



STUDY OF THE MECHANISM OF THE RETARDING EFFECT ON BREAD STALING BY USING NATURAL GUMS

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Abstract: The mechanism of natural gums' effect on the preservation of bread freshness has been studied. The stage of bread staleness was estimated from the deformation of bread's crumb. Hydrophilicity and texture of bread crumb were also considered. The mechanism of gum's effect on the process of bread staling was studied by determining the respective change in the state of flour starch crystal structure, which was assessed by qualitative Roentgen phase analysis and the change of bread matter moisture bonds with the addition of gums, which was determined by the method of differential thermal analysis. As the result of the research, it was found that addition of natural gums accommodates bread shelf-life extension by means of crumb texture change, as well as the effect on bread biopolymer moisture bonds.

Keywords: gums, bread, freshness, structure, starch, crystallinity, moisture bonds.

1. Introduction

Extension of shelf freshness of bread always has been and to this day remains a problem for the baking branch of food industry. Now, with the introduction of accelerated technology, slowing down the process of baked product staling is a priority for bread manufacturers.

The process of bread staling is generally associated with changes to its properties, caused by changes of the state of starch, proteins and changes to moisture bonds of the bread [1, 2].

Some researchers [1, 3] believe that primary causes of bread staling are changes to starch structure. The process of bread staling occurs due to the process of starch retrogradation after gelatinization during baking. This explains the changes to physical and chemical properties of the crumb and hydrophilicity in particular. Reduction of crumb elasticity is explained by an increase of starch density that occurs due to transition from amorphous to crystalline state.

Knyahinichev [4] sees the process of bread staling as changes in moisture bond forms (bound and unbound) during preparation and storage of food. The author believes the reduction of unbound moisture in bread samples leads to slower formation of a single structural system of water molecules, starch and protein. This system is compacted by the convergence of starch chains due to intermolecular interaction of starch and protein. Thus, it is possible to keep the system less dense by reducing the amount of unbound water in bread samples.

A definite relationship between the content of bound water and bread staling can be established. In a study [5], it is shown that, during storage, unbound moisture content decreases as a result of an increase in capillary specific surface area that occurs due to starch retrogradation.

Thus, factors that affect staling are the formulation, the technological parameters of production, ingredient quality, and its storage conditions.

Food additives application appears as one of the effective ways of the bread quality improvement and shelf life extension [6, 7, 8]. Hydrophilic colloids (carbullose, carboximethylcellulose) are being used in baking aiming at the slowing of bread staling and improvement of crumb structure of frozen bread products [9, 10, 11, 12, 13].

Natural gums are widely used as structure forming and water bonding ingredients in food production. It is easy to suggest that they will also effect the dough component moisture bonding and, probably, influence the process of bread staling.

It is also known that adding guar gum has a positive impact on the quality of defrosted bread in comparison to products without such additives [14]. However, the exact mechanism of the influence of gums on the process of bread staling is yet to be researched.

Among gums, gum from the Carob tree (*Ceratoniasiligua*), guar gum (*Cyamopsis tetragonolobus*) and gum from Tara trees (*Cesalpinia spinosa*), which are mostly contained in the seeds of these plants and prevent their dehydration, have industrial importance [11]. Chemical structure of the aforementioned natural gums is that of neutral polysaccharides consisting of (1,4)- β - glycosidically bound mannose residues to which side chains of α -D-galactose resi-

dues are attached at regular intervals via 1,6- links. The mentioned galactomannans have different ratios of mannose to galactose, which vary between 1,6:1 (for guar gum) and 3,5:1 (for carob gum) [11, 12, 15]. Galactose content in carob gum is 17 -26%, tara gum - about 25%, guar gum - 33 - 40%. Galactomannan guar, tara and carob gums are all non-ionic [15, 16].

The water absorbing ability and effect to the water system properties are one of the functional peculiarities of gums. Galactomannans also regulate texture, affect crystallization of starch containing products, prevent stratification or sedimentation, increase resistance to freezing and thawing processes, prevent syneresis, and retrogradation [12, 16]. Due to these properties, natural gums have found application in bakery products and pastry production in quantities around 1 - 5 gram of gum per 1 kilogram of product.

