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Comparison of the Physicochemical Characteristics of commercial margarines in Uzbekistan and formulate trans-free margarine recipe based on local raw materials

Akbarali Ruzibayev
candidate technical sciences, docent, Tashkent Chemical-Technological Institute
100011, Uzbekistan, Tashkent, A.Navoiy str., 32
Shakhnozakhon Salijonova
Doctor of Philosophy (PhD), Tashkent Chemical-Technological Institute
100011, Uzbekistan, Tashkent, A.Navoiy str., 32
Mansur Akbarov
PhD student, Tashkent Chemical-Technological Institute,
100011, Uzbekistan, Tashkent, A.Navoiy str., 32
Gulmira Rakhimova
PhD student, Namangan Engineering-Technological Institute
160115, Uzbekistan, Namangan, Kasansay str., 7
Zulfiyakhon Khakimova
PhD student, Tashkent Chemical-Technological Institute
100011, Uzbekistan, Tashkent, A.Navoiy str., 32

ABSTRACT

The results of the analysis of fatty acid composition, physicochemical and microbiological properties of margarine of 7 different brands from commercial margarine products are presented in the research work. It was found that all the properties of margarines meet the food safety requirements, only the quantity of trans fatty acid is higher than the norm. It was determined that the rate of formation of primary and secondary oxidized substances during the storage period of margarines depends on the fatty acid composition. Microbiological changes of margarines prepared in laboratory conditions during storage were analyzed. It was observed that the microbiological propertiesof the margarines obtained during the storage period were relatively stable.

Keywords: trans fatty acid, margarine, emulsion, microbiological properties, microorganism, peroxide value, anisidine value, fatty acid content, essential fatty acid.

Introduction

Margarine is a product created as a substitute for butter, and its composition mainly consists of a mixture of fat and water phases. The oil phase of margarine contains various fats and oils, emulsifiers and fat-soluble additives. The aqueous phase contains sugar, salt, milk, vitamins and other water-soluble substances. The type and quantity of substances contained in margarine depends on its assortment. For example, if milk is used only in dairy-based margarine, sugar is not used in some types of margarine [1].

Margarine is a product prepared in accordance with the properties of butter, which has undergone a manufacturing process, mixed with substances that give it smell, taste and color, and which contains, in whole or in part, other oils or fats than butter [2,3].

In the world, the margarine standard was established by the Codex Alimentarius Commission for products containing at least 80% fat and 16% water (No. 32-1981, Rev.1-1989). It defines margarine as "a food made primarily from non-dairy fats and oils, consisting primarily of water and fat, in the form of a plastic or liquid emulsion." The standard includes permitted additives such as vitamins, flavorings, colorants, emulsifiers and preservatives [4].

It can be seen that most of the fats in margarine consist of highly unsaturated and monounsaturated fatty acids, which differ depending on the oils used in production. Although margarine is lower in saturated fatty acids than butter, it does not contain the healthy saturated fatty acids, butylic and myristic acids [5].

Until January 1, 2006, margarines were derived from chemically hydrogenated fats, whose hardness depends on trans fats. Even today, food companies are exploring the possibilities of replacing partially hydrogenated trans fats in margarine[6,7,8].

Specialists have conducted extensive research on the preparation and development of various variants of fat mixtures with different composition and hardness for margarine. According to them, hydrogenated oils containing trans fatty acids have high hardness, retain their hardness when mixed, the main thing is that they are easy to process, crystallize well, and form a small crystalline structure. High-temperature soluble triglycerides of hydrogenated fats form strong crystal lattices. They reliably hold liquid triglycerides soluble at low temperatures, as well as water droplets dispersed in oil. Fats with a low content of trans fatty acids and high hardness, for example, partially hydrogenated palm olein, are preferred [9].

Since the beginning of the 21st century, in America, Europe and other developed countries of the world, since 2018 in our Republic, a strict standard was set for the quantity of trans fatty acids in margarine products [10,11]. In particular, the

content of trans fatty acids in margarine products produced in our Republic and imported from abroad should not exceed 2% [12]. However, most margarine products today do not meet this requirement. Some of them meet the requirements for the quantity of trans fatty acid, but do not meet the requirements for other quality indicators. This requires the margarine industry to find a source of trans-free fats.

It is known that the physicochemical, microbiologicaland sensoryproperties of margarines and the quantity of trans fatty acid directly depend on their fat base [13].

