nor does it swell to the same degree when gelatinized. Furthermore, it is probable that excessive drying damages gluten, but this is a question beyond the scope of this study.

We must remember also that in milling such very dry wheats there may be danger that large numbers of starch granules may be injured. To be sure, before the wheat is sent to the rolls it is tempered, that is, it is

moistened. However, moisture can enter the interior of the wheat berry only at the germ. Therefore, in tempering, the bran coat is the portion of the wheat that is moistened and thereby toughened. The miller takes care not to add so much water or to permit the tempering process to take so much time that much moisture enters the endosperm. If the endosperm becomes moist, it is toughened, and when ground between the rolls it tends to flake rather than to crack. It is possible, therefore, that very dry wheats still remain abnormally brittle after tempering, with corresponding danger that in grinding starch granules may be injured. This risk would be greater in softer wheats, like the Persian and Indian wheats, than in hard vitreous ones. To overcome excessive brittleness of very dry wheats, it is often the custom to temper in two stages. A portion only of the tempering water is added at the beginning and the wheat is allowed to stand for as much as two days to give time for some of the moisture to penetrate into the endosperm and render it less brittle. The rest of the water is then added and the wheat held for a few hours longer before grinding.²

The capacity of starch to absorb water during gelatinization by heat is its most important property in the oven. The importance in this regard of size of granules, chemical composition, and injury has already been pointed out; but the past history of a starch seems also to have a marked effect upon its gelatinization temperature. Whympers³ found that the temperature of gelatinization varies with the state of maturity of the starch granule. LaWall and Graves,⁴ Nyman,⁵ and Reichert⁶ state that the gelatinization temperature of a starch freshly isolated from living tissue is different from that of a starch which has been dried previous to gelatinization. Drying potato starch raises the gelatinization temperature from 59° to 65° C. According to Samec,⁷ the length of time a starch has been wet is also a factor modifying its gelatinization temperature.

Furthermore, starch grains very readily absorb ions of calcium, magnesium, potassium, sodium, etc.,⁸ much as does the mineral zeolite or the artificial mineral "permutite," which is used for water softening. The ab-

¹ *Op. cit.*

² Cf. Bailey, *op. cit.*, p. 124.

³ "Microscopical Study of Changes Occurring in Starch Granules during Germination of Wheat."

⁴ *Op. cit.*

⁵ *Op. cit.*

⁶ *Op. cit.*

⁷ M. Samec, "Studien über Pflanzenkolloide. I. Die Lösungsquelle der Stärke bei Gegenwart von Kristalloiden," *Kolloidchemische Beihefte*, December 10, 1912, III, 123-60.

⁸ H. Tryller, "Beiträge zur Chemie der Kartoffelstärkefabrikation," *Chemiker-Zeitung*, November 11, 1920, XLIV, 845-47; Lloyd, *op. cit.*

sorption of different metals seems to affect the physical properties of granules. Fernbach and Wolff¹ found that using water containing lime in the preparation of starch affects the viscosity of the paste. This would indicate that the presence of calcium in the granule affects the temperature at which it gelatinizes and also the degree to which it absorbs water. There are many observations indicating that the mineral-salt content of the water used to make dough is of some influence upon the baking quality of flour.² These effects have been assumed to be the result of action of the salt upon gluten, for salts contained in the wash water, especially calcium, have marked effects upon the properties of gluten as it is washed out of flour.³ Students of these questions have not considered that starch may absorb calcium and may be changed in its physical behavior thereby, thus contributing to the effect of the presence of mineral salts in dough and bread. Yet a part of these effects may well be starch effects.

It is entirely within the range of possibilities that variability in gelatinization temperature is a factor in causing variability of behavior in the oven. If the temperature of gelatiniza-

tion is raised a few degrees, the shift in water which occurs as the dough is converted into bread will be delayed relative to the coagulation of gluten. The spring in the oven, the porosity, and texture of the loaf might well be affected. However, no experimental evidence is available on these points.

Variability of the resistance of starch to diastase.—In preceding sections it has been shown that the number of starch granules that lie free and are unsurrounded by gluten and the number of granules that are injured play their part in contributing to the diastatic power of flour. Granules that have been injured by diastatic attack while still in the wheat before it was milled tend to increase the apparent diastatic power of flour because they are corroded, pitted, and even perforated and therefore expose more surface to attack.⁴ Such granules are especially numerous in flour made from sprouted wheat. For this reason, and also because they contain larger amounts of diastase than flour made from unsprouted wheat, such flours exhibit great diastatic power. Flour deficient in diastatic power may be improved by addition of flour made from slightly sprouted wheat.⁵ Or a little sprouted wheat may be blended with wheat deficient in diastatic power before it is milled.