The mechanism of the influence of gums on the process of staling may be caused by the mentioned technological functional properties. However, current literature does not offer enough data to reveal the exact mechanism of the influence of natural gums on the processes of bread staling, so a task of systematization of data on their influence on the quality of baked products and extension of their term of freshness was undertaken by the authors by course of examination of the impact natural gums have on the changes in bread crumb structure during staling, and of the investigation of the process of starch retrogradation, as well as of changes of moisture states in baked products during staling.

2. Materials and Methods

Decelerating effects of natural gums (guar gum, tara gum and carob gum) on the process of bread staling were studied. Gum

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samples of 0.25 - 0.50 % of the weight of wheat flour were used.

Preparation of bread

The gums used were: Guar gum VIDOGUM GH (E 412), tara gum VIDOGUM SP (E 417) and carob tree gum VIDOGUM L (E 410) UNIPEKTIN (Switzerland).

The dough was prepared according to formulation, which was 100% wheat flour (containing 0.73% ash in dry matter, 27 – 29 % wet gluten), salt 1,8 %, yeast 3 %, sunflower oil 2,0 %, gums 0.25 - 0.50 % of the weight of wheat flour and water to get moisture of dough 44.5 %. As a control, no gums were added to the formulation. The ingredients were mixed during 6 minutes in mixing bowl. After 170 min fermentation, the dough was divided into 250 g loaves, formed on dough former, proofed 45 min and baked in an electric oven during 30 – 35 °C at 200 - 220°C. Baking trials were performed in triplicate.

Bread crumb structure

Physical and mechanical properties of crumb were assessed based on its compressibility, which was measured on a model 'A Π 4/1' automated penetrometer. Readings were taken after 4, 24, 48 and 72 hours during storage. Baked products were stored at room temperature in conditions that prevent drying. Measurements were taken at 10 points on the bread slice 40 mm thick on both sides. The loading tip had a hemisphere form of 25 mm diameter. It could be loaded with the removable weights. Total mass of pressing system reached 300 g. During the experiments, total, plastic and elastic deformations of the crumb were been determined. Total deformation was been determined based on the reading of load penetration (H_1) and was expressed in penetration units. After these, an additional weight was been removed and, as a result, the tip partially moved back under the action of the crumb elasticity. The respective reading of the penetrometer (H₂) refers to a value of elastic deformation. The difference (H₁-H₂) refers the value of plastic deformation [2].

Crumb fragility

Evaluation of the freshness of bread was also carried out by taking measurements of crumb fragility after 4 hours and during the 3 days of storage and the amount of absorbed water. Crumb fragility was been determined in the following way: 2 rectangular pieces of bread with the mass of 5 g each were placed in a conical glass and shaken during 5 minutes on the vibration shaker. After that, the crumb particles were weighted with an accuracy of 0,01 g.

Crumb fragility was been determined as the relationship of crumb particles mass to the total mass of bread samples and was expressed in percent points.

Hydrophilicity of bread crumb

The amount of moisture absorbed was been determined by the addition of water which was delivered by drops at total quantity of 17 cm³ from the pipette during 5 minutes. Water drops were delivered to the sample of 3 g of crumbs which was placed on the laboratory sieve. The sample moisture was been removed from the sieve and weighted. The amount of water absorbed by bread, in percent to dry measure, was been determined as follows:

$$V = \frac{(G_1 - G_2) \cdot 100 \cdot 100}{G_2 \cdot (100 - W)}, \qquad (1)$$

where G_2 – sample mass after moisturisation, g;

 $ge G_1$ – sample mass before moisturisation, g;

W – moisture mass fraction in bread, %.

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Radiographic research

Effect of gums on the process of starch retrogradation in bread was investigated by radiographic procedures conducted on a 'ДРОН-УМ' diffractometer. The pieces of bread were placed in the standard container for taking diffractograms of powder samples and were sealed in the container [17]. All laboratory samples (with gums and control sample) were Roentgenographed in one regime. Therefore, the results could be compared in terms of diffraction maximum (reflections) for the qualitative characteristics in the starch structure. Diffractograms of the samples were first taken 16 hours after baking and after 7 days of storage of bread, because changes in diffractograms during the first 2-3 days are insignificant. They were compared with the diffractograms of the flour.

