OVERDRUK
VERSLAG
SÆRTRYKK
AV BERETNING FRA NORDISK CEREALKJEMIKERFORENINGS
KONGRESS I BERGEN 1950

H. M. R. HINTZER

THE STALING OF BREAD

The staling of bread

Drs H. M. R. Hintzer

(Head of the Cereals Department of the Central Institute for Nutrition Research T.N.O.)

1. INTRODUCTION

The staling of bread has of old been a central problem of bakers, a problem which still needs a solution in spite of the innumerable investigations devoted to the subject by nearly all civilized countries.

In 1942 in the U.S.A. more than 250 millions of loaves were returned to the bakers because they were stale and therefore unsaleable. This meant a loss for human consumption of about 175 thousands tons of wheat. And this occurred in a year in which already all possible precautions had been taken against the waste of foodstuffs (25). According to statistics it may be assumed that between the two world wars about 3 to 5 % of the total bread production was withdrawn from human consumption by staling. Before the first world war this quantity was even estimated to be about 10 % (1).

Such figures show in an outstanding way the great importance of efficiently overcoming this fault. Within the scope of this paper, it is impossible to give a complete discussion of the research work that has contributed to the clarification of this problem during the last 20 to 30 years. Only some broad lines will be reviewed, while fundamental opinions about the principal points will be discussed. For a more extensive study I may refer to the excellent review by Geddes and Bice (13), and publications of Alsberg (1), Cathcart (4), Hutchinson (16) and Pyler (29).

Successively will be dealt with

1. characteristics of the phenomenon;
2. measuring methods;
3. theories;
4. prevention.

2. CHARACTERISTICS OF THE STALING EFFECT

Every consumer of bread knows what staling means. For him it consists of a number of rather disagreeable sensations of taste, which he experiences in eating bread aged more than 24 hours. These disagreeable observations are connected with some definite alterations which have occurred in the crust and in the crumb.

2. 1. Staling of the crust.

While the crust of the fresh bread has a crisp consistency a certain toughness develops in the course of 24 hours. Moreover the pleasant shiny appearance of the fresh loaf transfers into a more or less wrinkled appearance. Finally the taste of the crust, so pleasant in a fresh state, decreases quickly.

2. 2. Staling of the crumb.

The crumb of fresh bread is soft and flexible. In staling considerable alterations occur in the course of 12 to 24 hours. Bread aged 1 day has a dry, hard crumb which crumbles with cutting. This process proceeds in the next days while the taste deteriorates too. The alterations in the crumb contribute to the development of a somewhat bitter taste. English investigators use the expression «Saw dust taste».

The staling of the crumb is the most important of both groups of phenomena. For this reason this problem only will be dealt with in this communication.

The external observations are connected with definite internal physical-chemical conversions. The swelling power of the crumb, which means the quantity of water the dry crumb is able to absorb per unit of dry matter weight, declines rapidly. Moreover a considerable decrease of the soluble carbohydrates occurs. Further the starch of the staled crumb proves to be considerably more resistant to the action of amylase than fresh crumb. Finally essential alterations in the X-ray diagram become manifest. The cause of these changes will be discussed later on. First the measuring of the staling effects based on the alterations mentioned will be reviewed.

3. MEASURING METHODS

3. 1. The measurement of the softness by means of a compressimeter.

A piece of crumb of definite measurements cut from the centre of the loaf is exposed to a certain stress. The compression caused by this action is enlarged and transferred to an index. Generally the apparatus is provided with a device with which the relaxation after removal of the load can be measured too. An apparatus of this kind has been developed in our laboratory (15) and has been called *panimeter* (fig. 1).

3. 2. The measurement of the degree of crumbliness.

Geddes and collaborators (12) have developed a determination of this property. Pieces of crumb of standard measurements are mechanically shaken in a sieve above wire-gauze of fixed mesh during a certain time; the crumbs which have passed the wire are measured and expressed as percentage of the original amount of crumb.

3. *3. Determination of the swelling power.*

According to Katz (17) a standard amount of crumb is ground with water and pressed through a sieve. The crumb paste is diluted with a certain amount of water in a measuring cylinder. After a definite time the volume of the sediment is measured. This figure is characteristic of the swelling power.

Several modifications of this method have been introduced. The most important is the use of the farinograph (11) for the measurement of the consistency. The amount of water absorbed by a certain weight of bread crumb in order to reach a standard consistency is connected directly with the swelling power.

3. *4. Extractable carbohydrates.*

This method means the extraction of a certain amount of crumb with water followed by filtration, precipitation of the

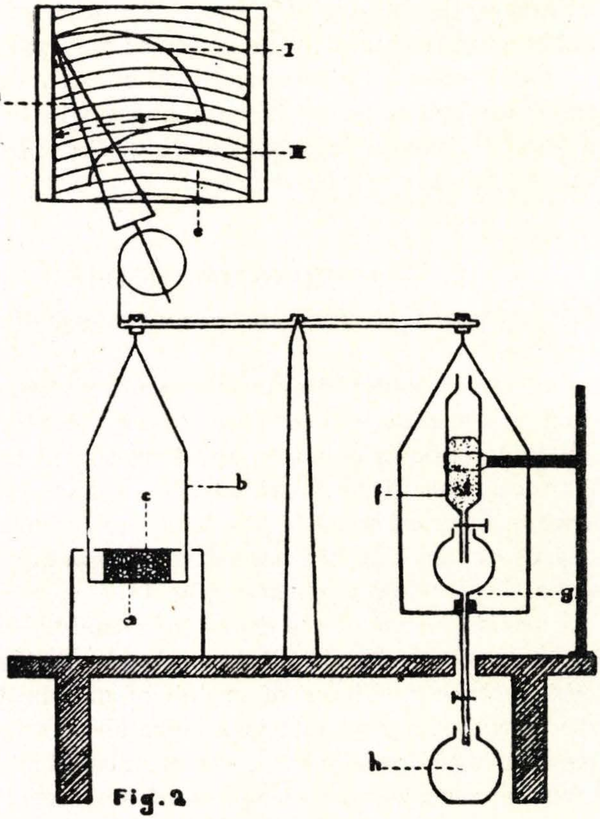

Fig. 1.