In years past much work was done upon the resistance of gelatinized starches to diastase,⁶ but these investigations are not significant for present purposes since we are interested in the resistance of raw starch as it occurs in flour. There is now considerable evidence that resistance to diastase varies from species to species and that in a single plant the starch may vary in this respect from organ to organ.⁷

Humphries and Simpson⁸ brought forward evidence to show that the rate at which the starch granules are attacked, and not the activity of the enzyme, is the prime factor that determines the gas-making capacity of a fermenting dough. Rumsey,⁹ on the basis of a review of the literature and his own experiments, reached the conclusion that such differences do exist. Collatz¹⁰ and Collatz and Racke¹¹ found the starch of different flours to possess different powers to resist diastase. Mangels¹² found different flours to differ in the

¹ *Op. cit.*

² For a discussion see Bailey, *op. cit.*, pp. 278 ff.

³ D. B. Dill and C. L. Alsberg, "Some Critical Considerations of the Gluten Washing Problem," *Cereal Chemistry*, September 1924, I, 222-46.

⁴ Malloch, *op. cit.*

⁵ R. C. Sherwood and C. H. Bailey, "Control of Diastatic Activity in Wheat Flour. I. Production of Diastatic Flour and Effect of Large Dosages," *Cereal Chemistry*, March 1926, III, 107-36; "II. Experiments with Flour Milled on a Commercial Scale," *ibid.*, May 1926, III, 163-82.

⁶ This literature is discussed in Oppenheimer, *op. cit.*, Vol. I, Part 9, pp. 640 ff.

⁷ Ziegenspeck, *op. cit.*

⁸ A. E. Humphries and A. G. Simpson, "Gas-Making Capacity as a Factor in the Estimation of Strength in Wheat Flour," in *Seventh International Congress of Applied Chemistry*, London, May 27 to June 2, 1909 (London, Partridge and Cooper, 1910), Section VI A, pp. 27-38.

⁹ *Op. cit.*

¹⁰ *Op. cit.*

¹¹ F. A. Collatz and O. C. Racke, "Effects of Diastase and Malt Extract in Doughs," *Cereal Chemistry*, July 1925, II, 213-27.

¹² C. E. Mangels, "Factors Affecting the Diastatic Activity of Wheat Flour," *ibid.*, September 1926, III, 316-32.

susceptibility of their starch to diastatic attack. He also found durum-wheat starch more readily attacked than starch from hard-red-spring wheat. Hermano and Rask¹ also noted that different wheat starches show significant variation in susceptibility to diastatic action. Malloch² noted differences in different kinds of wheat and in the same kind grown in different localities. His data also indicate that resistance increases with maturity.

There can therefore be no doubt that differences in diastatic power of different flours may depend upon difference in the resistance of their starches and that in this way starch properties may be an important factor in determining the baking quality of flours.

To what can this variability of starches be due? It may well be due to granule size or to chemical composition or to both.

In the discussion of the significance of granule size (see above), it was pointed out that, *a priori*, small-granule starches should yield sugar more rapidly under the influence of a constant proportion of diastase, because they present a larger surface per unit of mass than large granules. This suggestion does not necessarily imply that the individual small granule is more easily attacked by diastase than the large one. As a matter of fact, Barnstein³ has found that large wheat-starch granules are much more rapidly attacked than the small ones. We have, therefore, two factors working in opposite directions. Where there are proportionally many small granules, there is more surface exposed to attack, but more of the granules tend to be relatively resistant and vice versa. The relationships are too complex to warrant a positive statement.

Perhaps the reason why small granules are more resistant to diastase may be that they probably contain more α -amylose (see above), which is more resistant than β -amylose. Moreover, diastase does not attack that portion of

the α -amylose molecule where the phosphoric acid is attached.⁴

SUMMARY

Starch contributes not merely to giving flour and bread their food value and bulk but it also serves the following purposes:

(1) Starch absorbs moisture, and when flour is doughed its starch takes up about as much water as all the other flour components combined. It is responsible for about half of the total "absorption" of flours. While it absorbs only about one-third of its weight of water, it makes up nearly four-fifths of flour—hence, its important part in absorption.

It is impossible to say whether the starches of different wheats absorb different amounts of water; this problem has as yet been insufficiently investigated. Evidence is presented indicating that such differences probably exist. If further study proves this to be true, then variability of wheat starches with reference to their capacity to absorb water may be a factor in determining the absorption of different flours.

In the wheat berry, the starch grains lie imbedded in gluten. In milling, some of the granules are loosened so that they are no longer completely surrounded by gluten; they then absorb water more rapidly and more perfectly. The rate at which a flour absorbs moisture when doughed and probably the total amount absorbed depend to some extent upon the location of its starch granules with respect to the gluten. How many starch granules are freed from their gluten capsules depends upon the kind of wheat that is milled and the fineness to which it is ground. Soft-wheat flours tend to have more of the granules separated from their gluten covering than hard-wheat flours. Grinding a flour fine tends to free large numbers of starch grains and to favor absorption of water.

