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Research Article

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CHOICE RATIONALE OF MATERIALS FOR ROAD MARKING IN ORDER TO DEVELOP ITS PRODUCTION TECHNOLOGY

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Abstract. *The article is devoted to the study of coating for road markings. Because road marking coatings are highly weatherproof, resistant to temperature extremes, moisture resistance, and good anti-corrosion properties, they can be used to protect exposed steel structures, but their main purpose is to apply road markings. When choosing the type of materials for marking, it is important to take into account their technical characteristics. It is very important that the markings are clearly visible at any time of the day. During the day, visibility is affected by the size and brightness of the markup. This work describes a series of laboratory experiments with samples coated with paints and reveals their protective properties in contact with water and acid. The highest quality coverage was also identified. Work in this direction continues. Thus, the authors are currently conducting experiments to develop a polymer coating for the protection of concrete and concrete products.*

Keywords: coating, road markings, corrosion resistance, polymer, polymer coating.

1. Introduction

Everything in the world does not stand still, new technologies are constantly being developed, both in metallurgy [1- 5], engineering [6 - 8] and construction [9, 10]. One of the main problems is road surfaces and the durability and wear resistance of road markings. For the first time marking as a method of road traffic organization was applied in the early XIX century in Great Britain. In Shrewsbury, a row of white stones was laid on a small width of a bridge, marking the central line. In the XX century (1911) road markings began to be practiced in the United States of America.In Russia, the use of highway graphics began in 1933, when "piece-lines" made of nitro paint began to appear on Moscow streets. The first were Teatralnaya square and exits from Neglinka and Petrovka to Kuznetsky bridge [11, 12].

In the age of high speeds, the main reason for the accelerated pace of development of new technologies for pavements has been people's need for efficient transportation routes [13]. Infrastructure provision in the city needs to start with transportation routes. For this reason, special services pay special attention to signage on roads that are responsible for the safety of all road users. Road markings remain one of the most important elements in this system. It is used to ensure the regulation of traffic on the road. Road markings remain visible even in the dark through the use of special paint. The paint allows you to create distinct lines that are visible to the driver and signal to him how to behave on a particular section of the road [14].

The main functional purpose of quality road markings is to provide effective visual information to motorists and other road users in various conditions [15-18]. Traffic safety and road capacity depend to a large extent on the quality and condition of road markings. Road markings occupy a significant place within the technical means of traffic organization and are an integral part of the normal optical perception of a modern highway. Most importantly road markings shall be durable in terms of functionality [19].

The functional durability of road markings does not exceed two years, the cost of marking works is a significant part of the operational costs of road maintenance, and the time of their implementation is limited to the warm season of the year, especially in the northern regions of the Republic of Kazakhstan. During marking works, traffic conditions are significantly deteriorated, traffic safety is reduced, the cost of transportation is increased, and the environmental situation on adjacent road sections is worsened due to congestion. For these reasons, the problem of improving the functional durability of road markings is very relevant.

For example, the practical experience of using thermoplastic materials for markings in domestic and some CIS countries shows that a significant part of the destruction of markings made of thermoplastics is cracking with subsequent detachment of the material from the road surface. This is largely due to the imperfection or complete lack of methods for assessing the quality parameters of the materials used for road markings. These circumstances indicate the relevance of the development and improvement of methods of obtaining, testing and standardization of requirements for materials used for road markings [20]. The performance of coatings for road markings has been established through a series of laboratory experiments. An important research objective is to select the best quality pavement to improve the performance of road markings. Purpose of the work. Selection and formulation of initial components for road markings. The materials for pavements currently in existence are summarized in Table 1 [21 - 29].

