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ADHESION OF MARZIPAN PASTES BASED ON DRY DEMINERALIZED WHEY

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ABSTRACT
The results of researches of rheological and adhesion characteristics of marzipan pastes with dry demineralized whey (DDW) and glycerin are given. The positive effect of dry demineralized whey and glycerin on the characteristics of model compositions of marzipan pastes has been established. The component compatibility of DDW and almonds has been confirmed. It has been experimentally established that DDW and glycerin lead to changes in the structural state of marzipan pastes, changing the quantitative values of rheological characteristics. It is confirmed that with increasing DDW concentration, the indicators of deformation and plasticity increase. The indicators of elasticity and resilience of marzipan paste decrease, which in general leads to an increase in molding ability. The surface effect on the properties of marzipan pastes with dry demineralized whey and glycerin was carried out. The technological expediency of using glycerin in the composition of marzipan pastes with DDW to increase their plasticity and pliability while maintaining high molding properties is substantiated. The rational content of glycerin is established, which allows regulating the adhesion properties within the set limits for paste-like finishing semi-finished products from marzipan masses. The rational content of DDW and glycerin in the composition of marzipan pastes while ensuring high functional and technological properties in the application of confectionery flour on the surface is substantiated. Mathematical modeling of adhesion behavior of marzipan pastes is carried out. The adhesive properties of the pastes are mathematically substantiated and their ability to have flexibility under the action of the applied shear stress is confirmed within the established limits. Its currents are considered and substantiated. A study of moisture absorption by flour confectionery when covered with marzipan paste is provided. The wetting angle is considered and the work of adhesion is determined. Based on researches the directions of use of the developed marzipan pastes in confectionery production as finishing semi-finished products for a covering and as a layer for flour confectionery products and modeling of figured products are offered.

Keywords: marzipan paste; adhesion; whey powder; glycerin; rheological properties; modeling

INTRODUCTION
Confectionery production is an art, so there is a fleeting fashion. The quality of products significantly depends on how receptive the manufacturer is to the latest trends in the product market, how he/she knows the tastes of consumers, and their solvency. With the country's entry into a new level of market relations, the assortment policy of the food industry in general and confectionery, in particular, has changed. In the conditions of market competition more and more attention is paid to the level of aesthetics of confectionery products. The range of confectionery and semi-finished products produced in our country is diverse, constantly changing, and has about 5,000 items. Stricter consumer requirements for the taste of confectionery products with a limited raw material base and reduced quality of raw materials encourage scientists to create a new direction in the confectionery industry which is the development of compound foods based on raw materials in certain regions.

Improving technological processes is one of the main directions in the food industry. It involves the study of changes in physicochemical properties when using various methods of influencing natural raw materials used for human nutrition. Extensive opportunities in this direction open up when creating such process conditions that provide a comprehensive impact on raw materials. Therefore, the main technological directions in the development of new types of confectionery and semi-finished products are to improve the range of products for baby and dietary nutrition, increase the amount of protein, reduce carbohydrates, and especially sugar. To solve this goal, the addition of various fillers to the composition of sugar masses, which enrich the product with biologically active substances, has recently become widely used.

Modern semi-finished products for confectionery products are represented by a wide range of various creams, chocolate, marzipan, sugar, paints, toppings, cast caramel decorations, etc. A special place among the finishing confectionery semi-finished products is occupied by marzipan mass of a mixture of raw almond kernels, apricots, or nuts. Due to the exclusivity of organoleptic properties and versatility of use in various areas of confectionery production **(Tamova, Shchikarev, and Basyuk, 2015)**, the paste has the necessary set of substances for the human body. Due to the high level of import dependence **(Dmitrieva and Makarova, 2016)**, the production of marzipan in Ukraine is limited, because 80% of the almond kernel consumed in Ukraine is of foreign production. This necessitates the search for new ingredients of domestic production, which will reduce the share of imports of dependent raw materials in the recipes of marzipan masses and reduce the cost of finished products. At the same time, it is important to preserve the typical marzipan taste, aroma, and structure of the product, as well as to increase its biological and nutritional value. Such improvement of existing technologies of marzipan pastes should be based on the use of non-traditional vegetable raw materials aimed at increasing the biological value, reducing energy consumption, improving flavor and functional and technological properties.

Analysis of model approximations of medium types

Most confectionery consists of sugar or other sweet substances (honey, xylitol, sorbitol), as well as molasses, various fruits and berries, milk, butter, cocoa beans, nut kernels, flour and other components. These are mainly sweet products that have a pleasant taste and aroma, good appearance, high nutritional value, calories and good digestibility.

In the work of **Tamova, Shchikarev and Basyuk (2015)** and **Kozlova (2014)** it is noted that the choice of process parameters involves comprehensive research to identify the nature of changes in the structure and properties of both individual components of raw materials and raw materials as a complex. Therefore, the participation of scientists in the implementation of technology is to deepen the understanding of the importance of nutrition in human life, taking into account national traditions, transformations of individual food components in the body structure, their impact on organs and systems. Preservation of valuable nutrients and BAS, the formation of habitual consumer characteristics, high bioavailability and product safety is based on the development of production technologies with the necessary physiological properties by improving recipes, methods and modes of processing raw materials, technological parameters of production.

Developed technologies of marzipan pastes **(Apet and Pashuk, 2004; Pat. No. 2015152421, 2017)** the authors aim to find and study the physiological and technological properties of non-traditional raw materials, which in terms of biologically active substances (BAS) can be attributed to the so-called functional ingredients, studying their influence on the course of preparation and formation of product quality. The recipe mainly included walnuts, hazelnuts, cashews, pecans, peanuts, chestnuts, cherry stones, apricots and pumpkin seeds. Replacement of almonds with peach or apricot pits **(Chorrna et al., 2015)** was accompanied by the name of the made persipan paste. In the works **(Chorrna et al., 2015; Tamova et al., 2015)** it is noted that the optimal quality of marzipan mass can be obtained from sweet almonds with the addition of 1 – 2% bitter. Its limitation is due to the danger of the formation of hydrocyanic acid from amygdalin.