Water bond forms in bread

Study of the forms of moisture in the bread crumb and their relative change during storage were carried out by a model "Derivatograph Q-1000" differential-thermal analysis unit for temperatures ranging from 0 - 200 °C. Samples weighing 1 g were heated at 1.25 °C min⁻¹. Differentialthermal analysis readings were taken 16 hours after baking and after 3 days of storage. Analysis of temperature curves (TA) and mass change curves (TG), as well as their derivatives (DTA, and DTH, respectively) allowed to distinguish 4 temperature ranges with varying rates of moisture evaporation, which are seen as a measure of the strength of connection with the material.

Statistical analysis

Measurements of penetration values, crumb fragility and hydrophyllic qualities of crumb were carried out 5 times in 3 experimental series. Experimental data were processed using the mathematical statistic methods within a 95 confidence interval %. Roentgenographic and thermalgravimethrical measurements were triplicated with the averaging of data thus obtained.

3. Results and Discussion

3.1. Bread crumb texture during storage As is widely accepted, determining bread crumb compression with a penetrometer is one of the most veracious indicators during the assessment of the freshness of bread [1, 2, 18].

As shown by our study (Table 1), supplementing the dough with a mass fraction of gums in quantities of 0.25 and 0.5% marginally affects the overall, plastic and elastic deformation of crumb immediately after baking, but contributes to a significant improvement of overall and plastic strain indicators after 48 hours of storage, when compared to the control. Elastic deformation of bread test samples does not differ from the control, though on the 72 hours of storage, this effect is effectively lost. This illustrates that gums can be used as additives in bread in order to constrain the process of staling during the first and second days of storage. The best staling retarding effect is observed with the use of tara and carob gums. A more pronounced effect of freshness preservation of baked goods is obtained when using 0.5% mass fraction of gums.

It is known that during staling crumb pore walls lose their strength, which increases their tendency to crumble. Increase of crumb pore fragility during storage lies at the base of currently used methodology for bread freshness evaluation. Characteristics of hydrophilic colloids in bread are used as a basis for a crumb swelling in water method of freshness assessment [19].

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Table 1

Indicators of crumb deformation of bread with natural gum additives												
Indicators	Control	With the	addition of	gums in the	Control	of gums in						
	(no addi-	amount	of 0.25% b	y weight of	(no addi-	the amount of 0.5% by weight						
	tives)		flour	• •	tives)	of flour						
		guar	tara	carob		guar	tara	carob				
Total deformation of crumb,												
H_1 , instrument units												
after 4 hours	107±2	103±2	106±2	101±2	90±2	92±2	113±2	90±2				
after 24 hours	56±1	73±1	74±1	76±1	45±1	52±1	57±1	59±1				
after 48 hours	47±1	51±1	51±1	49±1	31±1	37±1	49±1	45±1				
after 72 hours	35±1	34±1	37±1	33±1	30±1	33±1	38±1	35±1				
Plastic deformation of crumb,												
H_2 , instrument units												
after 4 hours	86±2	82±2	83±2	81±2	69±2	70±2	90±2	67±2				
after 24 hours	45±1	60±1	61±1	62±1	35±1	41±1	46±1	48±1				
after 48 hours	38±1	40±1	42±1	40±1	24±1	29±1	42±1	38±1				
after 72 hours	28±1	27±1	32±1	27±1	23±1	26±1	30±1	28±1				
Elastic deformation of crumb,												
(H_1-H_2) , instrument units												
after 4 hours	21±1	21±1	24±1	21±1	20±1	22±1	24±1	22±1				
after 24 hours	11±1	13±1	13±1	14±1	10±1	11±1	11±1	11±1				
after 48 hours	9±1	11±1	9±1	10±1	7±1	8±1	8±1	7±1				
after 72 hours	6±1	7±1	5±1	6±1	7±1	6±1	7±1	7±1				

Indicators of crumb deformation of bread with natural gum additives

It is also proven that bread staling is accompanied by a decrease of hydrophilic properties of its crumb [1].

It was determined that crumb fragility of bread samples with gum additives is lower than in controls, both after 24 hours of storage and after 72 hours (*Fig. 1*). Hydrophilicity of bread samples with gum additives is higher when compared to control (*Table 2*) both 4 hours after baking and after 48 hours of storage. After 72 hours, this difference levels out. A more evident effect on crumb hydrophilicity was achieved with tara and carob gums.