Table 1. Road marking materials

Name	Advantage	Disadvantage	Note
Paints (Figure 1)	low cost of material per unit area of marking compared to the use of plastic materials; technological equipment for its application, short drying time; the possibility of stencil application of complex in configuration marking elements; brightness; easy to apply and use.	availability of non-ecological, flammable organic solvents (up to 60%); lack of light fastness and reflective effect (does not glow in the dark); rapid abrasion (service life is 3-8 months); at the same time, not suitable for busy federal high ways.	
Thermo-plastics (Figure 2)	does not contain solvents; has much greater functional durability than in the case of paints; brightness; layer thickness; ease and speed of application.	the need to heat up the material before use with special devices for infrared heating of asphalt concrete pavements; precise compliance with the plastic heating temperature and time for its melting and mixing.	flow properties of thermoplastics necessary for marking are acquired as a result of melting at 150-220°C.
Cold-plastics (Figure 3)	do not require heating for their application; as a result of their mixing, a material is formed that creates elements of horizontal road markings; have a good prospect of use in various climatic conditions; frost resistant; economical; has high adhesion and homogeneity of the layer.	high cost and small number of machines; use of marking machines with a special unit for mixing hardener and plastic; complete release of the node from plastic within a short period of time (30-60 minutes).	they are an alternative to plas-tics; in its original form it is a fluid mixture of basic components and a separately supplied hardener
Polymer-tapes (Figure 4)	high and consistent quality.	have not found wide application; the cost is very high and exceeds the cost of cold plastics.	are used on an experimental basis; careful compliance with the marking technology is required.
Light reflectors (cataphotes) (Figures 5, 6)	clearly visible in bright sunlight and dark night, which increases safety in any weather; increased service life by 10-15% due to the presence of glass beads; significantly increase the grip of car tires with the surface of the highway; does not contain organic solvents in contrast to paint, so it is not flammable and absolutely safe in terms of the environment.	fixed artificial lighting, when the significance of retro reflective parameters is reduced to a certain extent; precise compliance with the application technology; dependence on weather conditions; long drying time; rapid abrasion and high cost; moreover; the service life does not exceed 3-9 months.	glass beads with a diameter of (0.05-1.50 mm) are used to give the markings retro reflective properties.

Scientific novelty consists in the fact that in the proposed formulation of road markings there is a polymer matrix coating consisting of vinyl-n-butyl ether (VBE), which is a low-temperature additive at the molecular level, that is, provides elasticity of the coating at low temperatures and improves adhesive properties, which leads to an increase in the service life of road marking compositions. The presence of titanium and zinc metal oxides in the composition increases the corrosion resistance of these road markings.

The most important characteristics of road markings are the parameters that determine their visibility. During daylight hours, the visibility of the marking is characterized by its size, contrast of color and brightness (brightness factor) of the marking and the pavement on which it is applied (GOST R 51256-99), to which is also normalized the value of the brightness factor (or visibility factor in diffuse daylight and artificial illumination) depending on the characteristics of the road - its category, the material of the top layer of the pavement and the color of the marking.

Fig. 1. Road markingpaint.

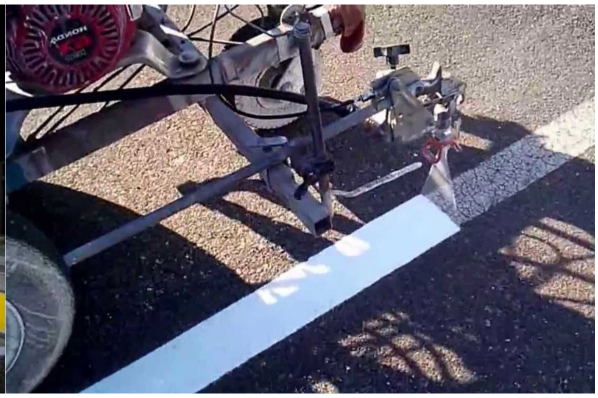


Fig. 2. Thermoplastic.

Fig. 3. Cold-useplastic.

Fig. 4. Polymertape.

Fig. 5. Glassmarbles.

Fig. 6. Glassbeadcoating.

It is now possible to use "structural" markings consisting of separate fragments or having a certain shape in the form of a checkerboard, comb, etc. Such markings provide better visibility of the markings at night when the pavement is wet in the reflected light of vehicle headlights. Another important property of "structural" markings is that when a vehicle wheel collides with it, the driver receives additional information in the form of vibration, which allows the driver to take timely action to return to the lane limits. Such markings are very promising given the country's climatic peculiarities [30].

Table 1 shows that paints and cold plastic are the most popular pavement marking materials for pavement markings. Their main difference is in the application technology. Paints, road enamels and cold plastics are applied at ambient temperature. These materials are applied by the so-called "cold method". The paint is applied to the road surface using a stencil. Road markings developed on the basis of a fluorescent surface and intended for use as directional, warning and/or side markings on roads, streets, embankments or parking lots are discussed in [31]. The markings contain a binder material that fluoresces when irradiated with UV(A) light, and translucent glass granules arranged in the binder material at 50-75% of their size. The size of the glass granules is 0.4-1.0 mm. Such a road marking material should resist water and tire wear during operation.