In the process of milling, some starch granules are injured; in fine grinding a great many may be. Injured granules swell at the site of injury and some of the starch substance dissolves. Therefore, a flour containing many injured granules absorbs more water than it would if it contained none, and it also contains

¹ A. J. Hermano and O. S. Rask, "A Consideration of Certain Reactions of Starches with Special Reference to Enzyme Hydrolysis," *ibid.*, November 1926, III, 361-92.

² *Op. cit.*

³ Cited by Neumann, *Brotgetreide und Brot*, p. 242.

⁴ M. Samec, *Kolloidchemie der Stärke* (Dresden and Leipzig, Steinkopf, 1927), p. 457.

more starch soluble in cold water. In good commercial practice few granules are injured and these phenomena are not important. However, it is well known to millers that heavy grinding or excessive manipulation of middling stocks tends to reduce flour quality; and this is perhaps due in part to injury to starch granules.

(2) Starch sustains fermentation. The enzyme diastase, present in flour, attacks the starch of dough with the formation of sugar which the yeast ferments to alcohol and carbonic acid. The carbonic acid together with water vapor formed during baking leaven the bread. If there were no starch or no diastase in flour, it would be necessary in some manner to furnish small amounts of sugar continuously to the yeast; otherwise leavened bread, as we know it, could not be produced.

The rate at which a flour can produce sugar from starch when doughed is known as its diastatic power. This depends, obviously, both upon how much diastase a flour contains and upon how resistant its starch is to diastatic attack. The resistance of starch depends both upon its location and upon its intrinsic powers of resistance.

If most of the starch is locked up inside clumps of gluten where diastase cannot easily reach it, because diastase diffuses with difficulty if at all through gluten, such starch granules are not attacked. If, however, the granules be free and not surrounded by a protecting envelope, there is nothing to prevent diastase from reaching them. Hence breaking up gluten clumps by grinding, or otherwise, tends to increase the diastatic power of flours.

There is considerable evidence, though not yet enough to be finally conclusive, that the starches of different wheats exhibit differences in their resistance to diastase. It is extremely probable, therefore, that the diastatic power of different flours may vary for this reason. The reason for such variability among wheat starches is unknown. It may be due to differences in the size of the granules or it may be due to differences in chemical composition. There is some evidence that in different wheat starches the percentages of α -amylose and β -amylose are not the same.

Intrinsic power to resist diastase may be

modified in various ways. Starch from sprouted wheat is less resistant than it was before sprouting began. Therefore if flour is made from parcels of wheat containing any material number of sprouted kernels, its diastatic power is increased, in part because its starch is less resistant, in part because sprouted wheat contains much diastase.

Gelatinizing starch, as by heating with water, lessens its resistance to diastase. Therefore, mixing in some scalded flour in dough favors early fermentation; this may also be accomplished by adding boiled potatoes or other gelatinized starchy material.

Injury to granules renders them easily attacked. Therefore not merely does fine grinding increase diastatic power by rendering more starch grains accessible to diastase, but if the grinding is severe enough to injure large numbers of granules these will be attacked rapidly, as will also that portion of the substance of injured granules which becomes dissolved. The diastatic power of such flours is much increased.

(3) Starch is probably the principal substance involved in the growing stale of bread. In the oven, gluten coagulates and loses capacity to hold water while starch is gelatinized to the extent that the water present permits and gains in water-holding capacity. In fresh bread, as a result, starch holds more water and gluten probably less water than in dough.

It is known that the gelatinization temperature of different starches differs somewhat and that in the same sample large granules gelatinize at lower temperatures than small ones. It is also known that the size distribution of the granules is different in different wheats. It may be that the differences in gelatinization temperatures are related to the size distribution of the granules. In any event, differences in the temperature of gelatinization will cause starch to swell and absorb water earlier or later in the oven and thereby affect the plasticity of the dough. It is therefore possible that the nature of the starch affects the "spring" in the oven and the loaf volume. This is a matter for future investigation.

In time, the gelatinized starch in bread undergoes spontaneous changes, and to such change the growing stale of bread has been

attributed. While more study is needed before the mechanism by which bread grows stale may be regarded as wholly solved, it seems clear already that starch plays the major rôle in that mechanism. The growing stale of bread is certainly not due to loss of water, i.e., drying out.

Much of what is presented in this study is hypothetical and speculative. This is deliberate. The aim is to attract the attention of investigators to the study of starch and of its rôle in the preparation of baked products and to indicate some of the problems that await solution.

This study is the work of Carl L. Alsberg

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