Schematical drawing of the panimeter.

carbohydrates with alcohol and finally the weighing of the dried precipitate (19).

3. 5.

The *decrease* of the *resistance* of the *starch* to *amylolysis* is suitable for a method of evaluation too (33). A certain weight of bread crumb is exposed to the action of standard amylase and after certain time the degree of break-down is measured by analysis of the reaction products.

As the concentration of this is lower, the resistance is higher and the degree of staling is also higher.

3. 6.

According to Katz (19, 20) *the change in the X-ray diagram* may be also used as a measure of the staling effect.

Although the alterations mentioned occur simultaneously, they are dominant at different times. Generally it can be said that the reduction of the compressibility, the swelling power and the solubility occur especially during the first 10 hours after baking, whereas the development of crumbliness becomes manifest later on, as a rule not before 24 hours. Remarkably, the consumer judges a loaf aged 10 hours as still practically fresh, although obviously several alterations have occurred. Nevertheless softness, swelling power and solubility are mostly used in order to determine the degree of staling.

This applies particularly to the softness which is highly appreciated by the bread consumer (28).

4. THEORIES

The conversions mentioned above indicate clearly that the staling is not a superficial phenomenon but that it is related to very essential alterations in the material of the bread. About the nature of these changes different theories have been developed in the course of time.

The oldest explanation, which is also the most obvious, is that staling is nothing else than the drying out of the loaf. Indeed the process is generally connected with a loss of moisture. In 1852, however, Boussingault (3) showed that by exclusion of drying, that is storage in a moisture-saturated atmosphere, the staling continues. This shows that loss of moisture cannot be the origin.

Consequently investigators have started to detect more fundamental conversions and in view of the character of the crumb during staling they have thought of certain alterations in the starch complex as the main constituent of the crumb.

In 1902 the French investigator Lindet (24) deduced from the decrease of the quantity of soluble carbohydrates, that during staling the starch is converted into a less peptizable and less hydrated state with liberation of water. The liberated water is partly absorbed by the gluten; the rest remains in a free state and evaporates if the loaf is stored in a dry atmosphere. This conversion called *retrogradation* by Lindet, is reversible as, by heating the crumb above 60° in the presence of sufficient water, a fresh state is reached again.

In the years 1912 to 1937 Katz approached the problem with a series of fundamental investigations that brought him to a theory, which is still accepted, on the whole, nowadays. As criteria for the staling he used the measurement of the swelling power and the determination of the soluble carbohydrates.

At first Katz ascertained that staling is connected with a certain optimum region of moisture content, lying between about 16 and 38 %. Crumb with less than 16 % or more than 38 % moisture can be stored in a fresh state during an unlimited time on the condition that deterioration of microbiological nature is excluded (19). These investigations have been confirmed by recent findings of Geddes (12).

Further Katz observed that staling is not only connected with an optimum moisture region but also with an optimum temperature range. No staling occurs at temperatures above + 60° or below ÷ 30°. The highest rate occurs about some degrees below zero (17, 19, 21).

These observations brought Katz to study whether in practice a loaf keeps fresh better at a very low or high temperature. In chapter 5 we will refer to this again.

Katz observed the same behaviour in investigating starch suspensions in the proportion starch: water = 1 : 1, a concentration similar to the proportion starch : water in the loaf. The suspensions were brought to a swollen state by heating and were then cooled and aged, while these conversions were followed by determination of the swelling power and of the soluble carbohydrates according to the techniques developed for bread crumb. In the same way as before he observed with the aging of the starch paste strong reduction of the swelling power and of the soluble carbyhydrates with gradual liberation of water (19). Moreover he established that the alterations in the X-ray diagram during the conversion of dough into bread crumb, staling and refreshening of the crumb on one hand and of the swelling of the starch suspension, aging of the starch paste and heating of it above 60° on the other hand show exactly the same trend (20). From this Katz concluded that the staling of bread may be reduced to a *reversible conversion* in the structure of the swollen starch grains, accompanied by dehydration, this means expulsion of water.

Later investigations were chiefly built on the ideas of Katz. New fundamental views were not developed.

The American Schoch, however, has approached the staling problem in a new way. Schoch who was strongly affected by the progress in modern starch research (K. H. Meyer, Hanes, Staudinger, Freudenberg, Rundle, Peat, French and Kerr) has considerably enlightened the conception of the staling phenomenon. Before entering into details it is first necessary to deal

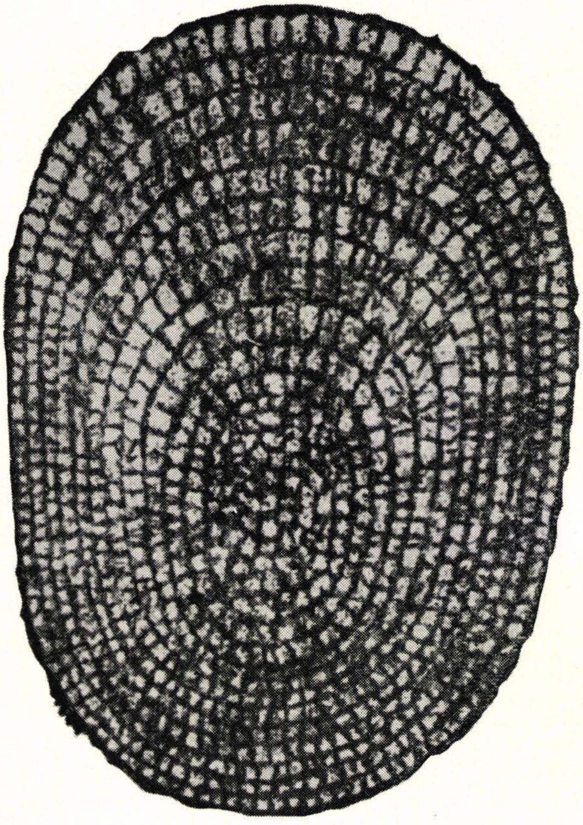

Fig. 2a

Structure of crystallites in the starch grain.

with some elementary ideas about the composition and structure of the starch grain and about the swelling process.