The authors of the paper propose a technology for road markings containing basic resins - n-butyl acrylate and methyl methacrylate, hardener, reactive resin on the basis of acrylic resins, gas pedal of the curing reaction; in this case the ratio of basic resins and reactive resin is in the range from 1:3 to 3:1. This technology will expand the possibility of using road markings in climatic conditions with reduced temperatures [32].

After analyzing the existing materials for road markings, the authors of this article offer their own technology for creating polymer coating for road markings.

2. Materials and Methods

All countries use white paint for permanent markings, so the university's chemistry lab used white components that were used as pigments. Reflective material (crushed glass) was also incorporated into the pavement to improve the visibility of the markings.

St.3 steel plates were used as samples (according to GOST 5272-82, in which steel plates are the analog samples). This underlayment was chosen because of its low porous permeability compared to asphalt-concrete; if the pavement performs well on steel, the quality performance on asphalt-concrete will be better compared to the experimental performance. (The porous structure of asphalt-concrete allows for improved adhesion properties of the proposed material, which in turn will affect performance). Coatings of different compositions were applied on degreased steel plates; quality control was performed by visual inspection after drying, and samples were tested in aggressive media such as water/NaCl (10% wt.), water/HCl (10% wt.). [35]

The main component of coatings is varnish (copolymer of methyl methacrylate/vinyl butyl ether, copolymer of methyl methacrylate/vinyl butyl ether, maleic anhedride ethyl acetate (solvent), adhesion additives, emulsifying agents), having a liquid or semi-liquid consistency and drying in a thin layer on an object to form a strong film, well resisting various external physical and chemical influences.

Methyl methacrylate and vinyl butyl ether (copolymer 1) were poured into a three-neck flask. After loading 100 g of solvent - ethyl acetate. Then dinitrilazoisobutyric acid polymerization initiator was added. To obtain varnish to coating #1, the components were heated to a temperature of 90 °C, during heating the components should be stirred constantly for their complete dissolution. Copolymerization occurs at slow heating to a temperature of 70-80 °C for 1-2 hours. The retention time after heating was 16 hours. [35]

Similarly, the synthesis of copolymer 2 (methyl methacrylate, vinyl butyl ether, maleic anhydride) with different ratio of initial components was carried out. After dissolution of maleic anhydride, 100 g of solvent, ethyl acetate, was loaded. Pigment powder was obtained by thoroughly abrasion from 5-40 μm using mortar and pestle. The obtained copolymers were mixed with fillers and crushed glass in order to change their technological and operational properties. Coating compositions containing pigments, fillers, retroreflective component and base are given in Table 2. The obtained coatings of different compositions were applied on degreased steel plates made of St.3 steel (according to GOST 5272-68, in which steel plates are the reference samples). This substrate was chosen because of its low porous permeability compared to asphalt concrete; if the coating performs well on steel, the qualitative performance on asphalt concrete will be better compared to the experimental performance. (The porous structure of asphalt concrete can improve the adhesion properties of the proposed material, which in turn will affect the performance properties) [34].

The drying time of the coating on the plates was 24 h. After drying of the coatings, quality control was carried out by visual method. Samples were weighed on analytical scales before and after coating (Table 3).

Table 2. Coating compositions

Component	Coating No. 1	Coating No. 2
Glass	20 g	40 g
Zinc oxide	60 g	20 g
Titanium dioxide	-	20 g
Components for varnish:		
Methylmethacrylate	100 ml	100 ml
Vinylbutylether	40 ml	40 ml
Ethylacetate/solvent	300 ml	
Dinitrilazobisisobutyricacid (DAA)	1.4 g	1 g
Dioxane	-	200 ml
Maleican hydride	-	50g

The purpose and description of the used components included in the polymer coating is given in Table 4.