In works (**Apet and Pashuk, 2004; Pat. No. 2015152421 (2017)** the ways of strengthening of taste and aromatic indicators of marzipan pastes are noted. Their prescription composition may include a variety of non-traditional raw materials, such as coffee meal, chicory powder, bunduk seeds. This approach gives marzipan pastes the smell of coffee and the taste of hot chocolate. At the same time, other works **(Apet, 2004; Pat. No. 20150211, 2016)** noted that the use of pear and amaranth seed powders not only enhances the taste and aromatic qualities of marzipan pastes but also improves rheological characteristics due to the high oil content. This creates the conditions for increased viscosity and adhesion stress, which improves the formation of these confectionery masses.

Reducing the caloric and glycemic content of finishing semi-finished products in their production happens by using different technological properties, origin, composition, caloric content and sweetness of sugar substitutes and sweeteners. Technologies of marzipan paste with low sugar content **(Pat. No. 20150141, 2016; Pat. No. 2016127117, 2017)** are represented by model compositions of sodium or potassium acesulfame, aspartame. The use of synthetic sweeteners indicates the lack of such compositions. Studies by the authors (**Fernandez and Santos, 2018; Zeynep and Sifa, 2014)** confirm their negative impact on human health.

The use of natural sweeteners in the technology of marzipan pastes, namely: agave syrup, erythrol, stevioside, palatinosis can significantly reduce the high caloric content **(Pat. No 20150211, 2016)**. Known technologies of marzipan masses **(Pat. No. 20150211, 2016; Pat. No. 20150141, 2016)** in which various types of flax, barley, buckwheat, corn, lentil, rice are used as fillers as well as pea flour, increase the internal forces of adhesion of the components of marzipan masses. Such fillers bind moisture better and promote the formation of a more homogeneous and plastic structure of the mixture during molding. However, despite the positive attitude, these compositions reduce the organoleptic characteristics due to the presence of a sharp cereal taste and aroma. Baby foods that are part of the diet of children need special care as objects of enrichment. Their bodies are more sensitive to non-traditional ingredients because children's metabolic systems are not yet sufficiently formed and are not able to withstand high loads, to respond adequately to them.

Dried chokeberry berries and medlar leaf powder are used as a functional additive in marzipan paste technologies. This allows not only to increase the nutritional and biological value but also to achieve the maximum possible preventive effect with a relatively small content of marzipan pastes. As an antioxidant use the drug "Cyclorar". This biologically active substance improves the nutritional value of marzipan masses and improves its molding properties.

The main disadvantage of marzipan pastes with these additives is reduced sensory characteristics. The use of additives to enrich the nutritional composition has a significant effect on changes in the color and taste of this product. As a result, there are problems with the toning of marzipan paste and obtaining the appropriate color scheme. This makes this type of finishing semi-finished product unsuitable for confectionery coating and modeling of figured finishing semi-finished products. The raw material for the production of marzipan pastes due to biological, physical, and mechanical factors changes its properties and acquires characteristic of this type of paste. The process of production of pastes can be considered as a set of processes of change of rheological characteristics of the formed semi-finished product according to a compounding under the influence of biological, physical, and mechanical factors. On the other hand, changes in rheological characteristics affect the choice of design and modes of operation of equipment. Therefore, the complex of rheological (structural and mechanical) properties of marzipan pastes are the most important, which predict their state in a variety of technological processes and characterize the physical state, dispersion, structure, structure, and type of interaction.

It is established that methods and means of determining the rheological characteristics of different types of deformation affect product quality **(Stadnyk et al., 2019)**. In our opinion, the works by **Kravchenko et al. (2019)** give some examples of calculations of technological processes and equipment aimed at studying the physical and mechanical properties of the environment. This approach allows to improve and intensify the technological process, to develop scientifically sound methods for calculating the technology of forming marzipan pastes.

Developed technologies of marzipan and praline masses **(Sirohman and Lozova, 2008; Pat. No 2008121837, 2009)** in the prescription composition of which included milk powder, in our opinion allowed to improve consumer properties and reduce production costs. It is known that DDW is used in the manufacture of confectionery as a substitute for condensed or powdered milk in the production of creamy caramel, iris, fondant, icing, chocolate **(Kravchenko et al., 2020)**.

As a result of the analysis of literature and patent sources, the wide use of glycerin in the prescription composition of paste-like finishing semi-finished products was revealed. Glycerin in the technology of sugar pastes is used to reduce the stickiness (adhesion) of the food system, it gives softness to the pastes, improves the molding properties, makes them more pliable in the manufacturing process of finishing semi-finished products **(Gulenko, Sibileva, and Zhyvotkevych, 2013)**. This determines the relevance of research on the feasibility of using glycerin in the technology of marzipan pastes with DDW.

The creation of a new technology of marzipan pastes with DDW, the feasibility of using glycerin in their composition requires in-depth studies of rheological and sensory characteristics of finished products to justify rational technological processes, which largely determine the consumer and functional properties of marzipan pastes. The relevance of the search for new recipe ingredients for marzipan masses in the partial replacement of almond flour, the use of which can simultaneously solve several technical problems to ensure the specified organoleptic and rheological properties, is quite high.

When calculating the recipe, the main difficulties arise due to the instability of the movement of the paste, and, accordingly, shear deformations, the impact of quality indicators. At the same time, the improvement of the technological process requires the establishment of a relationship between the characteristics of the components that affect marzipan pastes in the formation of products.

Therefore, the main approach to the choice of marzipan paste formulation is to establish rheological connections, which are the most realistic for solving the problem in the formation of semi-finished products and products. Accordingly, the study of the developed marzipan pastes requires in-depth knowledge of all the intricacies of the process, its mathematical description.

Scientific hypothesis

Creation and determination in the prescription composition of marzipan pastes of rational concentration of glycerol with dry demineralized whey to ensure the specified (desired) rheological, surface characteristics, which will help to some extent in ensuring the technological feasibility of use.