In the research work, the physico-chemical, microbiological and sensorypropertiesand fatty acid content of commercial margarines were studied, and compliance of margarines with safety requirements was evaluated. Also, a trans-free margarine recipe was created based on local fatty raw materials.

Materials and methods

Raw materials and samples

Margarines of 7 different brands were analyzed to determine the fat phase of margarines on the market. In order not to violate the rights of producers and to preserve anonymity, the analyzed margarines were marked as M-1, M-2, M-3, M-4, M-5, M-6, M-7.Dairy-based margarines of the brands "Mechta", "Shchyedroye leto", "Olmos", "Khozyayushka", "Maselko", "Appetito" were selected for analysis.

Cottonseed (CSO) and sunflower (SFO) oils were used as the main raw materials for the production of trans-free margarine. Refined, bleached, and deodorized SFO, CSO, cottonseed palmitin and interesterified fat were obtained from “Tashkent fat and oil industrial complex” JSC. An emulsifier, phospholipid concentrate was used to prepare the margarine emulsion.

Fatty acid analysis & Label Assessment

The fatty acid composition of the samples was measured by AGRO-KIMYO STANDART LLC (Tashkent, Uzbekistan). The determination was conducted using the AOAC 996.06 method (AOAC International). Fatty acids were saponified, methylated and methyl esters were extracted. Then, the methyl esters of the fatty acids were analyzed by Shimadzu GC2030 gas chromatograph (capillary column SH-2560; 0.25 mm ID; 0.2 mm df; 105 m). using external standards for quantitation. Trans fatty acid was determined by the method of Farag and etc. [14]. Acid and iodine values were determined according to the AOAC [15] methods. Solid fat contents (SFC) were determined using a nuclear magnetic resonance (NMR) spectrometer according to the AOCS Official Method Cd 16-81. [16].

Usually, solid vegetable fats, animal fats, butter and vegetable oils are used in the fat phase of margarine. The quality of these fats and oils and their quantities determine the sensory and physicochemical properties of margarine. The quantity and composition of the components in the margarine recipe are different depending on the type of margarine. The quantity of fat can be up to 25-82%[17].

It has been found that liquid vegetable oils are more useful for the human body than solid fats. These oils contain a lot of unsaturated fatty acids, which have the property of cleaning cholesterol and other fatty substances in the human body. The degree of unsaturation of fatty acids affects their digestion and absorption by the body. This explains the benefits of olive, sunflower, soybean, sesame and other such oils. Linoleic and linolenic acids contained in oils are considered essential fatty acids, that is, they are included in the group of non-exchangeable substances and are not synthesized in the human body, but enter inside of body by the food. These acids are considered necessary substances for brain activity [18].

The melting point of the simple mixture of fats and oils or the interesterified fats included in the margarine determine the expected melting properties of the final product. General characteristics of margarine, such as storage and packaging, as well as nutritional quality, are estimated from this characteristic. The physical properties of fats and oils directly depend on their fatty acid composition and structure of triglyceride. The quantity and ratio of saturated and unsaturated fatty acids in oils and fats determine their physical properties. Based on these data, we analyzed the fat content of the analyzed margarines and the fatty acid composition of the extracted fats and oils. For this purpose, methyl esters of fatty acids extracted from oils and fats were analyzed by gas-liquid chromatography (table 1).

Table 1

Fat content of commercial margarine products and their fatty acid composition

№	Sample number	Quantity of fat, %	$C_{14:0}$,$C_{14:1}$	$C_{16:0}$,$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	Trans FA	Other FA
1	M-1	74,4	0,7	26,6	5,1	34,5	32,3	0,1	5,2	0,7
2	M-2	60,8	0,5	22,2	5,8	42,8	27,8	0,1	5,8	0,8
3	M-3	75,0	2,6	25,3	4,0	26,2	33,8	0,1	0,4	8
4	M-4	60,6	0,4	16,9	8,7	54,7	18,7	0,1	7,6	0,5
5	M-5	55,0	1,1	21,1	7,5	51,6	18,0	0,1	7,7	0,6
6	M-6	46,5	0,9	32,4	5,6	45,4	14,3	0,4	4,3	1
7	M-7	60,0	1,1	25,7	5,4	36,3	30,4	0,2	8,5	0,9

From the data in Table 1 it can be seen that out of the seven samples of margarine analyzed, the quantity of fat in four was greater than the quantity indicated on the label, and in three it was the same. The fatty acid

composition of oils extracted from margarine samples differs from each other. There is a lot of palmitic acid in all samples of margarine, for example, 32.4% in sample M-6 and 16.9% in sample M-4. This indicates that all margarine samples contain cottonseed oil or palm oil.