Table 3. Difference in weight of samples before and after staining, g

Sample weight before staining	Sample weight after staining
$M_1 = 13.4$	$M_1=29.94$
$M_2= 14.2$	$M_2=29.41$

Table 4. Characteristics of varnish components

Material	Description and purpose
Zinc oxide	Has good optical properties and leads to a reduction in material consumption; used to save expensive titanium oxide.
Methylmethacrylate	Complex methyl ester of methacrylic acid; colorless; oily liquid with aromatic odor; easily evaporated and flammable.
Vinylbutylether	Used to produce polymer.
Solvent	A mixture of aromatic hydrocarbons with a small content of naphthenes, paraffins and unsaturated cyclic hydrocarbons; used for dissolving oils, bitumens, rubbers, etc.
Dinitrilazobisisobutyricacid (DAA)	Organic substance of nitrogen compounds and nitriles class; used as an initiator of radical polymerization and other radical reactions.
Dioxane	Good solvent for mineral and vegetable oils, paints; hygroscopic and miscible with water.
Maleican hydride	Raw material for the production of polyester resins; is an important component of varnish [24, 35].

To obtain the varnish for coating No.1, the components (see Table 2) were heated to a temperature of 90°C, during heating the components had to be stirred constantly to dissolve them completely. The settling time after heating was 16 hours. Pigment powder was obtained by thoroughly abrasion from 5-40 μm using mortar and pestle. [35]

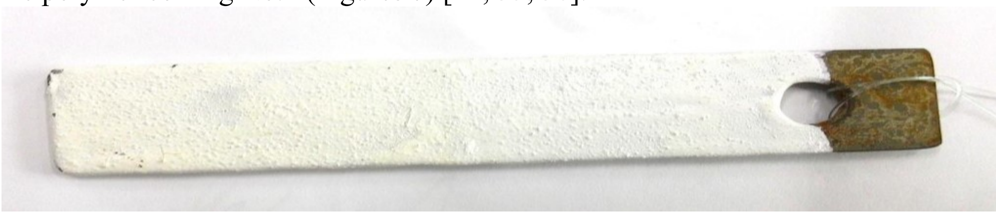
3. Results and discussion

After drying of samples exposed to aggressive media (10% aqueous solutions of NaCl and HCl) for 10 days, the corrosion resistance of protective coatings was determined by calculating the corrosion severity and adhesion by the scratch grid method according to GOST 5272-82 (Table 5).

Table 5. Test results

Sample	After 10% aqueous NaCl solution	Corrosion severity	After 10% aqueous HCl solution	Corrosion severity
No.1	After the test, the coating on the sample partially peeled off	3	After the test, the coating peeled off completely	2
No.2	After testing, there was only slight crumbling of the coating, but the coating itself held tightly to the sample and did not peel off	4	After the test there was a typical crumbling of the coating, the coating itself even at light contact leaves white prints. It should be noted that this coating has a good adhesion ability	3

According to Table 5, coating No.2 withstood the effects of aggressive environments, maintaining continuity, unlike polymer coating No.1 (Figures 7) [24, 35, 36].

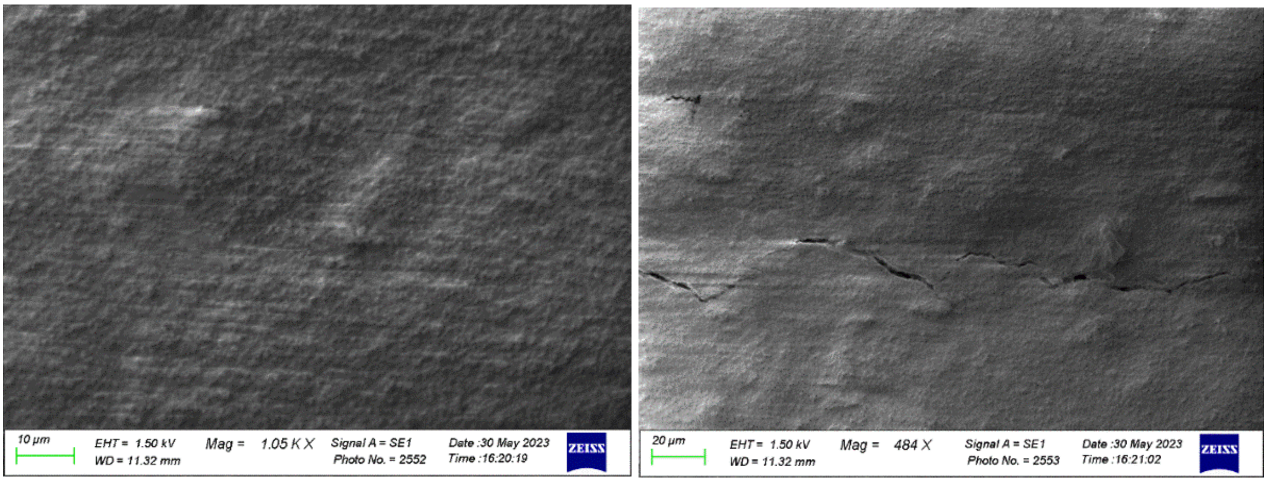


a)

b)

