

Обґрунтовано склад стабілізаційної системи для масляних паст на основі сухих концентратів молочного та сироваткових білків, що сприятиме зменшенню дефіциту білка у раціоні харчування сучасної людини та дозволить додатково підвищити збалансованість складу масляної пастки.

Із урахуванням функціонально-технологічних характеристик, умов гелеутворення та синергізму до складу стабілізаційної системи введено полісахариди – карагінан та гуарову камідь.

Досліджено динаміку градієнту граничного напруження білкових та білково-полісахаридних систем для масляних паст. Встановлено, що гелі на основі сухого концентрату молочного білка є пластичними системами, мають достатню міцність та тиксотропні властивості. Для зниження кількісного вмісту стабілізаційної системи у виробництві масляної пастки із структурним каркасом, подібним до вершкового масла, до складу системи було введено карагінан. Але збільшення його концентрації зумовлювало утворення міцно зшитих гелів, непридатних для виробництва масляних паст. Підвищити стійкість системи до циклів «заморожування – розморожування» дозволяє введення гуарової камеді. За показником граничного напруження при змінній швидкості деформації модельних зразків встановлено раціональне співвідношення складових стабілізаційної системи. До її складу входять: концентрат молочного білка: концентрат сироваткових білків: гуарова камедь: карагінан у співвідношенні 10,0:3,0:0,3:0,05.

Визначено раціональну концентрацію стабілізуючого компоненту на основі знежиреного молока, яка становила 13,35 %.

Визначено показник активності води модельних зразків обраних стабілізуючих речовин та сумішей у визначених співвідношеннях. Доведено, що стабілізуючі речовини виявляють виражені вологуютворюючі властивості, які підвищуються при їхньому комбінуванні.

Доведено ефективність розробленої системи за показниками активності води та ентальпії системи. Показник активності води для масляної пастки з масовою часткою жиру 40 % становив 0,981, що є близьким до відповідного показника вершкового масла з масовою часткою жиру 72,5 % (контроль) – 0,979. Показник ентальпії масляної пастки становив 61,35 Дж/г, контролю – 61,13 Дж/г. Це пояснюється додатковим зв'язуванням вологи функціональними групами компонентів білково-полісахаридного комплексу та свідчить про термодинамічну стабільність масляної пастки.

Визначено ефективність застосування розробленої системи у технології масляних паст: показник термостійкості масляної пастки з масовою часткою жиру 40 % становив 0,87 (контроль – 0,91), розмір краплинок водної фази на зрізі не перевищував 0,2 мкм

Ключові слова: масляна пастка, концентрат молочного білка, концентрат сироваткового білка, білково-полісахаридний комплекс

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A STABILIZING SYSTEM FOR BUTTER PASTES BASED ON THE DRY CONCENTRATES OF MILK PROTEIN

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1. Introduction

One of the main tasks for the dairy industry is the production of quality and safe products that meet modern nutritional requirements. The sedentary lifestyle, complicated ecological situation, the absence of main nutrients in human nutrition, cause the metabolic disorders, which is consequently accompanied by weight gain, leads to obesity, cardiovascular and a number of other diseases. Therefore, at present there is a need to restrict the consumption of high-calorie food products, especially those based on animal fats.

One of the ways to solve the problem is to develop a technology of analogs for high-calorie food products with the ratio of nutrients that is maximally close to the scientifically-substantiated norms.

These products include butter pastes, which are positioned as low-calorie butter-like analogs. Butter-based pastes are the products with a mass fraction of fat from 40.0 to 49.9 %, which could represent the emulsion of both the reverse type “water in fat” and the mixed type “water in fat” and “fat in water”. According to international standards [1], such products are denoted as the dairy spreads, or semi-fat butter [2].

Since butter-based pastes are characterized by high levels of milk plasma, additional functional and technological ingredients are needed to ensure proper structural-mechanical properties, organoleptic indicators of products and stability during storage. The purposeful combination makes it possible to maximally efficiently exploit properties of separate components of multicomponent dairy products [3]. Therefore, development of stabilizing systems for butter-based pastes as

complex emulsion systems is relevant, since it would allow obtaining products with the predefined structure, from that similar to the classical butter to the paste-like structure, thereby improving the economic efficiency of production.