The weight percent of saturated fatty acids was from 26.0% to 38.9%, and the weight percentof unsaturated fatty acids was from 60.1% to 73.5%. It was observed that linolenic acid in samples M-6 and M-7, and myristic acid in sample M-3 were more than other samples (2.6%). Also, 6.2% lauric acid was detected in sample M-3, unlike other samples. It can be concluded that this sample contains milk fat.

Trans fatty acids were detected in all margarine samples, the lowest quantity of which was observed in sample M-3 (0.3%). The quantity of trans fatty acids in all the remaining samples ranged from 4.3% to 8.5%. This is more than the quantity specified in the regulation (2%).

The shelf life of margarine products directly depends on their fat phase. If the percentage of polyunsaturated fatty acids in the fatty phase increases, the shelf life of margarine decreases. However, the antioxidants included in the recipe also have a serious effect.

The shelf life of margarines is evaluated by their peroxide value, acidity and microbiological property. The peroxide value represents the quantity of primary oxidation products of fatty acids in margarine. Therefore, the peroxide value depends on the composition of the fat phase and the nature of the antioxidant.

Due to the fact that the shelf life and food safety of margarine depend on the peroxide value of the fat phase, the peroxide values of the oils extracted from margarines was analyzed in the next experiments (Table 2).

According to Table 2, all margarine samples comply with food safety requirements (specified norm of 10 mmol of active oxygen/kg) in terms of peroxide value. In particular, it was found that the peroxide value in sample M-3 is the largest (1.7 mmol of active oxygen/kg) and the smallest in sample M-1 (1.2 mmol of active oxygen/kg). However, it is possible to positively evaluate the oxidation stability and shelf life of margarine samples based on the determined peroxide value.

In the next experiments, the physico-chemical and microbiological properties of margarine samples were analyzed. The obtained results are presented in Tables 2 and 3.

Table 2
Physico-chemical properties of commercial margarines

№	Sample number	pH	Acidity, grad. K	Content of moisture and volatile substances, %	Melting point, ˚C	Peroxide value, mmol active oxygen/kg
1	M-1	4,8	0,7	22,8	35	1,2
2	M-2	4,8	0,8	34,9	38	1,6
3	M-3	4,2	0,9	20,7	36	1,7
4	M-4	5,1	0,5	35,2	36	1,4
5	M-5	5,1	0,5	42	37	1,6
6	M-6	5,5	0,5	37,7	35	1,4
7	M-7	4,8	0,9	35,4	36	3,4

According to the data in Table 2, the physico-chemical properties of margarine samples are different. The pH value was in the range of 4.8-5.1, the acidity was in the range of 0.5-0.9%, the quantity of moisture and volatile substances was in the range of 20.7-42.0%. Melting points were almost the same, 35-38 ˚C. All margarines in terms of physico-chemical properties comply with the requirements specified in the regulation.

Food additives in margarine can seriously affect not only its physical and chemical properties, but also its microbiological property. Because milk and other components in margarine can be a favorable food environment for microorganisms. Therefore, margarines are analyzed microbiologically.

Microbiological properties of margarine are affected by ingredients, physico-chemical properties, processing conditions and packaging materials. In the production of margarine, the raw ingredients are controlled according to microbiological safety specifications, which are mainly implemented by the suppliers.

Spoilage of margarines is mainly caused by chemical events, and margarine is generally a microbiologically inert product. Considering the effect of the general composition of margarine, it prevents the growth of most microorganisms, because the presence of micron-sized fat droplets in the emulsion is an effective factor limiting the growth of microbes. Smaller droplets mean a smaller internal surface area and a limited number of nutrient molecules, thus extending the microbial growth time [19,20].

The composition of margarine prevents the development of most microorganisms, especially those considered to be potential pathogens. The composition of margarine added to the process of forming micron-sized aqueous phase droplets to form an emulsion is a very effective barrier to the growth of microbes.

In the next experiments, the microbiological parameters of margarine were analyzed (Table 3).