Therefore, gums contribute to a prolongation of bread freshness within two days of storage when compared with a control sample.

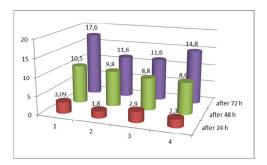


Fig.1. Change of bread crumb fragility during storage:1 - control (no additives), 2, 3, 4 - with addition of 0.5% guar, tara, carob gum respectively

The role of additives in enhancing hydration and crumb fragility reduction was apparently caused by their ability to absorb moisture, possible creation of complexes with amylose starch and the influence on starch retrogradation.

Ta	ble	2

Dread complex with the addition of come in the	Amount of absorbed water,% of bread dry matter								
Bread samples with the addition of gums in the amount of 0.25% by weight of flour	after 4 hours	after 24 hours	after 48 hours	after 72 hours					
Control (no additives)	300.0±5	284.5±5	258.5±5	249.4±5					
- with guar additives	334.5±5	317.8±5	298.9±5	239.2±5					
- with tara tree gum additives	340.8±5	319.6±5	309.3±5	256.6±5					
- with carob gum additives	344.0±5	323.6±5	299.0±5	246.7±5					

Changes in the hydrophilicity of crumb of bread with gum additives during storage

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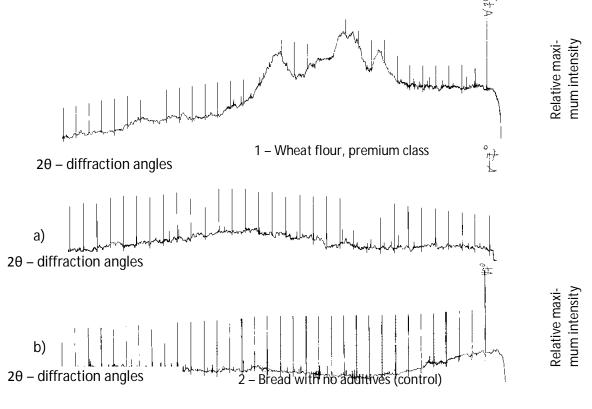
3.2. Radiographic research

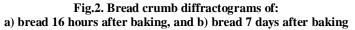
It is widely known that during baking, starch granules undergo partial gelatinization, thus binding unbound moisture and water that is released as a result of protein coagulation. At the same time, starch partially changes from crystalline to amorphous state, its grains swell, causing an increase in volume. During storage of bread, the reverse process is known to take place. Gelatinized starch transforms from amorphous state to partially crystalline, as its retrogradation takes place.

Radiographic studies of this process [1, 18] show that native flour starch results in diffractograms typical of crystalline structure of starch granules. During baking, starch partially gelatinizes, its structure undergoes changes, so diffractograms of the bread crumb show a combination of amorphous starch elements with elements in their crystalline state.

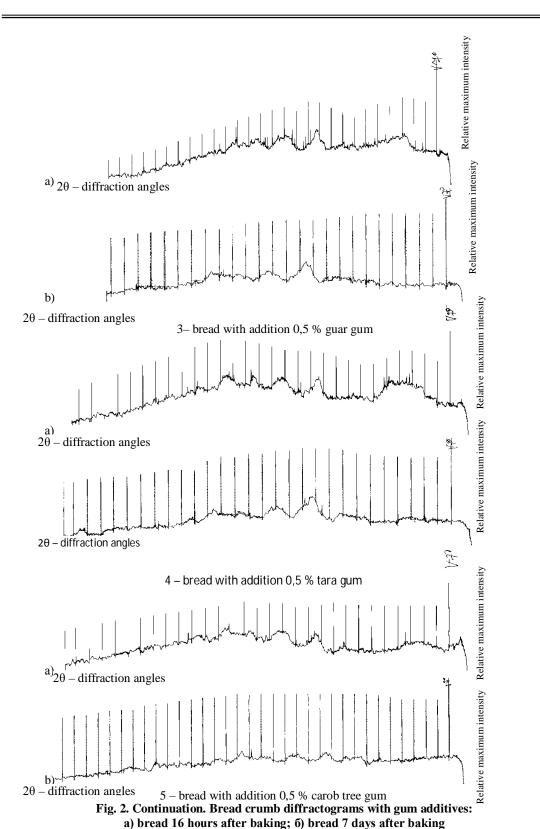
Diffractograms of stale bread crumb combine the elements of the previous two. The staler the bread, the closer the diffractogram is to that of flour. The diffractogram of stale bread has shown that starch returns into its initial crystalline condition, i.e. retrogrades.