MATERIAL AND METHODOLOGY

Materials

Dry demineralized whey made from cottage cheese with 90% level of demineralization under TU U 15.5-00413890-089:2014 **(Table 1)**; marzipan paste, made by traditional technology; model systems of marzipan paste with the addition of DDW in concentrations of 10 – 40% **(Table 2)**, and food glycerin TU U 10.8-40570177-001:2016: 1 – 6% **(Table 3)** of the total mass of dry components of marzipan mass (almond kernel and powdered sugar).

Table 1 Physical and chemical and organoleptic parameters of DDW.

Name of indicator	Characteristics and norm
Taste and smell	Sweet, without foreign tastes and odors
Appearance and consistency	Fine powder
Colour	Light cream
Mass fraction of dry matter, %	97.00
Mass fraction of ash, %	2.63
Mass fraction of lactose, %	75.92
Mass fraction of fat, %	1.0
Mass fraction of protein, %	15.45
The acidity is titrated	4.7
Acidity is active	5.825
Solubility index	Complete solubility

Table 2 Prescription composition of model systems of marzipan pastes, per 100 g.

Name of raw materials	Control	Samples with addition DDW, %			
		10	20	30	40
Powdered sugar	43.0	38.0	33.0	28.0	23.0
Treacle	14.0	14.0	14.0	14.0	14.0
DDW	-	10.0	20.0	30.0	40.0

Table 3 Prescription composition of model systems of marzipan pastes with MSSD, per 100 g.

Name of raw materials	Samples with the addition of glycerol, %					
	1	2	3	4	5	6
DDW 20 %						
Almond kernel	32.5	32.0	31.5	31.0	30.5	30.0
Powdered sugar	32.5	32.0	31.5	31.0	30.5	30.0
Treacle	14.0	14.0	14.0	14.0	14.0	14.0
DDW	20.0	20.0	20.0	20.0	20.0	20.0
Glycerin	1.0	2.0	3.0	4.0	5.0	6.0
DDW 30 %						
Almond kernel	27.5	27.0	26.5	26.0	25.5	25.0
Powdered sugar	27.5	27.0	26.5	26.0	25.5	25.0
Treacle	14.0	14.0	14.0	14.0	14.0	14.0
DDW	30.0	30.0	30.0	30.0	30.0	30.0
Glycerin	1.0	2.0	3.0	4.0	5.0	6.0

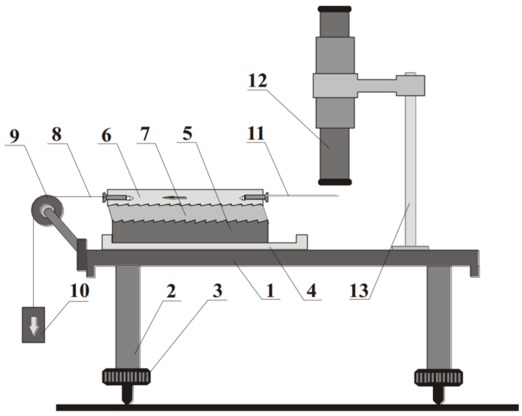

Figure 1 Installation diagram of a plane-parallel elastoplastometer Tolstoy. Note: 1 – table; 2 – support leg; 3 – adjusting screw; 4 – metal stand; 5 – metal plate; 6 – plexiglass plate; 7 – prototype; 8 – silk thread; 9 – block; 10 – cargo; 11 – observation needle; 12 – microscope; 13 – tripod.

Research methods

Sensory properties of model systems of marzipan pastes were determined according to the developed scales of organoleptic descriptors. Marzipan pastes with DDW were differentiated depending on sensory features of a consistence: marzipan pastes for a covering of confectionery; as a layer for flour and confectionery (LFC); marzipan pastes for making candies, bars, tiles; for modeling of figured products (MFP).

The study of the rheological properties of control and experimental samples was carried out using a plane-parallel plastomer of the Tolstoy modification, which is based on determining the shear deformation related to the thickness of the sample at constant stress **(Figure 1)**.

During the study of the rheological characteristics of the model systems, a fixed load was selected for all variants (65 g), provided the same temperature (+6 °C) and sample height (7 mm).

The study of the surface characteristics of the control and test samples was performed on a dynamometer connected to the MIG-1.3 measuring instrument. It allows characterizing the degree of adhesion of materials of a different structure at their surface contact. The adhesion strength was determined by the method of normal separation of the steel plate from the structured body (marzipan paste). The search for the obtained data of the results of the experimental array of the optimal mass fraction of DDW and glycerin in marzipan pastes was carried out according to known methods and methods of statistical processing using the known method of correlation and regression analysis of experimental results using differential operators qualitatively and quantitatively evaluate the characteristics in the selection of matrix ingredients.

Statistical analysis

This work is aimed at creating and studying the prospects of using marzipan paste based on a rational concentration of glycerol with dry demineralized whey. Estimation of the basic regularity of change of compounding structure and properties of marzipan paste is based on optimum parameters and modes at its rheological properties. The prescription composition establishes the probability of the obtained results of structure formation, necessary for the description of consumer properties. Features of the effect of glycerin and whey dry demineralized in the formation of the structure of marzipan paste and the conditions for achieving rational rheological parameters, it is possible to predict the adhesion of the paste.

A whole complex of rheological studies was carried out during the development of the prescription composition of marzipan pastes. To clarify the role of glycerol and dry demineralized whey, the planning and formulation of computational experiments were performed to obtain the appropriate regression equations. The dependence of the structural and mechanical properties of the pastes on the content of DDW and glycerin were constructed by the method of an arbitrary experimental design.

According to the results of rheological studies, it is not recommended to increase the concentration of glycerin by over 5%. These results are confirmed by the results of sensory analysis. The zones of rational concentrations of DDW and glycerin in the composition of marzipan pastes were determined by the method of compromise solutions. Accordingly, the variables, optimization criteria, as well as the area of the definition of factors were identified.

