

## BUILDING MATERIALS AND PRODUCTS

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### ACRYLIC OLIGOMER BASED ON BUTADIENE DIMER FOR ANTI-CORROSION SURFACING

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**Statement of the problem.** The objective of the work was to assess the effectiveness of the modifying effect of the 4-vinylcyclohexene co-oligomer with methyl methacrylate (OBMMA-50) on the properties of an anticorrosion coating based on KORS copolymer obtained using styrene rectification residues to increase the technological and operational physical and mechanical characteristics of the initial coating.

**Results.** The functional, structural and conformational features of the initial copolymer and oligomeric modifier are established, which ensure their compatibility in the formation of an anti-corrosion surfacing. The optimal prescription composition and effective range of the acrylic oligomer content were revealed, where there is an increase in technological and physico-mechanical parameters of the initial anti-corrosion surfacing from 15 to 100 %.

**Conclusions.** The features in the structure and composition of the starting polymer and acrylic modifier are shown that provide a significant increase in the physical and mechanical parameters of the coating containing the optimal concentration of acrylic oligomer in its composition.

**Keywords:** distillation residues of styrene rectification, butadiene dimer, acrylic co-oligomer, anticorrosive composite material.

**Introduction.** Currently when the issues of saving material, raw materials and energy resources are pushed into the top of the agenda, the problem of combating metal corrosion, which causes millions in losses to any country's economy, is becoming increasingly relevant. In order to protect metal surfaces from corrosion and weathering, polymer compositions based on a copolymer of styrene distillation residues (KORS) are extensively used [1, 2]. The chemical composition and structure of this copolymer are characterized by the linear structure of the macromolecule whose major chain contained styrene fragments interconnected by valence bonds over vinyl groups with an aromatic ring, and only at the ends of such a rigid, low-mobility and non-polar structure were monomeric units of polar maleic anhydride, which in combination with the above features of the backbone result in a low structural and adhesive activity of the KORS copolymer [3, 4].

The major disadvantages of the above compositions are long drying time as well as unstable physical and mechanical properties and adhesion of surfacings [5]. From the viewpoint of materials science of composite materials, the introduction of a polar acrylic co-oligomer with a lower molecular weight, high functionality, and mobility of an acrylic co-oligomer macromolecule into this composition can catalyze structural processes, increase adhesive contact, and generally improve the physical and mechanical properties of an anticorrosion polymer coating [6, 7].

The objective of the study was to establish the effectiveness of the modifying effect of the co-oligomer of 4-vinylcyclohexene with methyl methacrylate (DBMMA-50) in the composition of an anticorrosion coating based on the KORS copolymer obtained by means of styrene distillation residues.

The results were assessed by the level of improvement of the technological and operational properties of the anticorrosion surfacing based on the KORS copolymer by introducing into its composition a co-oligomer (DBMMA-50) obtained by means distillation residues of toluene rectification formed in the production of butadiene rubber [8]. The task is becoming increasingly important due to the development of the theory and practice of improving the physical and mechanical properties of anticorrosion surfacing by means of modifying the initial composition with a functional acrylic oligomer obtained based on the by-products of the existing synthetic rubber production.

### 1. Materials and methods for investigating the ingredients and anti-corrosion surfacing.

Based on the major properties of the synthesized low molecular weight copolymers 4-vinylcyclohexene (VCH) with methyl methacrylate (low molecular weight, unsaturation, the presence of ester groups) it seemed appropriate to test these products in the composition of a commercially available composition based on the KORS copolymer. The properties of these polymer products are shown in Table 1.

Table 1

Structural parameters of macromolecules of copolymers of anticorrosive composition [9]

Type of polymer	$\overline{M}_n$ , atomic mass unit	$N$	$a_{36}$ , Å	$L_{\text{макр}}$ , нм	$R_F$ , Å	$V_{\text{meop}}10^3$ , Å <sup>3</sup> /molecule
DBMMA-50	1500...5200	14...53	1.54	4.3...16.3	7.5...16.7	0.4...4.6
KORS	10000...15000	67...144	1.54	21...44	19.2...30.4	10.1...28.03

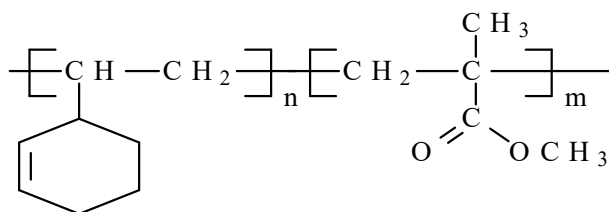
**Note:**  $\overline{M}_n$  is an average molecular mass;  $N$  is a general degree of polymerization;  $a_{36}$  is the length of the continuous area of the macromolecule;  $L_{\text{макр}}$  is the length of the macromolecule;  $R_F$  is the size of the clew of the macromolecule;  $V_{\text{meop}}$  is the volume of the free clew.