Analysis of diffraction patterns obtained during research (*Fig. 2*) shows a significant difference between diffractograms of freshly baked bread and wheat flour. Diffractograms of the crumb structure of freshly baked bread without gum additives show domination by an X-ray amorphous phase both after 16 hours of storage (*Fig.* 2A), and after 7 days (*Fig. 2B*).





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This indicates that the starch of the sample is almost completely gelatinized. On diffraction diagrams of bread with gum additives, crystalline structure of starch remains evident, especially after 16 hours of storage. After 7 days diffractograms of bread with gum additives indicate a dominant presence of starch of amorphous structure.

Because, as is widely accepted [1, 18], the nature of bread crumb diffraction diagrams and the rate of crystal structure formation depends on the moisture of the starch gel, it can be assumed that due to significant water absorbing capability of natural gums less starch undergoes gelatinization, as can be clearly seen on diffractograms of bread with gum additives.

Probably, as a result of the lower quantity of free moisture, partial gelatinization of starch, in the process of bread with gums baking, takes place. During storage of this bread partially gelatinized starch removes moisture from gums and swells. With this its level of amorphousness increases. Thus, the crumb of the bread with gums preserves its freshness significantly longer. So, prolongation of the freshness of bread with natural gum additives is associated with preservation or even increasing of amorphousness level of starch granules.

3.3. Water bond form changes in bread during storage

According to modern concepts, the process of staling is a set of several simultaneously flowing processes of starch retrogradation, denaturation of proteins and complex redistribution of moisture between the polymers in flour. The latter aspect is less studied and is quite controversial in terms of the distribution of moisture bond forms. The majority of conducted studies have determined that bread storage is accompanied by a decrease of bound moisture in the crumb [1, 5]. The influence of structure forming additives on changes in bond forms of moisture in bread during staling was not yet researched.

In the present work the method of differential-thermal analysis has been applied, which appears to be the most objective and approved testing method.

Results transcription is given in Table 3. During the first stage of moisture removal from food samples (Table 3) there is a significant loss of water. In the temperature range, corresponding to the first stage of drying, unbound moisture, moisture in macroscopic capillaries and immobilized water are removed. The amount of moisture removed during the first stage of drying varied in the different samples 12.2 -19.2% by weight of the sample, which amounts to 27 - 43% by weight of moisture in the dough. In samples of bread with gum additives, after 24 hours of storage, moisture content was lower when compared to the control sample of bread without additives. During storage, the amount of unbound water decreases, moreover in samples of bread with gum additives this reduction is less noticeable. In bread with carob gum additives, moisture content that corresponds to this temperature range virtually does not change during storage.

In the second temperature interval, ranging from 96 - 105 °C, the rate of moisture change of the samples is slightly lower, which is obviously due to removal of moisture from micro capillaries. During this interval, smaller amounts of moisture are removed, amassing to - 2.8 - 7.0% of sample mass or 6.3 - 15.7% of the total mass of water in the dough. Moreover, content of this form of moisture bond in samples of bread with gum additives is also lower than in the control sample.