The determined mathematical dependences of the main structural and mechanical parameters of marzipan pastes on the content of glycerin and DDW have the form:

1. by strength index:

$$Y_{1MFV}=-2.35x_1^2-1.25x_2^2-3.14x_3^2+0.13x_1x_2-$$
$$-1.52x_1x_3+0.89x_2x_3+7.27x_1+4.81x_2-6.73x_3+21.07$$

2. by extensibility index:

$$Y_{1MFV}=-1.08x_1^2-0.48x_2^2-0.26x_3^2+0.09x_1x_2-$$
$$-0.87x_1x_3+1.02x_2x_3+5.48x_1+3.48x_2-4.27x_3+7.12$$
$$Y_{2MFV}=18.6x_1^2-1.08x_2^2-0.67x_3^2+3.44x_1x_2-$$
$$-1.04x_1x_3+0.78x_2x_3+4.41x_1+5.48x_2-6.12x_3+122.12$$

3. by the ability to form index:

$$Y_{3MFV}=-0.18x_1^2-0.73x_2^2-2.61x_3^2+0.04x_1x_2-$$
$$-2.94x_1x_3+7.45x_2x_3+2.45x_1-3.57x_2+1.54x_3+2.8$$
$$Y_{3MFV}=-0.15x_1^2-0.46x_2^2-3.07x_3^2+2.01x_1x_2+$$
$$+2.01x_1x_3+6.37x_2x_3+1.76x_1-2.31x_2+1.04x_3+3.9$$

Where:
Y_{1MFV} is strength of marzipan paste *MFV*, points; Y_{2MFV} is extensibility of marzipan paste *MFV*, points; $Y_{3\ MFV}$ is ability to form, points; X1 is content of MJ and CP,%; X2 is content of glycerin,%; X3 is MSDS content,%.

By integration, the functions were obtained and the areas of optimal parameters of glycerol and DDW content in marzipan pastes were determined **(Table 4)**.

The optimal values are selected by rounding the optimized values within the compromise areas, to facilitate the dosing of the components of the formulation of marzipan pastes in the production environment.

Thus, the results of rheological and sensory studies confirmed the possibility of adding DDW to the prescription composition of marzipan pastes at a concentration of 10 – 20%, which allows the improvement of their sensory, technological, and functional properties.

RESULTS AND DISCUSSION

Meeting the needs for high-quality food is one of the main social and economic problems of today. Quality issues **(The European Commission, 2005; DSTU 3355-96, 1996; DSTU ISO 9001, 2015)** in particular the development of new products at domestic food companies, are now receiving increasing attention. Consumption or maintenance of a balanced and nutritious diet is ensured by the implementation of national programs to improve food quality and an integrated food safety system. That is why the problems of ensuring the safety and quality of products are becoming increasingly important for the food industry of Ukraine. This is facilitated by the country's transition to new political and economic relations with the European Union.

An in-depth analysis of rheological and sensory studies of newly developed formulations allows for their further use. Therefore, based on our determined optimal values of marzipan paste LFC, we analyze the effect on the strength of adhesion. The theoretical estimate of adhesion is currently very approximate, due not only to the imperfection of the equations used to calculate the strength of intermolecular bonds but also to the fact that it is impossible to estimate the actual number of bonds per unit area. Also, it is difficult to estimate the true contact area, which is always much larger during visual observation, due to the presence of roughness in the surface layer.

The study of the application of marzipan pastes on confectionery semi-finished products allows us to determine and justify their rationale prescription composition. Adhesion according to **(Adamson, 1976; Rydil, 1936)** as a surface phenomenon is associated with rheological parameters and characterizes the volumetric properties of marzipan pastes. It occurs at the boundary between two phases of heterogeneous condensed bodies: marzipan paste is one phase, the contact surface is the second phase, which causes adhesion.

The volumetric properties of the paste determine the area of contact of the two bodies, which affects the amount of adhesion and its consequence, which characterizes the state of the surface after removal of the adhering mass of the paste.

Adhesion has concomitant phenomena that characterize the bulk properties of food masses and significantly affect the adhesion interaction of the components of marzipan pastes **(Kravchenko et al., 2019)**. The influence of volumetric characteristics of food masses on surface properties can be traced by considering the ratio of adhesion and cohesion **(Stadnyk et al., 2019)**. In the case of adhesion, there is a limit of phase distribution, for cohesion such a limit is absent **(Wake, 1976)**. Cohesion is the body's resistance to destruction associated with overcoming the forces of interaction between atoms and molecules at the interface and means bonding within marzipan pastes, ie within a single phase.

Table 4 The range of optimal parameters of glycerol and MSDS content in marzipan pastes.

Model compositions of marzipan pastes	X_1(glycerin), %			X_2(DDW) %		
	$X_{1\ min}$	$X_{1\ min}$	Optimal value	$X_{2\ min}$	$X_{2\ max}$	Optimal value
Marzipan paste (LFC)	4.8	5.3	5.0	27.0	33.7	30.0
Marzipan paste (MFP)	4.4	4.5	5.0	18.2	22.4	20.0

In the process of applying effort to the marzipan paste when applied to the workpiece is the fractional interaction of their surfaces. The nature of the mass flow of marzipan paste in the form of different profiles is determined by the structural and mechanical properties and the strength of interaction (sticking) with the contact surfaces. Therefore, the amount of adhesion, in this case, is characterized by the force of separation, the specific work of separation relative to the unit area, the contact time to change the bonding conditions between the substrate and the adhesive under load. Therefore, the maximum increase in the forces of interaction of the paste with the contact area of the workpiece is characteristic. Violation of these relationships leads to the production of low-quality products and reduces the efficiency of the process. The phenomenon of the interaction of the above-mentioned bodies is rather little studied, and the nature of adhesion requires research. In works (**Zimon, 1974)** the nature of adhesion is often explained by diffusion and electrical theory. Adhesion is always the result of the intermolecular interaction of surfaces different in nature **(Deryagin, 1978; Zimon, 1974)**.