Based on Table 1, the base copolymer KORS exceeds the acrylic co-oligomer DBMMA-50 in terms of the average molecular weight from 2 to 10 times, which is also naturally reflected in

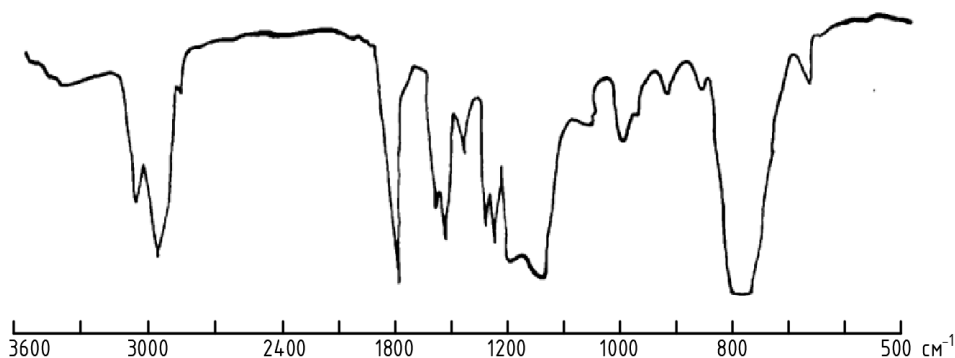
the values of the total degree of polymerization, the length of the macromolecule, the size and volume of its coil. Considering the above conformational features, having a higher penetrating ability the DBMMA-50 macromolecule can compact the loose structure of the base KORS copolymer and, due to the presence of polar ester groups give rise to structural, including adhesive, processes on the contact surface of the protected metal [10, 11].

Acrylic oligomer DBMMA-50, obtained at the initial mass ratio of butadiene dimer (WCG): methyl methacrylate (MMA) — 1 : 3, was employed as a modifying additive. The essence of the copolymer nature of WCG macromolecules with MMA manifests itself in the results of investigations of solutions of homopolymers and putative low molecular weight copolymers by turbidimetric titration [12], which indicate the formation of WCG cooligomers with MMA with the following structural formula [14, 15] (Fig. 1).

The specified structural formula of the acrylic co-oligomer (DBMMA-50) was confirmed by the IR spectral data presented in Fig. 2.



**Fig. 1.** Composition and structural formula of the co-oligomer DBMMA-50



**Fig. 2.** IR-spectrum of the co-oligomer WCG with methyl methacrylate (DBMMA-50) containing 55.3 % mole of WCG and 45.7 % mole of MMA

In Fig. 2 showing the IR spectrum of a low molecular weight copolymer of WCG with MMA at a molar ratio of structural units of 55.3 : 45.7, it is necessary to note considerable frequency characteristics near  $1730\text{ cm}^{-1}$  and some absorption bands in the range of  $1200\text{--}1050\text{ cm}^{-1}$  associated with stretching vibrations of the carbonyl ( $\text{C}=\text{O}$ ) and ether ( $\text{C}-\text{O}-\text{C}$ ) groups determining the presence of ester groups in the acrylic co-oligomer macromolecule. The synthe-

sis of an acrylic co-oligomer based on the double bonds of VCG and MMA is confirmed by the absence of characteristic bands for the coordinates 3080 and 1645  $\text{cm}^{-1}$ . The characteristic absorption bands in close proximity to the coordinate points 670, 1080, 3020  $\text{cm}^{-1}$  can be interpreted as vibrations of the double bond of the cyclohexene ring of WCG [16, 17].