While ten years ago this region of science was still in a chaotic state, during the last years some uniformity in opinons has been developed as a consequence of the application of modern investigation methods. As a synthesis of the most important view points the following conception results.

The starch grain is composed of concentric layers of radially orientated crystallites or micelles (figs. 2 a and 2 b). The

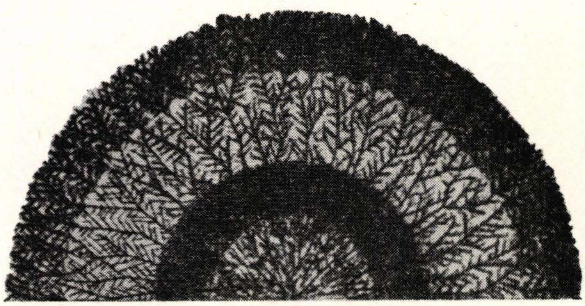

Fig. 2 b
Concentric layers of crystallites.

crystallites consist of two constituents. The first consists of glucose chains orientated near one another and linked by alpha-1,4 glucosidic bonds. This component is called *amylose.* The remainder of the crystallite consists of highly branched rather short glucose chains also linked by alpha-1,4 glucosidic bonds within the branch points 1,3 and 1,6 glucosidic bonds (10, 34). This component, called *amylopectin,* is the main constituent and amounts to 60 to 100 % of the starch grain (fig. 3). The amylose chains are completely and regularly divided between the amylopectin. The branches of the amylopectin of different micelles are coordinated too to a certain extent and create regions of crystalline nature (26). This means that a certain region of this kind may be involved in several micelles at the same time (fig. 4).

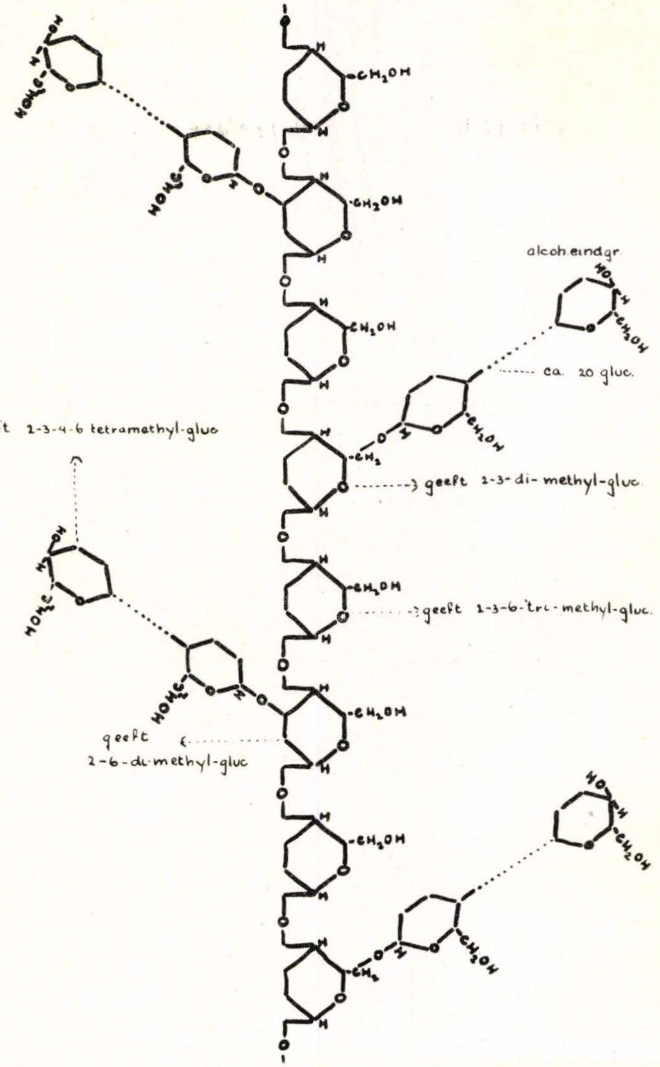

Fig. 3

Structure of branched chains according to Staudinger.

Also about the manner in which the coordinated regions arise a certain conception has been developed (22). It is assumed that secondary bonds arise between the free OH-groups of different branches with the aid of hydrogen bridges. These so-

Fig. 4

Amylopektin micelles in a natural starch grain; the thick parts are crystalline regions between the chains (according to K. H. Meyer).

called cross-links may arise directly or by means of one or more water molecules (fig. 5).