In the food industry, there are many processes in which the forces of friction and adhesion interact simultaneously. These phenomena occur when the relative displacement of the contact surfaces of the two bodies. In researches by (**Deryagin 1978),** simultaneous interaction of force of friction and adhesion is considered and their connection is established. The law expresses the proportionality of friction forces to a normal load. Some researchers as (**Souheng, 1982; Lee, 1979)** believe that the only cause of external friction is the forces of attraction between the surfaces of bodies. Chemical adhesion may occur during the adhesion of liquid and elastic and plastic food masses **(Berlin and Basik, 1974)**.

In our process, a liquid meniscus appears between the contacting phase parts. In this case, it seems to tighten the particle and the surface. The amount of adhesion will be determined by capillary force:

$$F_k = 4\pi\sigma_T r \quad (1)$$

Where:
σpn is the surface tension of the liquid condensed between the contacting bodies.

According to (**Vakula and Prytinin, 1984)** there is a spreading of a thin layer of liquid that is on a body surface.

If the "adhesion" or "adhesion force" is evaluated by the dependence of M. Stefan and Gorbatov, then such a process takes place in time, ie adhesion is evaluated as a process that must be performed to separate the samples **(Adamson and Gast, 1997; Rydil, 1936)**. Distance differences can characterize the phenomenon of cohesion. In this case, the pressing of the two bodies is a capillary interaction:

$$P = 2\alpha F\cos\beta / h = 2\alpha F_k / h \quad (2)$$

Where:
α is the coefficient of surface tension, $N.m^{-1}$; *cosβ* characterizes surface wetting; *α* 'is the coefficient of surface tension at full wetting, $N.m^{-1}$; *h* is the thickness of the layer of marzipan paste, m.

Assuming that the force applied from the outside to the paste increases linearly with time:

$$P = \omega c * \tau,$$

Where:
ωc is the rate of increase of force, $N.s^{-1}$; *τ* is an hour, s.

Assuming that the contact area also varies according to the linear law, we obtain:

$$S = S_0 \cdot C\tau \quad (3)$$

Where:
C is the coefficient of proportionality, which depends on the properties of the product and characterizes the rate of decrease in the area; *S0* is the current value of the area of actual contact, m2.

Substituting (2 and 3) into the dependence of M. Stefan and Gorbatov, taking into account that at the moment of separation his time is obtained:

$$P_0 = \frac{2\alpha}{h} \cdot \frac{\omega_c}{\omega_c + \frac{2\alpha \cdot C}{h}} \quad (4)$$

For convenience, the equation is represented as (5)

$$\frac{1}{P_0} = \frac{h}{2\alpha} \cdot \frac{C}{\omega_c} \quad (5)$$

Since it is assumed that the increase in force and the change in the contact area are linearly dependent on time, we can assume that *C/ωc* is a constant value of A, ie:

$$\frac{1}{P_0} = \frac{h}{2\alpha} + A \quad (6)$$

The amount of adhesion is directly proportional to the tension surface of the marzipan paste and inversely proportional to the thickness of its layer. This dependence (6) can occur at a small thickness of the product layer.

Using such thermodynamic concepts as free surface energy and surface tension, we can describe some stages of the adhesive interaction of the process of applying marzipan paste on the surface of the flour confectionery, **Figure 2** (wetting the adhesive surface of the substrate). Despite the extreme importance, the processes of wetting and adhesion are still not clear enough, their study continues in all developed countries. Researchers are now particularly interested in the kinetics of wetting, nonequilibrium wetting, and other aspects of wetting processes.

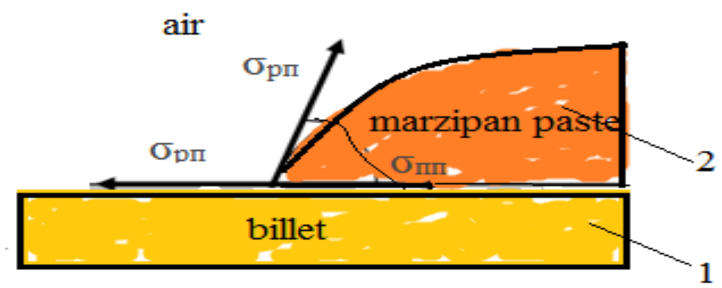

Figure 2 Equilibrium of forces affecting the angle of contact of marzipan paste 2 with the surface of the workpiece 1.

We consider the nature of their interaction as a process that occurs on the verge of contact of three phases. Wetting is also a manifestation of molecular forces, a manifestation of the affinity of the adhesive to the substrate **(Adamson and Gast, 1997; Rydil, 1936)**.

The paper by **(Shanina et al. 2019)** used the method of studying the surface tension at the interface between the phases, which allowed us to obtain very reliable research data. The study of wetting of different substrates is of interest in that it allows to identify the affinity of the adhesive to the substrate, to compare the molecular forces acting in different systems of adhesive which is the substrate.

All known methods and devices for determining surface tension are considered and analyzed in the works by **(Souheng 1982); Lee 1979); Adamson 1976); Rydil 1936)**. Moreover, in the work of the authors **(Fisher, 1979)** the technical means that allow automating the measurement process are described.

When applying marzipan paste on a hard surface of the workpiece, as noted earlier, there is a process of involuntary increase in the contact area, there is wetting. A layer of paste applied to the surface of a solid confectionery is a special physical object, the shape and structure of which is determined by the prescription composition.

In the work by **(Berlin and Basik, 1974)** it is noted that the application of a viscous liquid with its fluidity depends on the environmental conditions and the properties of the surface on which it is applied. Our offered marzipan pastes should ensure their smooth application (wetting) of the substrate surface, as well as interfacial contact between the adhesive and the substrate and interfacial or adsorption interaction at the interface of the two phases. To achieve a good application of the paste (wetting) with good adhesion, it is necessary that the surface tension of the adhesive was greater than the surface tension of the substrate. The wetting phenomenon is associated with the ratio of surface tensions (σ) of the adhesive and the substrate.