In the preparation of the surfacing composition, the KORS copolymer (TU 103 279-2003) and the DBMMA-50 oligomer were dissolved in xylene, a plasticizer (dibutyl phthalate) was introduced, and asbestos was added in portions with stirring. Stirring was performed until a homogeneous mass was formed. The resulting mixture was applied to the prepared metal surface in such a way that the layer thickness was 0.8—1.1 mm. The surfacing was dried at the temperature of 20 °C.

To compare (as a control), a metal surface was surfaced with a composition currently produced by industry (Engels, experimental mechanical plant). The composition had the following composition, % mass: copolymer KORS — 22.0; xylene — 52.0; dibutyl phthalate — 0.7; polyarylenealkyls — 0.3; chrysotile asbestos — 25.0.

A composition containing the DBMMA-50 oligomer was prepared with different ratios of ingredients (Table 2) and tested using the conventional methods [19, 20].

Table 2

Ratio of the ingredients of the anti-corrosion mix

Ingredients	Ratio of the mix ingredients, % mass, and experiment number					
	1	2	3	4	5	6
Co-polymer KOPC	20.0	21.0	23.5	25.0	26.0	28.0
Oligomer DBMMA-50	0.2	0.4	5.2	7.0	10.0	12.0
Plasticizer	0.5	0.7	0.9	1.0	1.1	1.5
Asbestos	12.0	15.0	20.0	22.0	25.0	28.0
Xylene	67.3	62.9	60.4	45.0	37.9	30.5

**2. Analysis of the research results.** The results of the tests of the compositions of anticorrosive surfacing shown in Table 2 are summarized in Table 3.

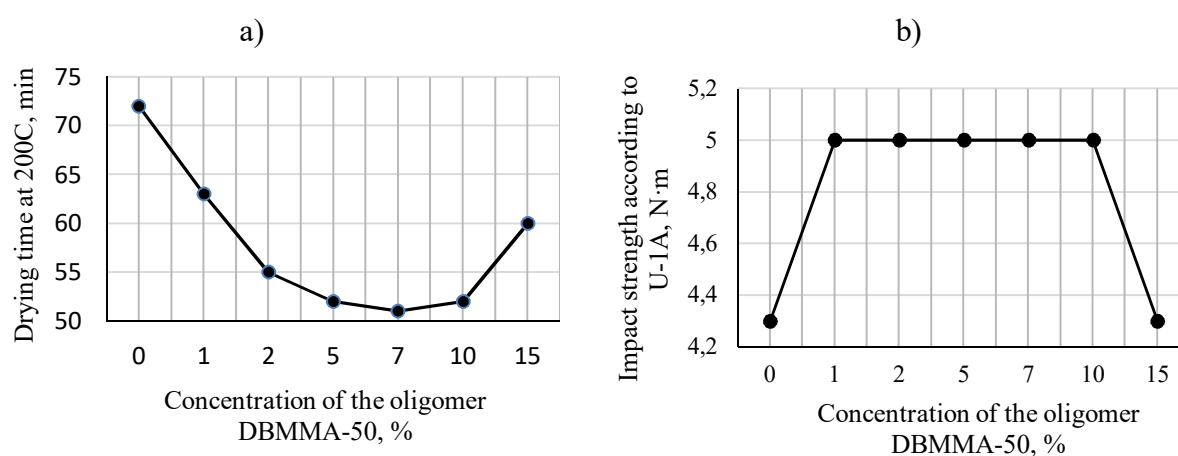
Based on Table 3, the introduction of DBMMA-50 into the composition helps to increase the adhesion strength to metal, impact strength, conditional tensile strength, and also considerably reduces the drying time of the surfacing.

For a more in-depth study of the effect of the acrylic co-oligomer concentration on the technological and operational properties of the original anticorrosion composition based on the KORS copolymer, the modifier content range was expanded for identifying the optimal range of its concentration. The results of studies of the physical and mechanical properties of the original and modified coatings are shown in Fig. 3, 4.