Table 3
Microbiological properties of commercial margarines

№	Sample number	Mikrobiologikko'rsatkichlar			
		CGB (coliforms), in 0,01 g	Pathogenic mikroorganisms, including Salmonella, in 25 g	Yeast, CFU/g	Mold, CFU /g
1	M-1	Negative	Negative	< 10	< 10
2	M-2	Negative	Negative	< 10	< 10
3	M-3	Negative	Negative	< 10	< 10
4	M-4	Negative	Negative	< 10	< 10
5	M-5	Negative	Negative	< 10	< 10
6	M-6	Negative	Negative	280	< 10
7	M-7	Negative	Negative	< 10	< 10

According to the data in Table 3, all seven analyzed margarine samples comply with food safety standards in terms of microbiological properties.

According to the "General technical regulation on the safety of fat and oil products", the number of yeasts should not exceed 500 and the number of molds should not exceed 50. Among the analyzed samples, the number of yeasts was 280 only in the M-6 sample. This sample is also considered suitable for consumption because it is less than the established standard.

The compliance of margarines with the food safety criteria was analyzed based on their fatty acid content, physico-chemical and microbiological parameters, and it was found that all of them comply with the safety criteria. All margarines do not meet the standard requirements for trans acid content. Therefore, based on the results obtained from the margarines analyzed above, in the next experiments, a trans-free margarine recipe was created in laboratory conditions based on local raw materials (Table 4).

Depending on the purpose, margarine products should have a certain melting point (smoothness) and flexibility. Melting is characterized by the complete melting temperature, which depends on the composition and quantitative ratio of solid and liquid fractions: the greater the quantity of solid fraction, the less the melted mass. Plasticity is related to the ratio of solid glyceride to liquid glyceride. Fats with a solid glyceride content of 15-30% are flexible and spreadable. The quantity of hard glycerides in dense and non-bending fat is more than 30%, and in very soft fats it is 10-12%.

Table 4
Fatty base of margarine formed from local oils and fats

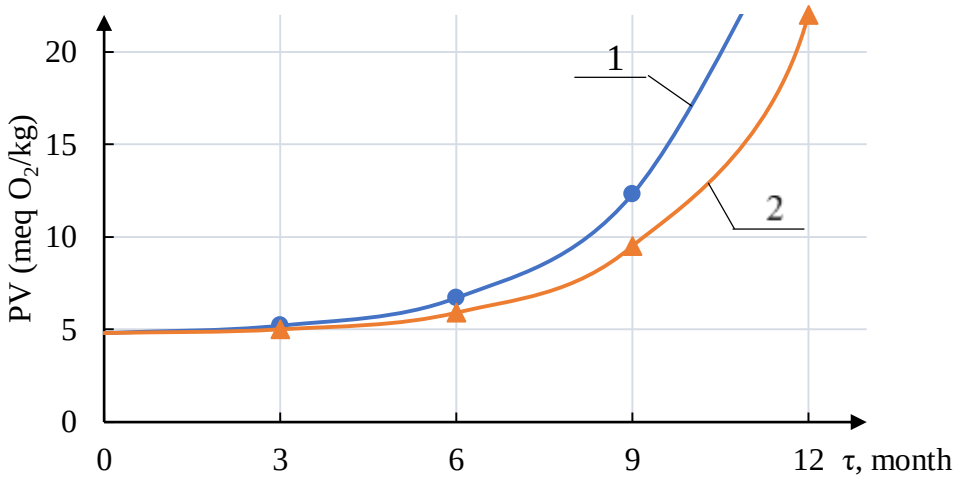
Fats and oils	Samples, %				
	existent			proposed	
	1	2	3	T-1	T-2
Hydrogenated oil, M_{pl} 31-34ºC, hardness 160-320 g/sm	50	45	-	20	-
Hydrogenated oil, M_{pl} 35-36ºC, hardness350-410 g/sm	25	30	-	30,0	-
Cottonseed palmitin M_{pl}20-25ºC	-	-	-	18	14
Sunflower oil(Soybean oil)	-	25	20	20	12
Cottonseed oil	25	-	-	10	-
Structure builder (fully hydrogenated oil)	-	-	-	2,0	2,0
Palm oil, M_p=43 °C	-	-	63	-	-
Palm oil, M_p=39 °C	-	-	17	-	-
Interesterified fatM_p 31-32ºC,	-	-	-	-	72
Jami	100	100	100	100	100

Table 4 shows that hydrogenated oils are partially replaced by vegetable oils and cotton palmin (recipe T-1). An increase in the quantity of liquid oils leads to an increase in essential fatty acids in margarine and a decrease in melting point and hardness. However, the addition of structure formers to the fat base of margarine increases its melting point and hardness.