Conditions for applying a paste (wetting) of a hard surface

If before the collision with the surface the paste layer had a surface *Sk*, and the surface of the solid workpiece was *St*, then in equilibrium, when the paste layer forms a drop of a certain shape on the body surface, the surface area of their collision will be *Sc*, and the paste surface area *Sp*. The total free surface energy at the initial moment is:

$$E = S_k\sigma_n + S_T\sigma_T \qquad (7)$$

Finally, after reaching equilibrium, the total free surface energy will be:

$$E_2 = S_n\sigma_n + S_{TP}\sigma_{TP}$$

It is known that a necessary condition for the spontaneous process of applying the paste is that there is a decline in free surface energy **(Berlin and Basik, 1974)**. In our case, when stopping the application (the action of shear stress), the decline occurs quite quickly:

$$\Delta E = (E_1 - E_2) \prec 0 \qquad (8)$$

For this condition of applying the paste, the inequality is valid:

$$\frac{\sigma_T - \sigma_{Tn}}{\sigma_n} \succ \frac{S_n - S_к}{S_{TП}} \qquad (9)$$

It follows that at σт> σтп there is an increase in the surface contact of the paste with the medium (Sp> Sk). Thus, the application (wetting) is thermodynamically possible under the condition σт> σтп.

The equilibrium of the paste layer on the surface of a solid body (excluding the surface roughness and the action of gravity) is subject to the Jung equation from which it follows:

$$\sigma_T = \sigma_{nT} + \sigma_n cos\theta$$

Where:

θ is the edge angle or wetting angle. From which it follows: $\cos\Theta = \frac{\sigma_T - \sigma_{TП}}{\sigma_П}$

Analysis of the state of equilibrium in the ternary system (solid-liquid – gas (air)) leads to the dependence of the form:

σт = σп (10) $\sigma_T = \sigma_П \frac{1+\cos\theta}{1-\cos\theta}$ $\frac{\sigma_T - \sigma_{Tn}}{\sigma_n} \succ \frac{S_n - S_к}{S_{TП}}$ (10)

Interfacial surface tension for two media is determined by Antonov's rule, according to which the surface tension is equal to the difference of surface tensions of each of the phases separately **(Adamson and Gast, 1997; Rydil, 1936)**.

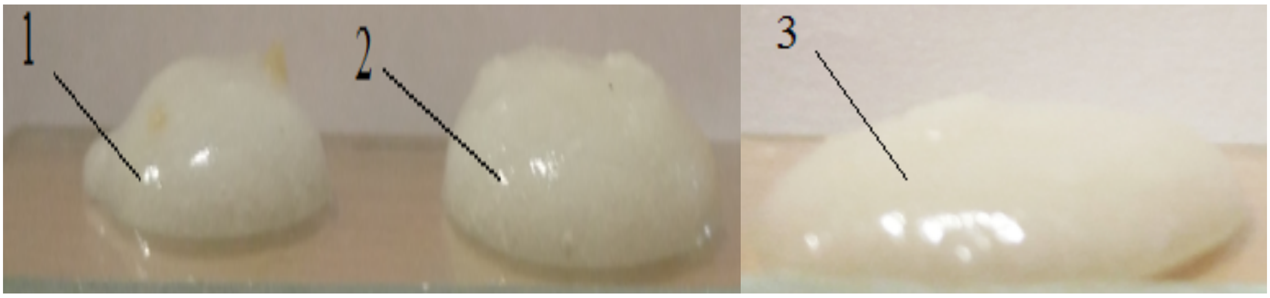

Figure 3 Blurring of marzipan paste.
Note: 1 – beginning of application, 2 – aging time 3 minutes; 3 – standing time 7 minutes.

Assuming this assumption for solid-liquid systems, we can write

$$\sigma_{тп} = |\sigma_т - \sigma_п| = |\sigma_п - \sigma_т|$$

Then, using Jung's rule **(Adamson and Gast, 1997; Rydil, 1936)** it is possible to receive a simple expression for the value of surface energy of a firm body:

$$\sigma_T = |\sigma_n - \sigma_T| + \sigma_n cos\theta \quad (11)$$

$$\sigma_T + \sigma_T = \sigma_n + \sigma_n cos\theta \quad (12)$$

$$2\sigma_T = \sigma_n (1 + cos\theta) \quad (13)$$

$$\sigma_T = \frac{1}{2}\sigma_n (1 + cos\theta) \quad (14)$$

It follows that the determination of the magnitude of the surface energy of a solid is possible by measuring the marginal wetting angle, ie the layer of paste **(Figure 3)**.

Determination of wetting angle of marzipan pastes

The study of the contact angle θ was determined by the method of dynamic measurement, provided that the phase boundary moves and there is a change in the contact angle over time is the method of changing the volume of the drop **(Figure 3)**. Among these processes, sorption and dissolution in the boundary layer of the two contacting phases promotes the diffusion of atoms (molecules) through the layer of confectionery and paste to desorb and release moisture.

The method of operative determination of the wetting angle was used to calculate the values of the derivative at the point of contact of the marzipan paste with the solid surface of the sponge blank. The surface of the marzipan paste is not described by simple analytical expressions. For an analytical description of the profile line of such a surface, you can use an approximation polynomial of the form:

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3$$

Where:
x and y are, respectively, the vertical and horizontal coordinates of the point on the surface of the marzipan paste;
$a_0, a_1, a_2 i a_3$ are polynomial coefficients.