2. Literature review and problem statement

Reduced fat content defines the peculiarities in the formation of butter paste structure. Thus, with an increase in the plasma fraction, its importance in the formation of the structure of butter grows. An important element of the structure of such products is the presence of a large number of continuous thin layers of milk plasma that penetrate the entire monolith. Stabilization of the water phase in liquid fat is achieved by the existence of mechanical strength of the interphase adsorption layers formed by the proteins of milk plasma and other surface-active substances at both surfaces. A combination of a large number of the interphase adsorption layers that possess mechanical strength associated with both phases is considered to be the second structure of such products [4]. Therefore, the development of the stabilizing systems for butter pastes would make it possible to purposefully regulate the structure of finished products and to ensure its stability during storage.

In order to stabilize the structure of low-fat products, it is proposed to use gelatin, cellulose derivatives, pectin, complex stabilizing systems Hamulsion, Palsgaard, which include hydrocolloids – carrageenan, xanthan and guar gums, modified starch, etc., which enables obtaining butter pastes with different structure [5–7]. However, the largest weight proportion among components of such stabilizing systems is typically taken by modified starch. The application of milk protein as a base of stabilizing systems would not only stabilize the structure of the butter paste, but could also contribute to increasing the biological value of the product and would allow partial compensation for the deficiency of protein in the diet of modern human.

In this regard, it is promising to use the whey protein concentrate, which is the most balanced in terms of the amino acid composition among most proteins and is inferior only to the chicken egg protein. In addition, the application of the dry concentrate of whey proteins makes it possible to obtain the more plastic gels that render the products tactile tenderness [8]. Furthermore, whey proteins exhibit the emulsifying properties that are important for use in the fat-based products, and have a high biological value, therefore, they could serve as an additional enriching component. Thus, there is a method for producing butter paste using the whey protein concentrate, obtained through ultrafiltration [9]. It was established that the product forms a double structural frame created by whey proteins and crystals of the milk fat glycerides. However, the use in the product composition of the dry concentrate of whey proteins alone predetermines a softer plastic consistency of a butter paste, which limits the choice of the type of packaging for packing the product. In addition, with an increase of the moisture content in the butter paste, which would require an increase in the amount of whey protein concentrate to be introduced, there is a risk of the occurrence of a foreign taste in the product. Therefore, it is advisable to combine the whey protein concentrate with the more active structure-forming agents.

Numerous studies have proven the effectiveness of the joint application of casein and whey proteins, which makes

it possible to enhance the biological value of the formulation mixture, to improve the emulsifying and moisture-retaining properties of the system [10]. Although the joint use of these proteins results in a product with the consistency similar to that of classical butter, the cost of such a stabilizing system is rather high, which can negatively affect the economic indicators of production.

In order to increase the efficiency of the stabilizing system, the synergistic components are introduced to its composition. Widely known in this field are the effects of interaction between milk proteins and individual polysaccharides, in particular carrageenan and galactomannans [11]. Therefore, in order to reduce the cost of the developed stabilizing system, it is expedient to introduce polysaccharides to its composition, which are the active structure-forming agents, and exhibit the synergism when interacting with milk protein, thereby performing the technological function: carrageenan and guar gum.

It is known that carrageenan, in the presence of protein, not only forms a weak gel, but also creates an additional structure due to the direct interaction with the positively charged amino acids and through the divalent ions – with the negatively charged amino acids of proteins at the surface of casein micelles. In addition, carrageenan can prevent moisture loss in a product during storage [12].

The guar rubber gels, although being not too strong, are characterized by high resistance to the cycles of “freezing-defrosting” [13]. Since the butter paste is expected to be stored at negative temperatures as well, it is advisable to introduce a component to the stabilizing system that would exhibit stability during freezing.

Thus, development of the stabilizing systems, based on the protein polysaccharide complexes, would make it possible to purposefully form the structure of butter pastes thereby promoting the biological value of products.

3. The aim and objectives of the study

The aim of this work is to develop a stabilizing system for the emulsion dairy products with an elevated biological value.