Today, many enterprises in our Republic widely use palm oil in order to produce margarine with a normalized quantity of trans fatty acids. Due to the fact that these fats are imported from abroad, the cost of the product is increasing. Therefore, palm stearin and palm oil in the recipe have been replaced with interesterified fat and fully hydrogenated oil.

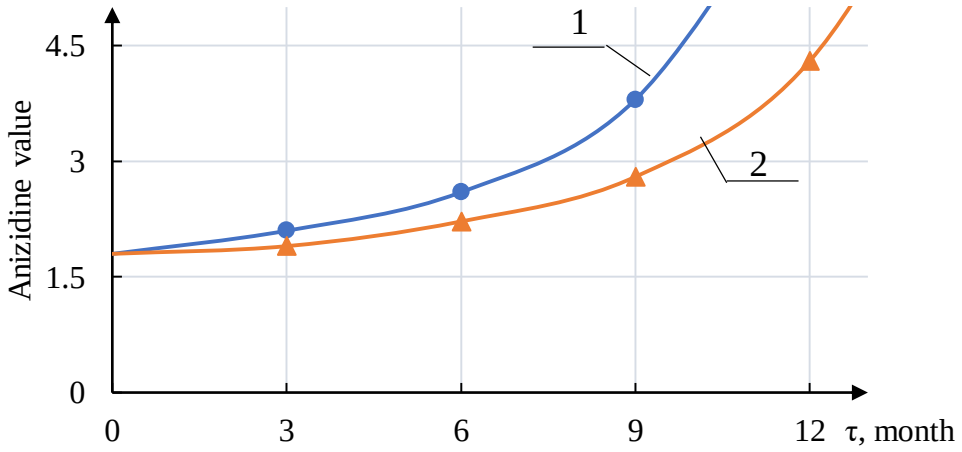
Analyzing the recipes of commercial margarines, we developed a margarine recipe that meets the standard requirements based on local fatty raw materials. The composition of the recipe is as follows: fat base 71.6%, dye 0.1%, emulsifier 0.2%, milk 10%, salt 0.4%, sugar 0.4%, phosphatide concentrate 0.5%, antioxidant 0.05%, water 17.25%. Margarine products were prepared in laboratory conditions based on established recipes. For this, the components of the recipe were mixed and an emulsion was formed, then the emulsion was cooled and crystallized. The physical and chemical properties of the prepared margarine products were analyzed.

Figure 1 shows the change in the peroxide values of the proposed and traditional recipe margarines. As can be seen from this picture, the peroxide values changed little during the specified storage period (6 months) of the offered margarine. During 12 months, the peroxide value of this margarine increased from the specified value (10 mmol/kg). This situation was also observed in the study of secondary oxidized products formed in margarine. Figure 2 shows the change in the anisidine value in these margarines.



1-control;2-proposed

Figure 1. Changes in the peroxide values prepared margarines during the storage period



1-control;2-proposed

Figure 2. Changes in anisidine values of prepared margarines during the storage period.

As can be seen from Figure 2, margarine forms secondary oxidized products, aldehydes, ketones, etc. This is confirmed by the increase in their anisidine numbers.

It is known that the substances contained in milk added to the margarine recipe create a favorable environment for microorganisms to live, that is, microorganisms can develop well in it. Therefore, pasteurized milk is added to margarine, and the prepared emulsion is also pasteurized before cooling. In the next experiments, the microbiological properties of margarines prepared in laboratory conditions were analyzed. Microbiological analysis was carried out in accordance with the general technical regulation "On the safety of oil-oil products" and the quantity of mesophilic aerobic and facultative-anaerobic microorganisms (MAFAnM), bacteria belonging to the group of enterococci (coliforms), pathogenic microorganisms (including Salmonella), yeasts and molds were analyzed. The obtained results are presented in Table 5.