The value of the angle, in this case, can be found by determining the derivative at the point of three-phase contact:

$$y' = tg\theta = a_1 + 2a_2 x + 3a_3 x^2$$

Obviously, at σт <σ тп and cos Θ <0, ie when the marzipan paste does not stick (wet) to the surface, the edge angle Θ must be less than 90 °. If the wetting angle is more than 90 °, partial wetting occurs. At Θ = 0, when the edge angle is not formed, there is a complete wetting, or spreading, which in our conditions does not occur.

$$\sigma_т > \sigma_п + \sigma_{тп}. \quad (15)$$

Thus, the wetting edge angle Θ or cos Θ is a measure of the application of marzipan paste. In the manifestation of physicochemical hysteresis, the wetting angles of the marzipan paste depend on the contact time of the phases during application to the surface of the workpiece. The surface of the workpiece marzipan paste covers completely, without the formation of voids. Therefore, the shape of the drop corresponds to a minimum of free energy. In our case we use the formula:

$$\theta_z = |arctg\,(a_1 + 2a_2 x + 3a_3 x^2)|$$

According to our research and data processing, the contact equation of applying the paste at an angle will be:

$$y' = -0.677 + 1.641x + 0.013x^2 + 2.454 \cdot 10^{-3} x^3$$

The equation for determining the angle will be:

$$\theta_z = |arctg\,(1.641 + 0.013x + 2.454 \cdot 10^{-4} x^2)|$$

Therefore, to achieve high adhesion, the surface tension of the paste must be of great importance.

It is also necessary that the surface tension of the solid confectionery was greater than the surface tension of the paste in contact with it.

Under such conditions, the application of adhesive on the surface of the substrate will be provided:

$$\Sigma \text{ substrate} > \sigma \text{ adhesive} \quad (16)$$

High-quality application of marzipan paste on flour confectionery allows moisture to penetrate some of its layers.

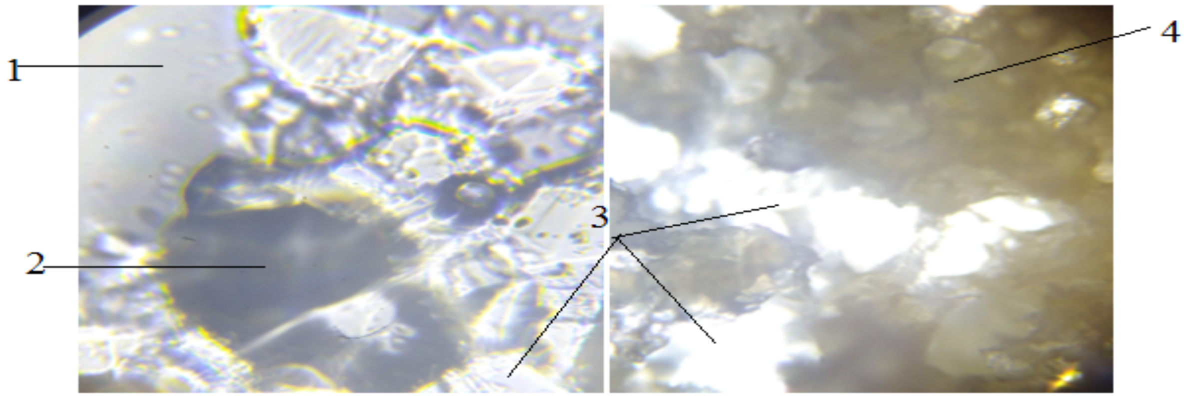

Figure 4 Photos of penetration of moisture of marzipan paste into a firm surface of flour preparation.
Note: 1 – marzipan; 2 – workpiece; 3 – air cavities in the workpiece; 4 – moisture penetration of the paste.

We made a section of applying the paste before and after 30 s of its contact. Photographs of the section under the microscope are presented in **Figure 4**.

According to the developed recipe, to determine the rate of penetration of moisture of marzipan pastes into the surface of the confectionery was used by weight method of research at a temperature of 25 °C.

The amount of moisture that penetrated through the surface of the confectionery was periodically weighed with an error of not more than 0.001 g. The change in the mass of the workpiece determines the amount of moisture that has penetrated through the test material. The experimentally established dependences of the change in the mass of the experimental samples in the time measured in min are shown in **Figure 5**.

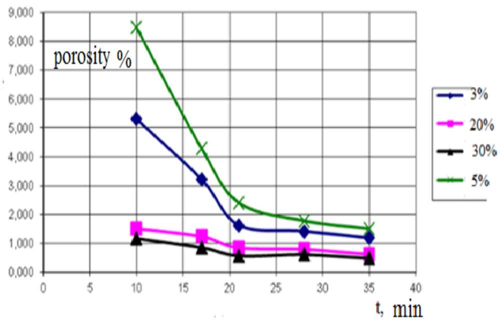

Figure 5 The rate of moisture permeability of marzipan pastes in the workpiece surface.

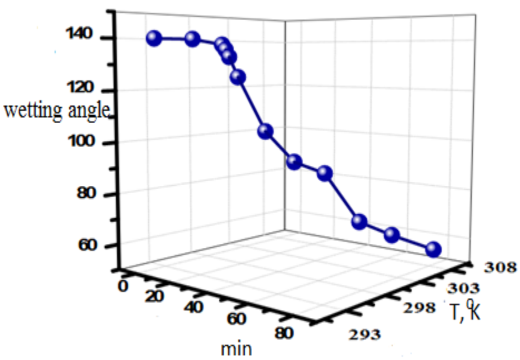

Figure 6 Dependences of the wetting angle on the ambient temperature and holding time for the pasta-confectionery system.

From the graphs shown in **Figure 5**, it follows that the absorbency of the sample coated with marzipan paste with a content of 20% and 30% DDW remained stable for 15 – 20 min from the beginning of the experiment. The less-dense molecular structure of marzipan paste with glycerin causes a greater ability to pass moisture into the workpiece. It may be desirable for the active application and coating of confectionery semi-finished products.

Calculation of the process

The effectiveness of this modification can be assessed by calculating the work of adhesion (Wa), which is determined **(Zimon, 1974)** by the ratio of surface energies of the adhesive, substrate, as well as interfacial energy:

$$W_a = \sigma_{ng} + \sigma_{Tg} - \sigma_{Tn} \qquad (17)$$

Where:

σ_{ng} is the surface tension of the paste (adhesive) on the border with gas (Air), MJ.m^{-2}; σ_{Tg} is the surface tension of solid body (substrate) at the boundary with gas (air), MJ.m^{-2}; σ_{Tn} is interphase surface tension, MJ.m^{-2}.