To accomplish the aim, the following tasks have been set:

- to substantiate the choice of components in the stabilizing system for a butter paste and to determine the rational ratio of components in the stabilizing system;
- to examine the index of water activity in the protein-polysaccharide complex at different ratios of components and in the butter paste with its presence;
- to prove the efficiency of using the developed stabilizing system in a butter paste technology based on analysis of the indices for enthalpy, thermal stability, distribution of moisture, and organoleptic properties.

4. Materials and methods used in the study

4. 1. Examined materials and equipment used in the experiment

The study was conducted within the framework of the scientific research (R&D) “Scientific principles for the development of resource-saving technologies of protein-containing polyfunctional concentrates for food products for special purposes” (State registration number 0117U001243), Ukraine.

The base of the stabilizing system for a butter paste was the milk protein concentrate, with a mass fraction of dry

substances of 85 %, and the whey protein concentrate with a mass fraction of dry substances of 96 %, obtained using the ultrafiltration method.

In order to increase the efficiency of the stabilizing complex at the expense of synergy from the interaction between proteins and polysaccharides, the use of carrageenan and guar gum is implied.

Since the base of the stabilizing system is a complex of milk proteins, in order to utilize the synergistic interaction, we used kappa-carrageenan E-407. Carrageenan is insoluble in milk at a temperature of 20 °C, but reveals its thickening and gel-forming properties when heated to 80 °C. For better dissolution, kappa-carrageenan was used in a mixture with potassium chloride.

Model samples were prepared on the basis of skimmed milk (protein content is 3.2 %). To this end, the ingredients under the specified experimental conditions were mixed in the dry form, they then at continuous stirring were added to the skimmed milk heated to a temperature of 35...40 °C, whose mass was determined based on the estimation of obtaining the mixture with a total weight of 100 g (the ratio of components was varied depending on the conditions for a particular experiment; the sample preparation was the same). The mixture, continuously stirred, was heated to (82±2) °C, followed by cooling to (20±2) °C.

The rheological properties of model samples were determined at the rotary viscometer “Reotest 2” (GRANAT, Russia) with the measuring system cylinder– cylinder S/N by acquiring the curves in the kinetics of deformation (flow).

Measurements were conducted at a temperature of 20 °C. The measuring cylinder (rotor) N was selected in such a way so that the gradient layer propagated along the entire thickness of the layer of the product, placed in the annular gap of the measuring device in the viscometer. The measurement of shear stress θ (Pa) was conducted based on 12 values for the gradient of shear rate γ in the range from 0 to 100 s^{-1} during the direct and reverse movement. For this purpose, the α indicators were taken at the maximum angle of deviation of the arrow in the instrument scale [14].

The shear stress (Pa) was calculated from formula:

$$\theta = Z \cdot \alpha,$$

where Z is the cylinder constant, Pa/divide of the instrument scale; α is the measured parameter, number of divisions in the scale of the device.

The study into water activity (A_w) (relative humidity, %) was performed at the HygroLab 2 (Rotronic, Switzerland) water analyzer at a temperature of 20 °C in the measurement range 0...1 A_w (0...100 % rh) [15].

The device “HygroLab 2” (Rotronic, Switzerland) (Fig. 1) is a desktop laboratory humidity and temperature analyzer with a display and control keys, which is connected simultaneously to 1 to 4 probes of water activity. The analyzed sample is taken to the container and placed to the measuring chamber. Atop it is a probe of water activity. The measurement cycle lasts 3–5 minutes, after which the values for water activity and temperature for each probe are shown by the display.

The heat resistance of the butter and the butter paste was determined by thermostating the sample, selected by a special probe, with a diameter of 20 mm and a height of 20 mm at a temperature of (30±1) °C for (120±5) min, followed by measuring the diameter of the sample. The coeffi-

cient of thermal stability was determined as the ratio of the initial diameter of the cylinder (20 mm) to the final (after thermostating). Thermal resistance is considered to be good at the coefficient' value ≥ 0.86 ; fair – from 0.70 to 0.85; and unsatisfactory if it is ≤ 0.70 [16].