If such starch grains are brought into contact with a restricted amount of water comparable with dough in the bak-

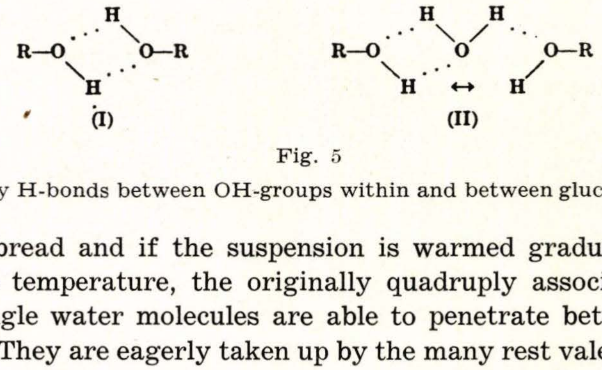

Fig. 5

Secondary H-bonds between OH-groups within and between glucose chains.

ing of bread and if the suspension is warmed gradually to a definite temperature, the originally quadruply associated but now single water molecules are able to penetrate between the chains. They are eagerly taken up by the many rest valences and included as links in the hydrogen bridges (26, 22). Consequently the whole complex will be torn up (fig. 6 and 7). By further heating, more and more water molecules penetrate within and between the micelles and more and more are caught in the hydrogen bridges. Finally the available water has been used up and a conglomerate of partly swollen starch grains results. If a piece of bread crumb is observed under the microscope such

Fig. 6

Amyiopectin micelles torn out of the original configuration by swelling. (according to K. H. Meyer).

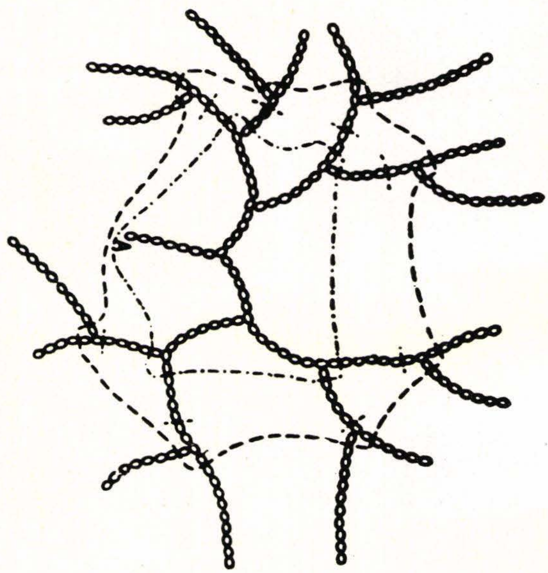

Fig. 7

Swollen amylopectin configuration enlarged (according to K. H. Meyer).

starch grains can be perceived between the gluten membranes.

With gradual cooling of such a swollen grain, which is in fact a small piece of starch gel, a definite arrangement in the gel arises. The glucose chains are beginning to orientate to spirals or helices (fig. 8). Each winding contains 6 glucose units while the 6-CH_2OH-groups of one winding are arranged between the 2 — and 3 — OH-groups of the next winding (8, 9, 14). Consequently the greater part of the rest valences of the CH_2OH- and OH-groups are intramolucularly saturated. This means that fewer OH-groups than originally, remain available for H-bridges between the spirals, so that a part of the original bound water molecules is liberated or more water molecules are involved in the bridges.

Thanks to the orientated structure the spirals are able to coornate loosely according to a simple rhombic (pseudo-hexagonal) scheme (fig. 9), which only needs few cross-links (7, 30). The result is a gel of a loose, flexible and elastic consistency.

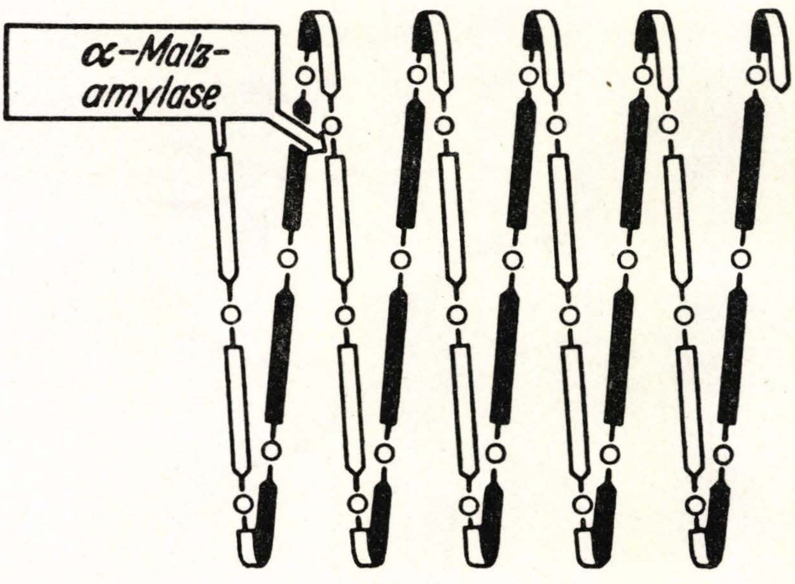

Fig. 8
Helical glucose chains (according to Hanes)

The staling process in the gel starts with the formation of *direct* hydrogen bridges between the CH_2OH- and OH-groups of different chains with liberation of the originally involved

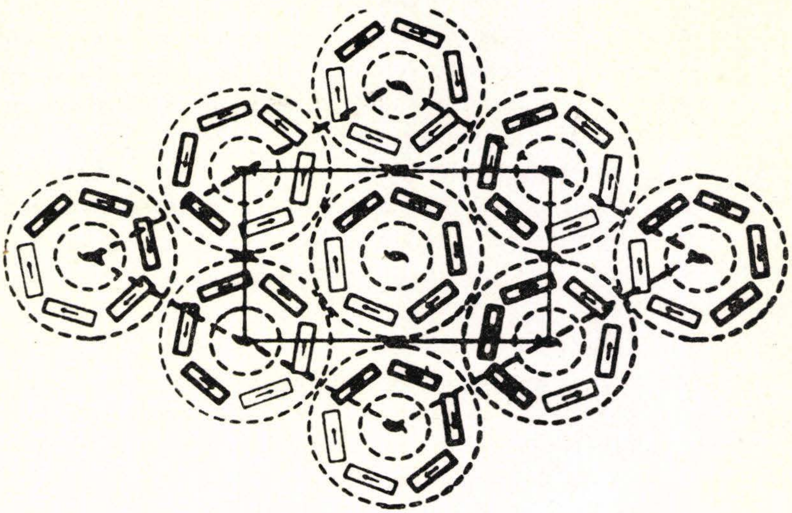

Fig. 9

Rhombic (pseudo-hexagonal) orientation of glucose spirals.

water molecules. These water molecules are expelled (syneresis). On behalf of the formation of these cross-links certain glucose units have to be turned, so that the winding and therefore also the spiral is torn more or less out of the original configuration. This phenomenon will particularly occur with the unbranched amylose chains which in this way get a chance to orientate firmly near one another, linked by several hydrogen bridges. The mutual bonds between the amylose chains are so tight that it is difficult to reverse the phenomenon by heating and to regain the original spiral structure. For this reason retrogradation of amylose is not reversible.