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Table	3
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	Bread moisture loss during dehydration in different temperatures ranges															
Bread samples	interval I				interval II			interval III			interval IV					
		oisture l	moisture loss			moisture loss				moisture loss						
	Tem- pera- ture, °C	mg	% of sam- ple mass	% of over all mois ture mass	Tem- perature °C	mg	% of sam ple mass	% of over all mois ture mass	Tempera- ture, °C	mg	% of sam- ple mass	% of over all mois ture mass	Tem- pera- ture, °C	mg	% of sam- ple mass	% of over all mois ture mass
No additives	No additives (control)															
- after 24 h	15-99	192	19.2	43.15	99-105	68	6.8	15.28	105-116	114	11.4	25.62	116-13	9 5	6 5.6	12.58
- after 72 h	16-96	160	16.0	35.96	96-104	56	5.6	12.58	104-113	108	10.8	24.27	113-13	8 6	0 6.0	13.48
With 0,5% gu	ar gum															
- after 24 h	17-99	176	17.6	39.55	99-101	32	3.2	7.19	101-114	138	13.8	31.01	114-13	9 5	8 5.8	13.03
- after 72 h	19-98	152	15.2	34.16	98-105	54	5.4	12.13	105-116	120	12.0	26.97	116-14	1 5	6 5.6	12.58
With 0,5% ta	ra gum															
- after 24 h	17-96	130	13.0	29.21	96-103	62	6.2	13.93	103-117	132	13.2	29.66	117-14	4 6	2 6.2	13.93
- after 72 h	16- 101	122	12.2	27.42	-	0	0.0	0.00	101-119	210	21.0	47.19	119-14	66	2 6.2	13.93
With 0,5% c	arob gum															
- after 24 h	17- 101	174	17.4	36.85	101- 102	28	2.8	6.29	102-114	146	14.6	32.81	114-13	96	0 6.0	13.48
- after 72 h	18-98	166	16.6	37.30	98-104	70	7.0	15.73	104-114	102	10.2	22.92	114-13	7 6	4 6.4	14.38

Thus, the total amount of moisture that is removed in the 15 - 105°C temperature range for the control sample on the first day of measurements is 26% of the sample total mass, or 58.5% of the total mass of the content of water in the dough. For bread samples with gum additives, losses of moisture in the 15 - 105°C temperature range on the first day of measurements were 19.2 - 20, 8% of the sample total mass or 43.1 - 46.8% of the total mass of water in the dough. After 72 hours of the storage of the samples, moisture content of these bond forms in the control decreased by 4.4%, while moisture content in samples of bread with gum additives remained virtually unchanged.

The third and fourth temperature intervals, ranging from 105 - 117 °C and 110 - 146°C respectively are marked with an enbound by adsorption, which corresponds to the fourth temperature range, during the

dothermic peak on the DTA curve, i.e., in these bounds an endothermic process takes place and it may be associated with the removal of moisture with substantial binding energy, such as osmotically bound moisture and adsorbed moisture.

As can be seen from *Table 3*, the amount of moisture removed during the third temperature range is higher for different samples of bread with gum additives by 1.8 -3.2% when compared to a control sample of bread and amounts to 13.2 - 14.6% of the sample weight or 29.7 - 32.8% of the total mass of water in the dough. After 72 hours of storage, the amount of moisture of this form of bond in bread without additives is slightly reduced while reduction in samples of bread with gum additives is much more evident. Bread with tara gum additives is an exception. Amount of water first day of storage of samples totals to 5.6 - 6.4% of the sample weight or 12.6 -

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14.4% of the total mass of water in the dough both in the control and samples with additives. After 72 hours of storage, the amount of water bound by adsorption in all of the samples of bread is almost identical.

Thus, the analysis of forms of moist identical. Thus, the analysis of forms of moisture bonds in samples of bread with gum additives suggests that a reduction in the speed of staling of these samples is connected with a lower content of unbound moisture, lower content of water in macro- and micro capillaries after baking and an increase of the amount of osmotically bound moisture. Tara tree gum shows a profound slowing effect on staling, which correlates well to the data received about a decrease in moisture content that was removed from samples during the first and second temperature intervals.

4. Conclusions

Use of natural gum additives in the amount of 0.25 - 0.5% of the weight of flour improves the elasticity of crumb, slows down staling, judging from the parameters of crumb deformation, crumb fragility and hydrophilicity. Best improving effect is observed in the case of tara tree gum.

A more evident effect on the preservation of the freshness of bread is achieved with gum dosages of around 0.5%.

Roentgenographic studies and studies of moisture bonds form during bread storage allowed an insight of the mechanism of natural gums' staling slowing effect. Diffraction patterns obtained of bread with gum additives showed that prolongation of the freshness of bread with natural gums takes place due to the increase in amorphousness level of starch granules. The slowdown of staling that took place in the studied samples can be explained as a result of a lower content of unbound moisture, lower content of water in macro- and micro capillaries at the beginning of the storage period and an increase of the amount of osmotically bound moisture.

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