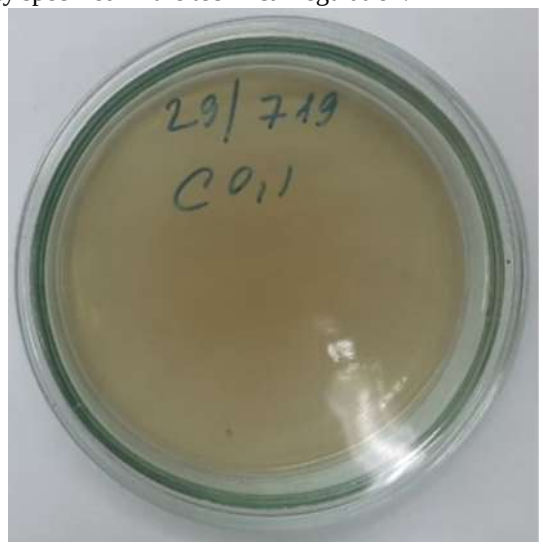
Table 5

Changes in microbiological properties of margarine during storage

Microbiologicalproperty	The norm specified in the general	Margarines

	technical regulation "About the safety of oil and fat products"	M-1 (control)	MT-1	MT-2
Quantityof mesophilic aerobic and facultative-anaerobic microorganisms, CFU/g	$1*10^5$	1*10	$1*10^2$	1*10
CGB (coliforms), g	0.01	Negative	Negative	Negative
Pathogenic mikroorganisms, including Salmonella, g	25	Negative	Negative	Negative
Yeast, CFU/g	$5*10^2$	Negative	1,5*10	Negative
Mold, CFU /g	50	Negative	Negative	Negative

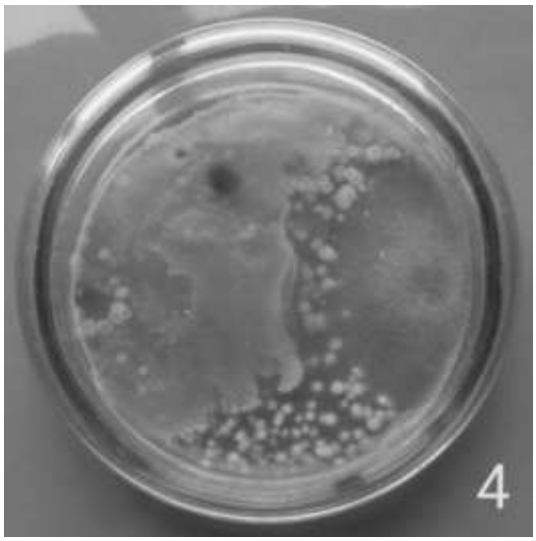
From the given data (Table 5), it can be seen that microorganisms such as bacteria belonging to the group of enterococci (coliforms), pathogenic microorganisms (salmonella) and mold were not observed in all types of margarine during the storage period. It was found that the quantity of MAFAnM and yeast did not exceed the quantity specified in the technical regulation.



Margarine M-1 (control)


Margarine M-1 (storedimproperly)

MargarineMT-2



MargarineMT-2 (storedimproperly)

Figure 3. Microbiological analysis of margarines

The obtained results allow us to conclude that margarines are nutritionally safe products. Their consumption satisfies the daily consumption of essential fatty acids. This serves as a basis for recommending it in the daily diet of patients with cardiovascular disease.

However, improper storage of margarine can lead to deterioration of its quality. The reason for the deterioration of the quality of margarine is that the water-milk phase is moldy and damaged by other microorganisms. When the air humidity in warehouses is high, the mold process is fast. Margarine made from well-

selected dripping milk will keep for a long time. This indicator is affected by the technological regimes of product preparation, the composition of the fatty base, and the density of the packaging containers.

Conclusion

The fat content, fatty acid composition, physico-chemical and microbiological properties of margarines of seven different brands from the available commercial margarines in Uzbekistan were analyzed. All their indicators were found to be in compliance with food safety requirements. Only one of the analyzed margarines (sample M-3) met the requirements of the standard for the quantity of trans acid, and the remaining margarines were found to be higher than the norm. Only one of the analyzed margarines (sample M-6) contained a large quantity of yeast microorganisms (280 CFU/g), but this quantity did not exceed the standard (500 CFU/g). Based on local fats and oils, a margarine recipe with an optimized quantity of trans acid was formed, and margarine was prepared on its basis in laboratory conditions. The peroxide value, anisidine value and microbiological properties of prepared margarines were analyzed. It was found that the change of microbiological indicators of margarine depends not only on the recipe, but also on the storage measures.

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