Table 3

Physical and chemical properties of the surfacing

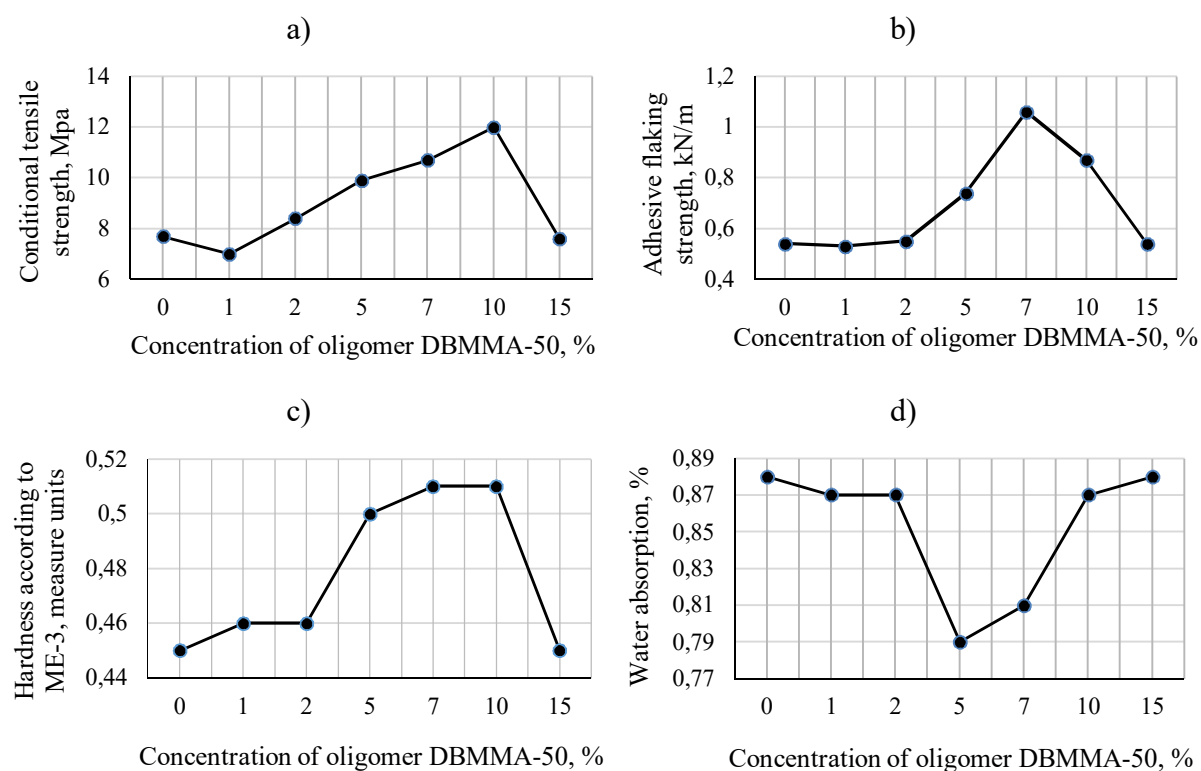
Index	Control	Composition in the experiments from Table 1					
		1	2	3	4	5	6
Drying time at 20 °C	72	63	55	52	51	52	60
Impact strength according to U-1A, N·m	4.3	5.0	5.0	5.0	5.0	5.0	4.3
Hardness according to ME-3, measure units	0.45	0.46	0.46	0.50	0.51	0.51	0.45
Conditional tensile strength, MPa	7.7	7.0	8.4	9.9	10.7	12.0	7.6
Adhesive flaking strength, kN/m	0.54	0.53	0.55	0.74	1.06	0.87	0.54
Water absorption, %	0.88	0.87	0.87	0.79	0.81	0.87	0.88
Water resistance, days	360	360	360	360	360	360	360



**Fig. 3.** Dependences of technological (a) and operational (b) indicators of anti-corrosion coating based on KORS copolymer from the content of the OBMMA-50 modifier

It should be noted that except the drying time (Fig. 3a) and impact strength (Fig. 3b) where the properties of the modified composition are considerably higher in a wider range (1—10 % mass), narrower intervals of optimal values are identified for other surfacing properties. Hence for the physical and mechanical parameters of the investigated modified anti-corrosion surfacing (Fig. 4a, b, c, d), mostly of an operational nature, the optimum is in a narrower range of acrylic oligomer concentration and amounts to 5—10 % mass. This might be due to the features of surfacing structuring under the impact of the modifier.

A rise in the strength characteristics of a surfacing containing from 5 to 10 % DBMMA-50 is obviously due to the structuring of the unsaturated DBMMA-50 oligomer along double bonds, which causes strengthening of the surfacing matrix. A further rise in the content of the acrylic oligomer is accompanied by the formation of defective microregions (due to the difference in the polarity of the KORS copolymer and the DBMMA-50 oligomer) which disrupts the uniformity of the surfacing and reduces its physical and mechanical properties [21, 22].