Fig. 1. Laboratory analyzer “HydroLab 2”

5. Results of studying butter pastes with a protein-polysaccharide complex

One of the main indicators of effectiveness for using stabilizing substances is the capability to form the structure. When adding the milk protein concentrate to the skimmed milk, warmed to 35...40 °C, in the amount of 15 % by weight, there formed the dense plastic mass due to the hydration of the surface layers of casein micelles and the gradual restoration of the casein micelle structure. At further heating, the degree of hydration of the fine-dispersed particles of casein increased, the process of gelling did not occur, and the system lost its structural strength.

The structuring of the system can be achieved by the introduction of multi-base salts – phosphorus or citric-acid salts of potassium or sodium. For a given series of studies, sodium triphosphate was used. The action of such salts is associated with the adsorption of anions at the surface of the protein. The anions of phosphorus or citric (or other polybase) acids increase the negative charge of the protein and improve its hydrophilic properties. In addition, the cations of salts (sodium and potassium) enter the exchange reactions with proteins, resulting in that the low-soluble calcium para-caseinate partially transfers into the readily soluble sodium caseinate (potassium) [17].

To increase the efficiency of the stabilizing system, a combination of dry concentrate of milk protein with kappa-carrageenan is proposed. The rational ratio between the dry milk protein concentrate (DMPC) and carrageenan as part of the stabilizing system is determined. To this end, the model samples with such a composition (per 100 g of sample) were produced: 1.0 g of dry salt of sodium triphosphate and carrageenan in the amount from 0.025 to 0.100 g were added to 15.0 g of DMPC with an interval of 0.025 g (in the mixture with dry potassium chloride (food), the ratio of 3:1). It was established that as the dosage of carrageenan increased, the viscosity grew in proportion to the amount of carrageenan, while during cooling the formation of a gel-like structure occurred.

The dependence of the stress gradient on the rate of deformation of model samples at different ratios of DMPC to carrageenan is shown in Fig. 2 (butter with a mass fraction of fat of 72.5 % was used as control).

It was established that at the concentration of carrageenan not exceeding 0.05 %, the strong spatial structure is not formed, the system is plastic and will organically combine

with the fat base. As the dosage of carrageenan is increased, the density of the structure increases and at the concentration of 0.1 % the spatial structure of the protein-polysaccharide gel forms, which is subject to destruction under mechanical stresses. The gradient of shear stress increases at initial velocities, and then it almost does not grow, which indicates the destruction of the structure of the protein-polysaccharide gel. The introduction of the structured system to the butter paste would worsen the tactile perception of the product. Therefore, the ratio of DMPC: carrageenan of 15.0:0.075 is rational.

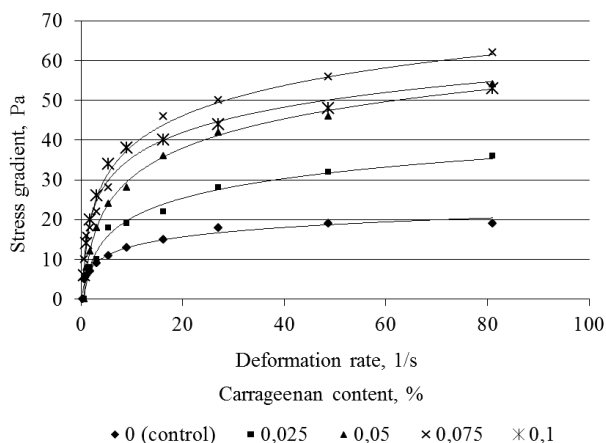


Fig. 2. Dependence of shear stress on the deformation rate of model samples based on the skimmed milk stabilized by DMPC and carrageenan

The next stage was to determine the rational amount of the concentrate of whey proteins obtained by ultrafiltration (SPC-UF) as part of the stabilizing system.

To determine the rational correlation of DMPC: carrageenan: SPC-UF, model samples were prepared, whose components were mixed in the ratios given in Table 1. Next, the ingredients were mixed with skimmed milk in the quantities required to obtain a sample with a total weight of 100 g.