The conversions mentioned before find expression in the X-ray diagram. Obviously the X-ray diagram of freshly swollen starch grains and also of fresh bread crumb points to a simple configuration within and between the chains. This arrangement is of pseudo-hexagonal nature and the diagram is called V-spectrum. On the other hand the X-ray diagrams of unswollen starch grains as occur in the unbaked dough, of aged swollen starch grains and of stale crumb point more to an arrangement *between* than *within* the micelles. In view of the discussion above this means that this arrangement arises by hydrogen bridges between the chains, in other words by cross-links, whereas the chains internally show little orientation and no helical structure (B-spectrum).

In view of the strong tendency to retrogradation of the amylose fraction it is conceivable that former investigators have related the staling effect chiefly to this constituent, in spite of the fact that the amylose is the smallest part of the starch grain.

Schoch (31, 32) states, however, that with staling of swollen starch grains the branched amylopectin chains show also a tendency to a tighter arrangement by cross-links under expulsion of water. This phenomenon is called *internal coacervation.* However, as by the branched structure parallel arrangement is impossible, the bonds have a much looser nature than the links between the amylose chains. This explains why the retrogradation phenomenon may easily be reversed.

Schoch bases his assumption on the observation that the retrogradation of the amylose already occurs during the baking process and eventually too during cooling of the bread. This follows from the extremely small amounts of soluble amylose in the fresh bread.

Several arguments support Schoch's point of view. In the first place he has succeeded in observing with pure amylopectin gels by X-ray investigation the transfer of a simply coordinated structure into a more complicated, less orientated one.

A second argument is the fact that amylopectin, just like bread, retrogrades gradually and reversible contrary to the quick and irreversibly retrogradation of amylose.

A third support for the theory of Schoch is the observation that through whole or partial masking of the side chains of the amylopection molecules e. g. by oxidation of the OH- or CH_2OH-groups or through break down of the side chains under the action of beta-amylase, retrogradation occurs to a much less extent. Further the staling can also be repressed by the addition of aldehydes, which are able to block the rest valences through the formation of loose, complex bonds with the free OH-groups.

Schoch, who had to leave his tests too early, was not able to check by baking tests whether a greater or less degree of blocking of the side chains is indeed correlated with the extent of staling of the bread. If it should be shown that Schoch is right, a new approach is given for combating staling. Such investigations are in progress now in our laboratory.

5. PREVENTION

In principle two ways of approach are possible.

5. 1. Retardation or elimination of the actual retardation process.

The most obvious method is the storage at very low or very high temperature. Concerning the first, investigations were carried out in a bakery in Rotterdam thirty years ago (27). Indeed it was possible to maintain bread in a state equivalent to 8 hours after baking during some weeks by storage at about ÷ 30°. As a consequence of the relatively high costs of this procedure resulting in a higher price of 1¾ cent a loaf, this technique proved not to be suitable in practice. Storing at high temperature, that is at 60° has two disadvantages. In the first place a heavy loss of moisture occurs which influences especially the nature of the crust in an unfavourable way. In the second place there is a good chance for development of certain thermal-resistant micro-organisms like rope. Katz has constructed some apparatus with which the loaves can be stored at a relatively high temperature in an atmosphere of controlled moisture content. In practice, however, this apparatus was not satisfactory (18, 19).

It must be emphasised that there are still more simple means to retard staling to a certain extent. These are a correct choice of the flour and a correct dough and baking procedure. It has been proved that a flour with much gluten of high quality produces bread of better keeping quality than flour with less and inferior gluten. The baking quality of the flour plays actually an important role (1, 16).

Moreover much may be improved by carrying out fermentation in the correct way. Particularly it is important to give sufficient time for fermentation. A fermentation temperature which is not too high and correct punching of the dough are in favour of the keeping quality of the bread, too (16). Involuntarily one is reminded here of the theory of Schoch. Long fermentation means plenty of time for the side chains of the amylopectin molecules to break down to a certain extent. Consequently the chance of cross-links between the chains in the swollen starch complex is decreased.

5. 2. The addition of certain adjuncts (bread improvers).

Generally these adjuncts don't affect the real cause of the staling effect. These adjuncts are able to achieve, however, that certain favourable properties like softness and tenderness are retained during a certain time. Materials of this kind are fats, glycerides, glycerol-mono- and distearates, lecithins, sugars, dextrins, swelling adjuncts (cellulose derivatives, bentonites) and malt extract.

The action of fats and lecithins is chiefly based on a refinement of the structure and consequently a refinement of the crumb walls, resulting in a greater softness and tenderness of the crumb.

The influence of swelling adjuncts can be explained as means for introducing an excess of water in the bread. This means, as has been discussed before, a retarding effect on the staling process. In this connection the favourable effect of the use of a good flour can be explained too. Much and excellent gluten means a strong swelling capacity, by which the water absorption of the dough increases. For the rest the action of these adjuncts are thoroughly discussed in the review of Geddes and Bice mentioned before (13).