**Fig. 4.** Dependences of the physical and mechanical parameters of the anticorrosion coating based on KORS copolymer from the content of the OBMMA-50 modifier

The synthesis of co-oligomers based on butadiene dimer — WCG — in the presence of radical initiators does not call for special equipment. Thus the organization of the production of DBMMA-50 on the existing equipment of any synthetic rubber plant does not pose any particular difficulties.

According to the approximate cost calculation, the cost of the DBMMA-50 oligomer is 16.2000 rubles/t (the cost is largely determined by the price of methyl methacrylate — 15.5000 rubles/t according to TU PEA 29-66). The cost of KORS copolymer is 45.000 rubles/t. The introduction of DBMMA-50 into the composition rises its cost. However, this improves the quality of the surfacing, which, in turn, will extend its service life by 5–10 years [23]. To compare: the cost of styrene-alkyd varnish (extensively used) is 7.200–86.000 rubles/t [24, 25].

## Conclusions

1. Comparison of the properties of the experimental and base compositions shows that while using the DBMMA-50 oligomer as part of the mix, a considerable effect is achieved in improving the technological and operational physical and mechanical properties of the original surfacing.

The synthesis of co-oligomers based on butadiene dimer — WCG — in the presence of radical initiators does not call for special equipment. Thus the organization of the production of DBM-

MA-50 on the existing equipment of any synthetic rubber plant does not pose any particular difficulties.

2. The experimental oligomer DBMMA-50 was obtained by means of waste products from the production of butadiene rubber. Up till now, practically acceptable solutions for using this waste have not been made available and are not expected to. Hence in terms of saving raw materials, the suggested technical solution is of great practical importance, since it contributes both to improving economic performance and addressing environmental issues.

3. The effective composition of the modified surfacing and its physical and chemical properties are shown. The optimal ratios of ingredients have been identified and a mechanism has been suggested for the modifying effect of the acrylic oligomer on the initial composition of the anticorrosive surfacing. Recipe and technological methods for the qualified improvement of the properties of anti-corrosion composite materials based on recycled polymer raw materials are suggested.

#### References

1. Askadskii A. A. *Lektsii po fiziko-khimii polimerov* [Lectures on the physico-chemistry of polymers]. Moscow, Fizicheskii fakul'tet MGU im. M. V. Lomonosova Publ., 2001. 222 p.
2. Vinogradova S. V., Vasnev V. A. *Polikondensatsionnye protsessy i polimery* [Polycondensation processes and polymers]. St. Petersburg, Nauka Publ., 2000. 624 p.
3. Zhuravleva I. I., Akop'yan V. A. *Vysokomolekulyarnye soedineniya. Ch. VI. Sinteticheskie polimery* [High-molecular compounds. Part VI. Synthetic polymers]. Samara, Samarskii universitet Publ., 2014. 528 p.
4. Irzhak V. I., Mezhevikskii S. M. *Kinetika otverzheniya oligomerov* [Kinetics of oligomer curing]. *Uspekhi khimii*, 2008, vol. 77, no. 1, pp. 78—103.
5. Kozlov D. Yu. *Antikorroziionnaya zashchita* [Anticorrosive protection]. Ekaterinburg, Origami Publ., 2013. 440 p.
6. Korolev G. V., Mogilevich M. M., Il'in A. A. *Assotsiatsiya zhidkikh organicheskikh soedinenii: vliyanie na fizicheskie svoystva i polimerizatsionnye protsessy* [Association of liquid organic compounds: influence on physical properties and polymerization processes]. Moscow, Mir Publ., 2002. 264 p.
7. Semenova I. V. e.a. *Korroziya i zashchita ot korrozii* [Corrosion and corrosion protection]. Moscow, Fizmatlit Publ., 2002. 335 p.
8. Kurbatov V. G., Il'in A. A., Indeikin E. A. Protivokorroziionnye pigmenty i napolniteli s obolochkoi iz polianilina [Anticorrosive pigments and fillers with a polyaniline shell]. *LKM i ikh primeneniye*, 2012, no. 11, pp. 49—52.
9. Mezhevikskii S. M., Arinshtein A. M., Deberdeev R. Ya. *Oligomernoe sostoyanie veshchestva* [Oligomeric state of matter]. Moscow, Nauka publ., 2005. 254 p.
10. Mezhevikskii S. M., Irzhak V. I. *Khimicheskaya fizika otverzheniya oligomerov* [Chemical physics of oligomer curing]. Moscow, Nauka Publ., 2008. 270 p.
11. Moskvichev Yu. A., Fel'dblyum V. Sh. *Khimiya v nashei zhizni (produkty organicheskogo sinteza i ikh primeneniye)* [Chemistry in our life (organic synthesis products and their application)]. Yaroslavl, Izd-vo YaGTU, 2007. 411 p.
12. *Novyi spravochnik khimika i tekhnologa. Osnovnye svoystva neorganicheskikh, organicheskikh i elementoorganicheskikh soedinenii* [The new handbook of chemist and technologist. Basic properties of inorganic, organic and organoelement compounds]. St. Petersburg, Mir i Sem'ya Publ., 2002. 1280 p.
13. Bazhenov S. L. e.a. *Polimernye kompozitsionnye materialy: prochnost' i tekhnologiya* [Polymer composite materials: strength and technology]. Dolgoprudnyi, Intellect Publ., 2010. 352 p.
14. Kerber M. L., Vinogradov V. M., Golovkin G. S. e.a. *Polimernye kompozitsionnye materialy: struktura, svoystva, tekhnologiya* [Polymer composite materials: structure, properties, technology]. St. Petersburg, Professiya Publ., 2009. 560 p.