Table 1

General characteristics of the structure of model samples on the base of skimmed milk stabilized by DMPC, carrageenan and SPC-UF

No	Component content, weight, %			
	DMPC	Sodium triphosphate	Carrageenan	SPC-UF
1	15.0	1.5	0.075	1.5
2	15.0	1.5	0.075	3.0
3	15.0	1.5	0.075	4.5
4	15.0	1.5	0.075	6.0

The resulting model samples were characterized by a homogeneous gel-like, dense, and sufficiently plastic, consistency. With an increase in the content of SPC-UF above 4.5 %, the consistency became too dense and somewhat lost plasticity.

The dependence of the stress gradient on the deformation rate of the model samples for different content of SPC-UF in the system is shown in Fig. 3.

It was established that the model samples were characterized by the similar dependences of the indicator of stress gradient on the deformation rate; this indicates the formation of plastic gels.

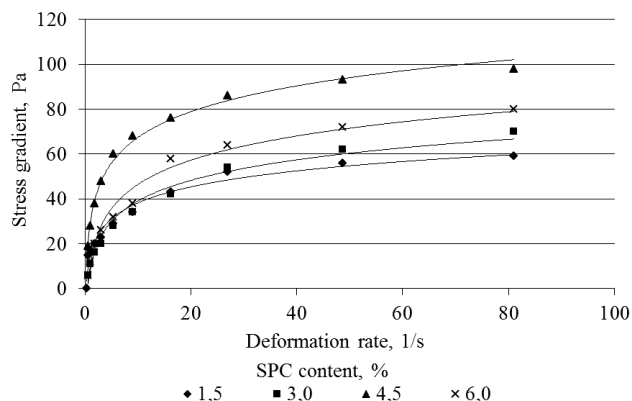


Fig. 3. Dependence of shear stress of the model samples based on skimmed milk stabilized by DMPC, carrageenan, and SPC-UF

With an increase in the content of SPC-UF above 4.5 %, a decrease in the stress gradient indicator is observed across the entire scale of the deformation rate, indicating a decrease in the strength of the gel structure because of the introduction of SPC-UF. Therefore, for the further research, the following ratio of components is accepted: DMPC: carrageenan: SPC-UF – 15.0: 0.075: 4.5.

In order to reduce the cost of the stabilizing system, it is proposed to introduce to its composition the guar gum, capable of forming sufficiently dense plastic gels, resistant to the cycles of “freezing – defrosting”. To determine the rational ratio of the four-component system, samples were prepared in accordance with the conditions from Table 2. The mass fraction of the mixture of components of the stabilizing system in a model sample was 10.0 %. The process of preparation of the samples was conducted in a manner similar to that described above.

The dependence of the stress gradient on the rate of deformation of the model samples at different ratios of DMPC, carrageenan (CAR), SPC-UF and guar gum (GUAR) is shown in Fig. 4.

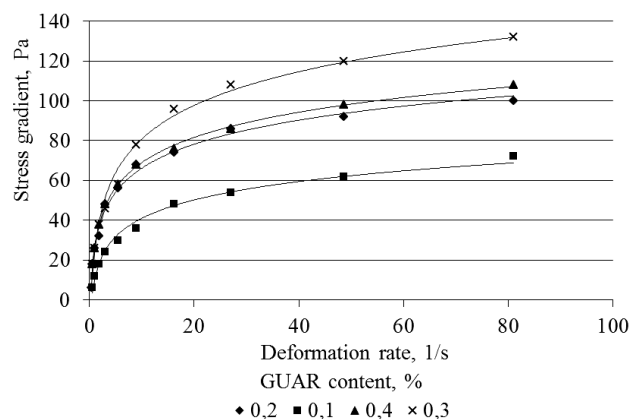


Fig. 4. Dependence of shear stress of the model samples based on skimmed milk stabilized by DMPC, carrageenan, SPC-UF and guar gum

It was established that with an increase in the content of guar gum in the composition of a stabilizing system to 0.3 %, the stress gradient indicator increased by 60 Pa on average. With a further increase in the content of guar gum to

0.4 %, the value for the stress gradient indicator was decreased. Since the stable amount of the stabilizing mixture components (10.0 %) was used in the preparation of the model samples, an increase in the proportion of guar gum predetermined a decrease in the proportion of all other components, in particular carrageenan, which negatively affected the indicator of the stress gradient.