A particular place is taken by certain high polymers which have been prepared in several countries during the last years. As a whole these materials exercise a strong surface-active influence. For this reason they have been introduced into several other industries e. g. the cosmetic industry. An outstanding action has been observed with the polyoxyethylenestearate to which is given the following structure (31):

$$CH_3\text{-}(CH_2)_{16}\text{-}\underset{\underset{O}{\|}}{C}\text{-}O(CH_2\text{-}CH_2\text{-}OCH_2\text{-}CH_2\text{-}O)_8\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_{16}\text{-}CH_3$$

Obviously the molecule consists of a chain of 8 oxyethylene-units connected on both sides with a stearic acid, resulting in a remarkable division of hydrophobe and hydrophilic regions.

According to Favor and Johnston (5, 6) this product exercises a remarkably favourable action on the softness and structure of the crumb if added to the dough in quantities of 0,5 to 1 %. In our own laboratory, in collaboration with a group of bakers, extensive investigations have been carried out about the value of the polyoxyethylenestearate (2). Moreover the toxicologic aspects of the problem have been studied in connection with the «Hearings on Bread Standards» which have proceeded in the U.S.A. during the preceding year (23).

The results of these investigations are only summarized here: «It has been proved that addition of polyoxyethylenestearate of about 0.5 % to the dough results in a better retention of the softness of the crumb and an improvement of several other properties such as volume, texture and palatability. This effect was most outstanding with flour of rather high (85 %) extraction rate. Opposite to these favourable experiences the crumbliness and the cutting quality of the bread is unfavourably influenced by the addition.

Concerning the crispness of the crust the addition has no effect. The fact that the crumb by addition of polyoxyethylenestearate retains the softness to a large extent is economically of considerable importance. For, by using this adjunct, it may be possible to spread the bread production over the whole day because it is not necessary to sell the loaves on the day on which they have been baked.»

In illustration (fig. 10) we show graphically the influence of the polyoxyethylenestearate on the softness of the crumb for four flour types. For comparison fig. 11 shows the influence of glycerol-mono-stearate on the softness of the crumb. It is clear that this adjunct cannot at all compete with the favourable properties of the poly-oxyethylenestearate.

With regard to the mechanism of the action of polyoxyethylenestearate it is impossible to draw definite conclusions. Our first impression is that a real effect on the retrogradation process is out of the question here. It is believed to be more likely that, thanks to the strong surface active influence and consequently the refinement of the structure, the retention of favourable properties is facilitated. In this connection it is

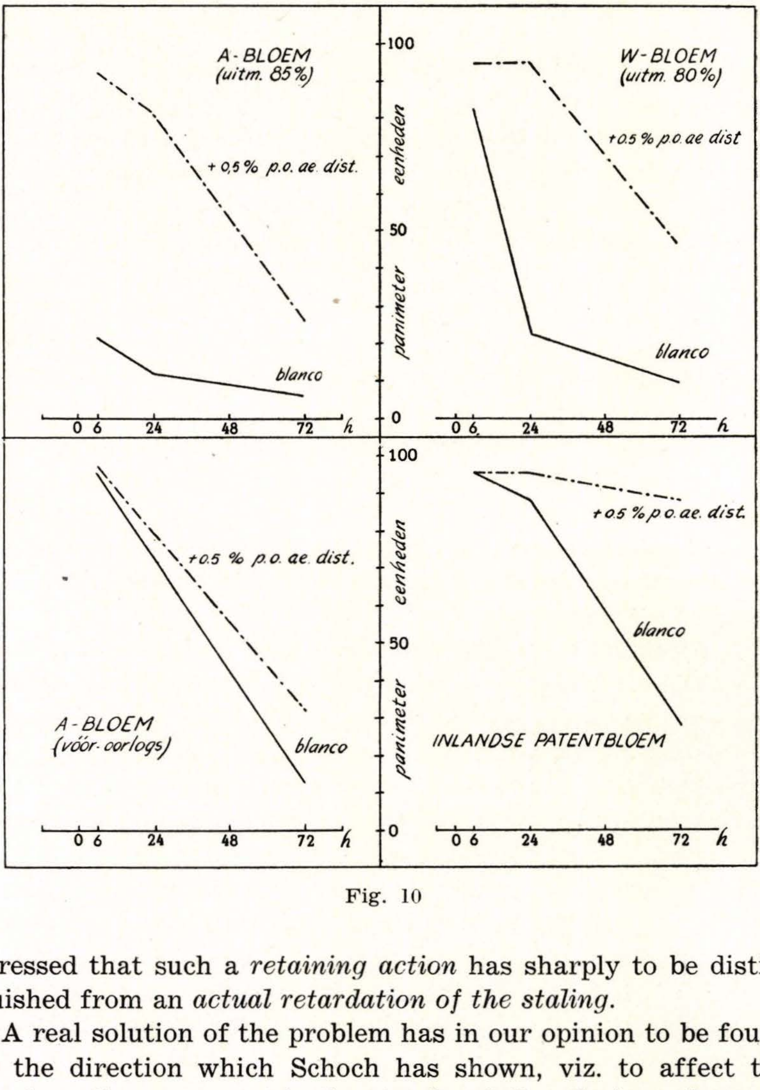

Fig. 10

stressed that such a *retaining action* has sharply to be distinguished from an *actual retardation of the staling.*

A real solution of the problem has in our opinion to be found in the direction which Schoch has shown, viz. to affect the amylopectin component in the starch gel directly in such a way that cross-linking between the branches is repressed.