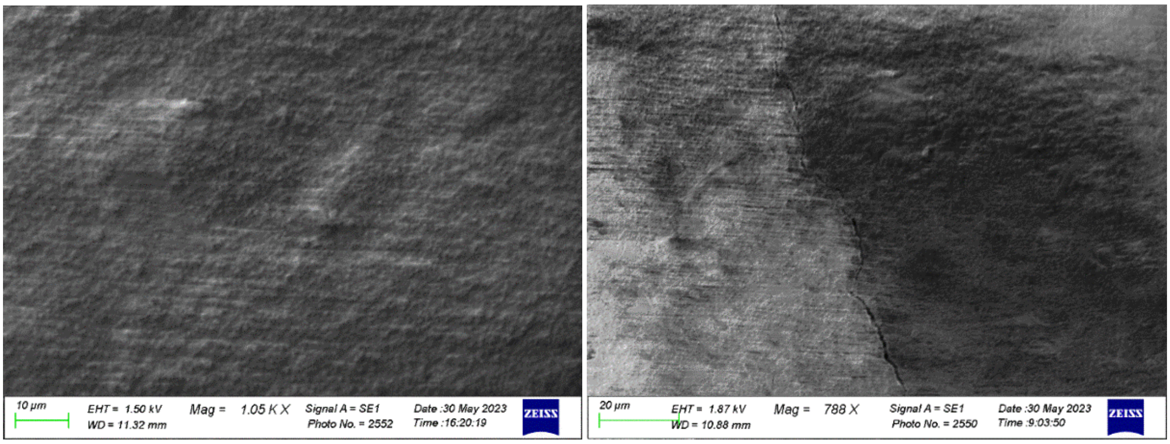
Fig. 7. Coating of sample No. 2 after exposure to a - 10% aqueous NaCl solution, b - 10% aqueous HCl solution

On the scanning electron microscope of the German brand "Zeiss" (JSC "Qarmet") the surfaces of the obtained protective coatings were investigated before and after exposure to aggressive media (Fig. 8-11).



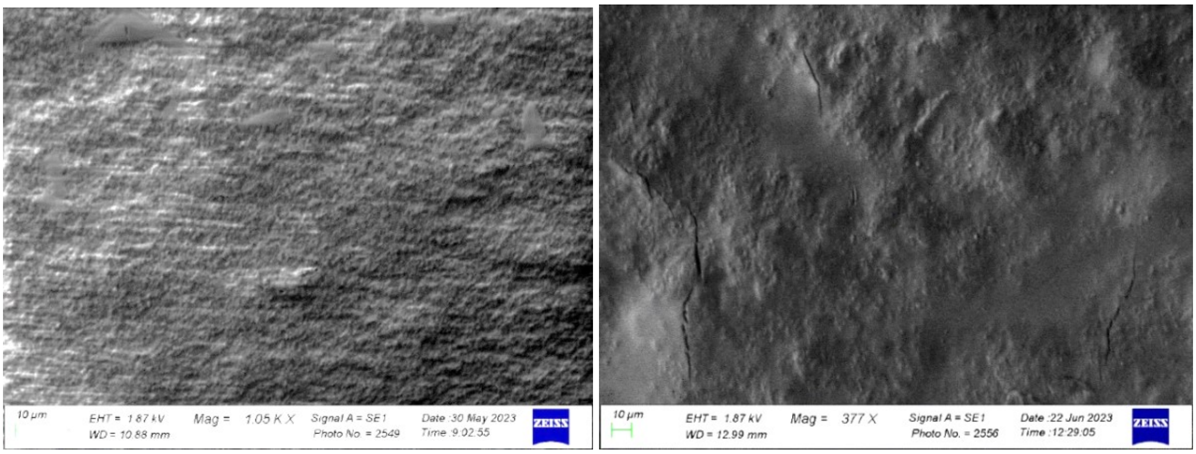
a b

Fig. 8. Polymer coating No.1 before (a, 1000x) and after (b, 480x) exposure to aggressive medium (10% aqueous NaCl solution)