Table 2

General characteristics of the structure of model samples based on skimmed milk stabilized by DMPC, carrageenan, SPC-UF and guar gum

No	Component content, %				
	DMPC	sodium triphosphate	Carrageenan	SPC-UF	guar gum
1	10.0	1.0	0.05	3.0	0.1
2	10.0	1.0	0.05	3.0	0.2
3	10.0	1.0	0.05	3.0	0.3
4	10.0	1.0	0.05	3.0	0.4

The indicator of water activity in the protein-polysaccharide complex at different ratios of components and butter paste that contained it was investigated. The composition of model samples of gels of stabilizing components, their mixtures and the butter paste with a mass fraction of fat of 40.0 %, stabilized by the protein-polysaccharide complex, is given in Table 3.

Table 3

The indicator of water activity in the protein-polysaccharide complex at different ratios of components and the butter paste that contained it

Component name	Component content, %					
	in sample No.					
	1	2	3	4	5	6
Milk protein concentrate (mass fraction of dry substances is 85 %)	15.0	15.0	15.0	10.0	15.0	4.48
Whey protein concentrate, obtained by ultrafiltration (mass fraction of dry substances is 96 %)	–	–	4.5	3.0	4.5	1.35
Sodium triphosphate	1.5	1.5	1.5	1.0	1.5	0.45
Food potassium chloride	–	0.025	0.025	0.002	0.025	0.008
Carrageenan	–	0.075	0.075	0.050	0.075	0.022
Guar gum	–	–	–	0.3	0.45	0.14
Butter (mass fraction of fat is 72.5 %)	–	–	–	–	–	55.17
Skimmed milk (mass fraction of fat is 0.05 %)	85.0	83.4	78.9	85.7	78.45	38.38
Total	100.0	100.0	100.0	100.0	100.0	100.0

Values for the water activity indicator of the model samples of gels of stabilizing components, mixtures, and the butter paste, stabilized by the protein-polysaccharide complex, are shown in Fig. 5. We used, as control, butter with a mass fraction of fat of 72.5 %.

Analyzing the data from Fig. 5, one can conclude that the stabilizing substances exhibit the moisture-binding properties, reducing the indicator of water activity of model mixtures. With an increase in the concentration of model solution (sample 4 – 14.352 g/100 g, sample 5 – 20.050 g/100 g), while maintaining the predefined ratio of components in the stabilizing system, the water activity indicator of sample 5 was lower compared to the respective indicator of sample 4. However, with the further use of model sample 5 in the production of a butter paste, we observed heterogeneity of the product’s consistency with the inclusions of dense particles. This effect can be explained by the insufficient amount of free moisture required for the proper spatial arrangement of functional groups of the protein-polysaccharide complex.

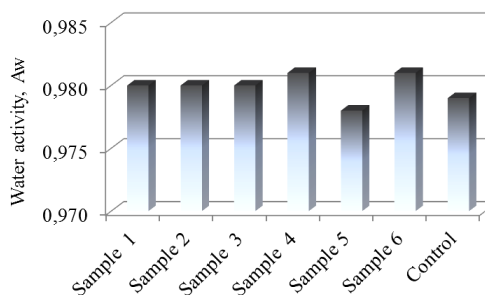


Fig. 5. Water activity of the model samples of gels of stabilizing components, their mixtures, and the butter paste, stabilized by the protein-polysaccharide complex

Enthalpy of the system increased with the introduction of stabilizing substances to the system (Fig. 6).

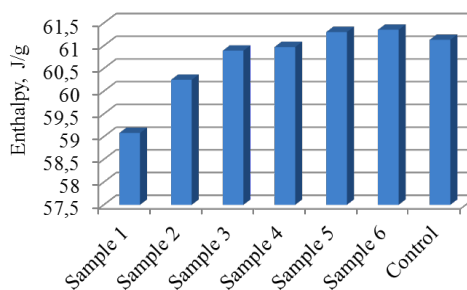


Fig. 6. Enthalpy of the model samples of gels of the stabilizing components, their mixtures, and the butter paste stabilized by the protein-polysaccharide complex

The largest increase in the enthalpy index occurs when we introduce the system to the composition, which is predetermined by the formation of the strong frame kappa-casein – carrageenan. The enthalpy index of the butter paste is somewhat higher than that in butter, which is associated with the additional binding of moisture in the butter paste by the components of the stabilizing system. Thus, the butter paste, produced using the developed protein-polysaccharide complex, is a rather thermodynamically stable system, which would ensure the stability of product quality indicators during storage.