Moreover it will be necessary to include the gluten in the investigations. Although it has already been established by Katz and by later investigators too that the swelling power of the gluten does not change during staling and that the contribution of the gluten to the staling effect only consists of the

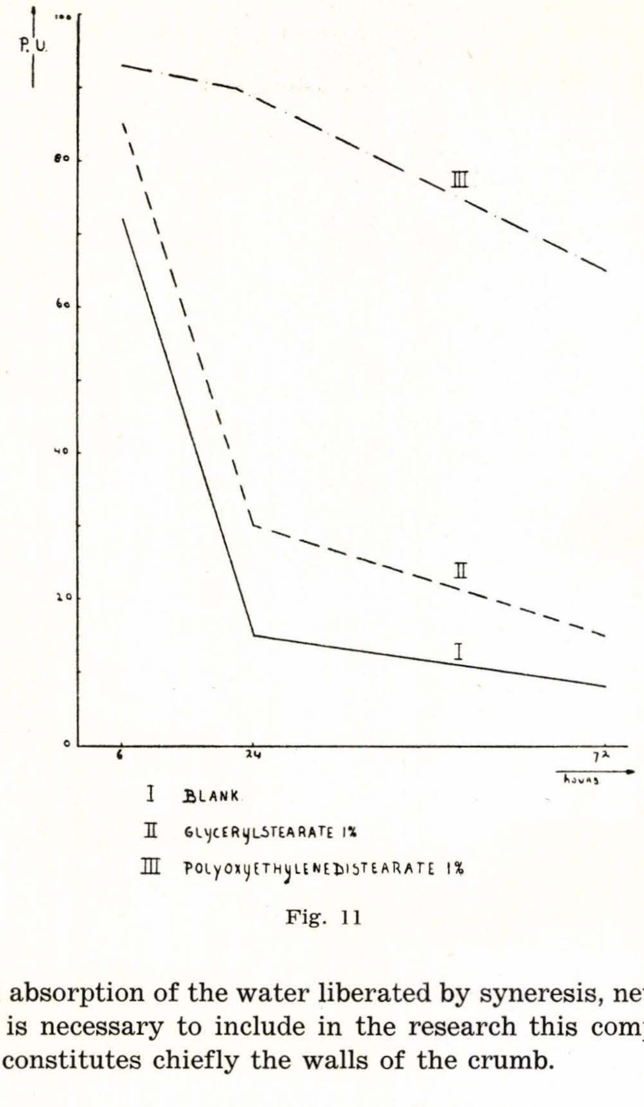

Fig. 11

partial absorption of the water liberated by syneresis, nevertheless it is necessary to include in the research this component, which constitutes chiefly the walls of the crumb.

Literature.

1. *Alsberg, C. L.,* The stale-bread problem. Wheat Studies Food Research Inst. *12,* 221—247 (1936).
2. *Bekkering, J. J.* en *Hintzer, H. M. R.,* De waarde van poly-oxy aethyleen-distearaat als middel ter bestrijding van het oudbakken worden van brood. Chem. Weekblad *45,* 605—614 (1949).

3. *Boussingault, J. B.*, Expériences ayant pour but de déterminer la cause de la transformation du pain tendre en pain rassis. Ann. chim. et phys. (3) *36*, 490—494 (1852).
4. *Cathcart, W. H.*, Review of progress in research on bread staling. Cereal Chem. *17*, 100—121 (1940).
5. *Favor, H. H.* and *Johnston, N. F.*, The effect of polyoxyethylene-stearate on the crumb softness of bread. Cereal Chem. *24*, 346—355 (1947).
6. *Favor, H. H.* and *Johnston, N. F.*, Additional data on effect of polyoxyethylenestearate on the crumb softness of bread. Cereal Chem. *25*, 424—425 (1948).
7. *French, D.*, Dissertation Iowa State College, Ames, Iowa (1942).
8. *Freudenberg, K.* und *Boppel, H.*, Die Lage der Verzweigungsstelle in der Stärke, Ber. *73 B*, 609—620 (1940).
9. *Freudenberg, K. Schaaf, E., Dumpert, G. und Ploetz, T.*, Neue Ansichten über die Stärke. Naturwissenschaften *27*, 850—853 (1939).
10. *Frey-Wyssling, A., Submicroscopic* morphology of protoplasma and its derivatives. Amsterdam 1948, blz. 219.
11. *Fuller, C. H. F.*, Starch and bread staling. Chemistry and Industry *1938*, 562—568.
12. *Geddes, W. F.*, et al., Study on the physical and chemical changes occurring in bread during storage. Project Report. Committee on Food Research, Office of the Quartermaster General. Project BS-3. Report 2 and 3 (Nov. 1, 1945—April 1, 1946).
13. *Geddes, W. F. and Bice, C. W.*, The role of starch in bread staling. Quartermaster Corps Report QMC 17—10 (1946).
14. *Hanes, C. S.*, Action of amylases in relation to the structure of starch and its metabolism in the plant. I—VIII. New Phytologist *36*, 101—141, 189—239 (1937).
15. *Hintzer, H. M. R.*, De Panimeter. Bakkersvakblad *8*, nr 4 (1949).
16. *Hutchinson, J. B.*, The staling and keeping quality of bread. Research Association of British Flour Millers Report Nr 15 (1936).
17. *Katz, J. R.*, De oorzaken van het oudbakken worden van brood (physiologisch-chem-gedeelte). Chem. Weekblad *9*, 1023—1058 (1912).
18. *Katz, J. R.*, Vers houden van brood. Chem. Weekblad, *18*, 317 (1921).
19. *Katz, J. R.*, Gelatinization and retrogradation of starch in relation to the problem of bread staling. In: *Walton, R. P.*, A comprehensive survey of starch chemistry. New York 1928, blz. 100.
20. *Katz, J. R.*, Abhandlungen zur physikalischen Chemie der Stärke und der Brotbereitung. XX. Über den Zusammenhang der Änderungen der Stärke beim Altbackenwerden des Brotes und beim Retrogradieren von Stärkekleister. Z. physik. Chem. *A 169*, 321—338 (1934).
21. *Katz, J. R.*, The influence of heat on the staling of bread crumb Baker's Weekly *87*, 26, 36 (1935), July 13.
22. *Kerr, R. W.*, Chemistry and industry of starch. New York 1944, p. 178—187.