Temperature and time dependences of wetting are investigated. **Figure 6** presents the results of the experiments. It is shown that in the temperature range 293 – 308 the conditions for wetting the workpiece surface (θ >90 deg) are not created. The dependence of the wetting angle in the system of marzipan paste (sponge cake) on the temperature is nonlinear, which may indicate a chemical interaction. The calculation of temperature changes showed that the probability of such a process significantly depends on the temperature of the experiment. The process of flow at the adhesion boundaries at the contact of the paste with the workpiece is best at temperatures that are present in the production premises: 20 – 250 °C, which is an improvement in wetting in the system.

σ_{ng} is the surface tension of the paste (adhesive) on the border with gas (Air), $MJ.m^{-2}$; σ_{Tg} is the surface tension of solid body (substrate) at the boundary with gas (air), $MJ.m^{-2}$; σ_{Tn} is interphase surface tension, $MJ.m^{-2}$.

Taking into account Young's equation, the work of adhesion can be determined by the formula, which uses the values available for experimental determination:

$$W_a = \sigma_{ng}(1 + cos\theta) \quad (18)$$

Taking into account the interfacial interaction, a more accurate value of the adhesion can be determined by the formula:

$$W_a = \sigma_{ng}(2 + b \cdot \sigma_{кr}) - b \cdot \sigma_{kr}^2 \quad (19)$$

Where:
b is the coefficient of proportionality equal to the tangent of the angle of inclination, depending on cosθ = f (σn) to the abscissa.
Σkr is the critical value of the surface tension of the adhesive, which provides complete wetting, $MJ.m^{-2}$ (equal to the value of the surface tension of the substrate).

Dependence (19) is the equation of the parabola, the vertex of which is at the following value of the surface tension of the adhesive:

$$\sigma_{ng} = \frac{1}{b} + 0.5\sigma_{kr} \quad (20)$$

The maximum adhesion work is determined by the dependence of the type:

$$W_{a\max} = \frac{1}{b} + \sigma_{kr} + 0.25b\sigma_{kr}^{\ 2} \quad (21)$$

Figure 7 shows the dependence of the adhesion on the surface tension of marzipan paste with different compositions.

The performed calculations and constructed graphical dependences testify to an increase of work of adhesion and

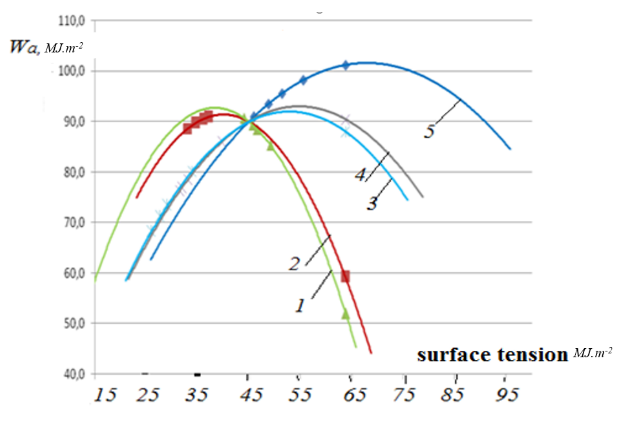

Figure 7 The dependence of the adhesion on the surface tension of marzipan paste according to the recipe.
Note: 1,2 – glycerol 3% and MSDS 20%, 3,4 – glycerin 4% and DDW 25%, 5 – glycerin 5% and DDW 30%.

the use of paste with DDW of 20% and 30% and glycerin to 5%. The most effective indicators of marzipan **pastes (Figure 7 item 5)** with 30% DDW and 5% glycerin. Therefore, this recipe has the most significant effect compared to other recipes. This is due to the quality distribution of marzipan paste and its adhesive properties. Partial replacement of almond flour with DDW in the prescription composition of marzipan pastes leads to changes in the structural state and quantitative values of rheological and sensory characteristics.

Indicators of the total deformation with increasing concentration of glycerol do not increase in direct proportion and depend on the mass fraction of DDW in the composition of marzipan pastes. Accordingly, at a concentration of DDW of 20%, the indicators of total deformation increase depending on the glycerol content in 1.0 – 1.2 times, at a concentration of DDW of 30% increase in 1.0 – 1.3 times, respectively. Irreversible deformation at a concentration of DDW of 20% is constant and does not depend on the concentration of glycerol. At a concentration of DDW of 30% with increasing concentration of glycerol, the reverse deformation increases by 1.5 times. The inverse deformation increases in direct proportion to the total deformation

CONCLUSION

The current direction of improving the preparation of marzipan pastes is and remains the search for promising sources of raw materials and the establishment of rational methods of their introduction, which will create optimal conditions with given biotechnological properties and establish mechanisms and factors of their formation. From the given mathematical analysis the compounding and selection of parameters of preparation of marzipan pastes are substantiated. Thus, in the process of formation, an increase in the strength of adhesion with an increase in the concentration of DDW, which is confirmed by sensory studies, a significant increase in stickiness. The surface properties of the pastes depending on the time of contact with the adhesive and air confirmed the fact of lengthening the working time, which is a very important factor in the modeling of shaped finishing semi-finished products made by hand. Based on the carried out sensory and rheological characteristics the directions of technological use of marzipan pastes which basis is based on structural properties are offered. Marzipan paste PKV is intended for a covering and as a layer for flour and confectionery products as the main indicator of consistency is extensibility. The best indicators were found at the concentration of DDW of 25% and glycerol of 4.5%. For marzipan paste, LFC used for the manufacture of candies, bars, tiles, as well as modeling of shaped products, the main criterion for the characteristics of the consistency is the forming ability of the paste. The best indicators are established at a concentration of DDW of 30%.

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