We determined the indicator of heat resistance of the butter paste, produced in accordance with conditions from Table 3, which was 0.87 (for control – 0.91). The butter paste was characterized by clean, pleasant taste and aroma, characteristic of butter, with a homogeneous, gentle plastic

consistency, with a good moisture distribution, without the visible drop of plasma at the cut when applying a sheet of filter paper impregnated with bromophenolblau.

6. Discussion of results of studying the development of a stabilizing complex for butter pastes

Based on an analysis of experimental results, the composition of the protein-polysaccharide complex for butter pastes with a mass fraction of fat of 40 % was substantiated. Dry concentrates of milk and whey proteins, which reveal the moisture-retaining and structurally-forming properties, were selected as a base. In addition, the protein complex will serve as an enriching component, which will improve the balance of the butter paste composition and contribute to the reduction of protein deficiency in the diet of modern human.

The presence of SPC-UF gives products a gentle plastic consistency due to the high dispersion of whey proteins and the patterns in gel formation.

In order to maximally utilize functional capabilities of the stabilizing substances, the composition of the protein-polysaccharide complex, including the synergists of milk proteins – carrageenan and guar gum, has been substantiated. The following auxiliary substances were used: to increase the hydrophilicity of milk proteins – sodium tripolyphosphate, to create the optimal conditions for the gelation of carrageenan – food potassium chloride.

The rational correlation between components of the stabilizing system was defined: DMPC:SPC-UF: carrageenan: guar gum – 10.0: 3.0: 0.05: 0.3 – based on the gradient of the limiting stress of model solutions of protein-polysaccharide gels.

In order to confirm the effectiveness of the developed stabilizing system and predict the capability of storing the butter paste with its use, the water activity indicator was investigated. It was proven that the addition of skimmed milk to a butter paste does not increase the water activity indicator. The butter paste with a mass fraction of fat of 40 % is characterized by the same indicator of water activity as the butter with a mass fraction of fat of 72.5 %. This is explained by the additional binding of moisture by the functional groups in the components of the protein-polysaccharide complex. Reducing water activity would slow

down the microbiological processes that occur during storage and cause product damage. That is, the relatively low value of water activity in a butter paste allows further studies into microbiological parameters of butter pastes in order to justify the regimes and storage terms that are closer to the respective conditions for butter.

Based on the indicator of thermal stability, the organoleptic properties and moisture distribution, the butter paste, which was made using the developed stabilizing system, could be positioned as low-calorie analog of butter.

Thus, the result of our scientific research is the development of the stabilizing system for butter pastes with the structure similar to that of butter. Introducing a wider range of stabilizing components would make it possible to obtain butter pastes with the predefined structural-mechanical properties.

Further study is required to reveal the patterns in the crystallization of glycerides of milk fat in the presence of components of the stabilizing system, as well as the subsequent formation of the structure of butter pastes with a different mass fraction of fat.

7. Conclusions

1. The choice of components for the stabilizing system for a butter paste is substantiated. DMPC-UF and SPC-UF and the polysaccharides carrageenan and guar gum, which provide for the synergistic effect when interacting with protein, were taken as the base.

2. The rational correlation of components in the stabilizing system is determined – DMPC: SPC-UF: carrageenan: guar gum – 10.0:3.0:0.05:0.3.

3. The thermodynamic stability of the butter paste with the protein-polysaccharide complex is determined based on the water activity indicator and the enthalpy of the system. For the butter paste with a 40 % fat mass fraction, the water activity and enthalpy indicators of the system are 0.981 and 61.35 J/g, respectively. For butter with a 72.5 % fat mass fraction (control), they are 0.979 and 61.13 J/g, respectively.

4. The efficiency of using the developed stabilizing system in the technology of butter pastes has been proven: the indicator of thermal stability of the butter paste with a mass fraction of fat of 40 % is 0.87 (control – 0.91), the size of droplets in the aqueous phase at the cut does not exceed 0.2 mm.

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