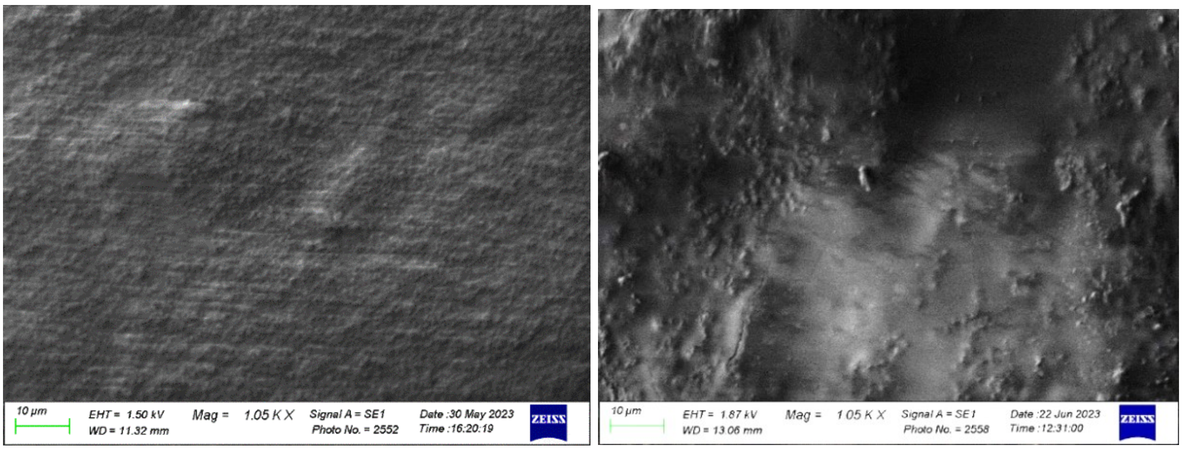
a b

Fig. 9. Polymer coating No.1 before (a, 1000x) and after (b, 780x) exposure to aggressive environment (10% aqueous solution of HCl)



a b

Fig. 10. Polymer coating No.2 before (a, 1000x) and after (b, 380x) exposure to aggressive medium (10% aqueous NaCl solution)



a b

Fig. 11. Polymer coating No.2 before (a, 1000x) and after (b, 1000x) exposure to aggressive environment (10% aqueous HCl solution)

As can be seen from Figures 8-11, the developed coatings No. 1 and No. 2 are homogeneous and solid before exposure to aggressive media. Similar structure has polymer coating No. 2 after exposure to aggressive medium of 10% aqueous solution of HCl (Fig. 11a, b). After exposure to 10% aqueous NaCl solution, polymer coating No.2 has small non-continuities (Fig. 10b). In polymer coating No. 1 after exposure to aggressive medium already at low magnification microcracks are observed in some places, and the coating itself is smooth, homogeneous (Fig. 8b and Fig. 9b).

4. Conclusion

Thus, coating No.2 withstood the exposure to aggressive media of 10% NaCl and HCl aqueous solutions (corrosion score of 3 and 2, respectively), compared to coating No.1 in the same media (corrosion score of 4 and 3, respectively). In this regard, the authors of this work plan to carry out approbation of the obtained results of the laboratory experiment by experimental-industrial means.

Conducting such research will solve the problem of selection of durable, corrosion-resistant, cheap and reliable pavement marking coatings, given the large supply of different materials on the market.

Currently, there are no production facilities for the creation of new polymer systems in Kazakhstan. Creation of such production will allow to receive own protective polymer coatings, solve the problem of choosing durable, corrosion-resistant, cheap and reliable coating for road markings, guarantees the expansion of the raw material base of the country, increase import substitution and, thus, increase the competitiveness of Kazakhstan.

Conflict of interest statement
The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

CRediT author statement
Conceptualization, G.U.; Methodology, V.M.; Software, I.V.; Validation, G.A., D.Y and I.V.; Formal Analysis, I.V. and V.M.; Investigation, V.M.; Resources, G.U.; Data Curation, I.V. and V.M.; Writing – Original Draft Preparation, V.M; Writing – Review & Editing, I.V.; Visualization, I.V.; Supervision, D.Y. and V.M.
The final manuscript was read and approved by all authors.

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