15. Semchikov Yu. D. *Vysokomolekulyarnye soedineniya* [High-molecular compounds]. Moscow, Akademiya Publ., 2006. 368 p.
16. Nikulin S. S., Sakhokiya I. A., Dmitrenkov A. I. e.a. Sopolimery na osnove kubovykh ostatkov rektifikatsii stirola — modifikatory drevesiny [Copolymers based on cubic residues of styrene rectification — wood modifiers] // *Izvestiya vuzov. Lesnoi zhurnal*, 2002, no. 2, pp. 78—86.
17. Tager A. A. *Fiziko-khimiya polimerov* [Physico-chemistry of polymers]. Moscow, Nauchnyi mir Publ., 2007. 576 p.
18. Nikolaev A. F., Kryzhanovskii V. K., Burlov V. V. e.a. *Tekhnologiya polimernykh materialov* [Technology of polymer materials]. St. Petersburg, Professiya Publ., 2008. 544 p.
19. Filimonova O. N. Pererabotka i primeneniye kubovykh ostatkov rektifikatsii stirola [Processing and application of cubic residues of styrene rectification]. *Uspekhi sovremennogo estestvoznaniya*, 2010, no. 2, pp. 115—117.
20. Bayramoglu G., Vezir M., Nilhan K., Apohan K., Güngör A. Synthesis and characterization of UV-curable dual hybrid oligomers based on epoxy acrylate containing pendant alkoxy silane groups. *Progress in Organic Coatings*, 2006, vol. 57, no. 1, pp. 50—55.
21. Mathew A. M., Predeep P. Styrene butadiene co-polymer based conducting polymer composite as an effective corrosion protective coating. *Progress in Organic Coatings*, 2012, vol. 1, no. 7, pp. 174—181.
22. Ozyilmaz A. T., Akdag A. Polyaniline, poly (N-methylaniline) and poly (aniline-co-N-methylaniline) coatings on stainless steel. *Transactions of the Institute of Metal Finishing*, 2011, vol. 4, no. 89, pp. 203—215.
23. Shi H., Liu W., Yang M., Wang Zh. Hydrophobic Waterborne Epoxy Coating Modified by Low Concentrations of Fluorinated Reactive Modifier. *Macromolecular Research*, 2019. vol. 4, no. 27, pp. 145—157.
24. Xie Y., Liu Ch., Liu W., Yang M. A novel approach to fabricate polyacrylate modified graphene oxide for improving the corrosion resistance of epoxy coatings. (February 2020). *Colloids and Surfaces a Physicochemical and Engineering Aspects*. DOI: 10.1016/j.colsurfa.2020.124627.
25. Xu Y., Li M., Liu M. Corrosion and fouling behaviors of phosphatized Q235 carbon steel coated with fluorinated polysiloxane coating. *Progress in Organic Coatings*, 2016, vol. 57, no. 34, pp. 177—188.