23. *Klokgieters, J. M.*, De «Bread Standards Hearings» 1948—'49 te Washington. Bakkerijwetenschap *2*, 38—43 (1949).
24. *Lindet, L.*, Sur les états qui présente l'amidon dans le pain tendre et dans le pain rassis. Bull. soc. chim. France *27*, 634—639 (1902).
25. *Magruder, M.*, Bread waste is charged to bakers. United Press Dispatch, St. Paul Pionier Press (April 22, 1946).
26. *Meyer, K. H.*, Recent developments in starch chemistry. Advances in Colloid Sci. *1*, 143—183 (1942).
27. *Onnes, H. J.*, Rotterdam experiments with bread freezing. Food Inds. *9*, 584 (1937).
28. *Platt, W.* and *Powers, R.*, Compressibility of bread crumb. Cereal Chem. *17*, 601—621 (1940).
29. *Pyler, E. J.*, The staling of bread. Baker's Digest *22*, 99 (1948).
30. *Rundle, R. E.* and *Edwards, F. C.*, The configuration of starch in the starchiodine complex. IV. An X-ray differaction investigation of butanolprecipitated amylose. J. Am. Chem. Soc. *65*, 2200—2203 (1943).
31. *Schoch, T. J.* and *French, D.*, Fundamental studies on starch retrogradation. Project Report. Committee on Food Research, Office of the Quartermaster General. Project BS-1. Report 1 to 5 (June 4, 1945 to December 31, 1945).
32. *Schoch, T. J.* and *French, D.*, Studies on bread staling. I. The role of starch. Cereal Chem. *24*, 231—249 (1947).
33. *Schultz, A. S.* and *Landis, Q.*, The hydrolysis of starch in bread by flour and malt amylase. Cereal Chem. *9*, 305—310 (1932).
34. *Staudinger, H.*, Über die Bedeutung der Gestalt der Makromoleküle in der Kolloidchemie. (Über hochpolymere Verbindungen, 184. Mitt.) Compt. rend. trav. lab. Carlsberg. Sér. chim. *22*, 494—503 (1938).

DISCUSSION

Dr J. Van der Lee.

Are there any possibilities in bakery practice to retard retrogradation of the starch as is suggested by Mr Hintzer?

Answer:

Indeed this is a difficult and rather complicated problem. The affection of the side chains of the amylopectin molecules presupposes that the starch is present in a susceptible form. This is the case during the baking stage. On the other hand in this stage amylolytic enzymes lose their activity.

Nevertheless I think that there are possibilities to evade this difficulty.

Professor Jörgensen stressed, that one must distinguish between staling of crumb and staling of crust. In Denmark, staling of crust is by far the most important factor.

C. W. Brabender:

I wonder whether or not the changes in the physical properties of crust play a greater part in causing staling effect than crumb. The structure of «Brown'n Serve»rolls' seems to prove this statement. It looks as if the crumb in a semi-baked roll is completely developed during the first stage of the baking process carried out in the commercial bake shop. There is no crust at this stage, but a thin skin. During the second stage the crust is formed as thick and dark as one likes it. There is, in my opinion, no change in crumb structure during the second baking stage which takes place in the domestic kitchen. If there is a change, it is only due to loss of water during the second heating.

As to preventing of staling precision adjustment of malt addition is one, favoured by many American bakers. The great Bakery Service Organisation C. G. Patterson of Kansas City recommends this procedure as the best way to obtain a soft slightly humid crumb resulting in a delayed staling effect. This Company has even developed a slight rule to calculate the right amount of malt flour, based on the Amylograph figure.

Dr. Schulerud:

According to our experiences, p-oxystearates act on wheat flour only, not on rye. However, rye flowers of the «hard» type, for instance milled from south American rye, may be favourably influenced by malt diastase. Such flours sometimes behave badly under Norwegian baking conditions, the loaves show a tendency to burst and be torn up during baking in the oven. The reason for this probably is, that the starch of such flours has an unusually high gelatinization temperature. Since rye flour has no gluten, it must be the outer layer of gelatinized starch first formed which holds the loaf together when it rises in the oven, and in the case of hard flour, this layer is formed too slowly to obtain the necessary strength. A suitable quantity of malt diastase lowers the gelatinization temperature so that normal bread is formed, and the rapid staling, which is usual for bread from such flours, is retarded. This, together with the lacking activity of p-oxystearates, indicates that the staling process must be rather complicated.

Civilingenjör S. Hagberg.

Concerning the influence of amylase activity in the dough on the rate of staling of bread alfa-amylase may have a different action compared with beta-amylase. As is known the linear-chain fraction (A-fraction or amylose) of the starch is considered to retrograde already during the cooling of bread. The coacervation i. e. heat reversible aggregation of the branched-chain fraction (B-fraction or amylopectin) however is regarded the best explanation of the bread staling process. This coacervation is attributed to intermolecular association between the linear side chains of branched molecules (Schoch and French). The removal or modification of these side chains as in beta-amylase treatment may result in decreased ability to form coacervates. Alfa-amylase may have a different action on the staling of bread as more linear side chains of branched molecules is formed in alfa-amylase treatment at least in the first stages. Investigations made in our laboratory seem to favor this view.

The primary alcohol groups on the sixth carbon atom of the glucose unit is claimed to form more stabile associative bonds than the secondary alcohol groups. The efforts to retard the staling of bread thus may be directed on to remove or block the primary alcohol groups. It is possible that polyoxyethylenstearate and monoglycerids are acting in that way but the action of these compounds is so far not well understood. Also the influence of other substances i. e. the proteins is not thoroughly elucidated.

TRYKT HOS
FABRITIUS & SØNNER
OSLO