The effect of titanium nanoparticles on the corrosive activity of de-icing agents

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Abstract. The article considers the processes of corrosion of the vehicle body influenced by road pollution components. It is noted that the support frameworks, especially their bottom, are most susceptible to corrosion damage. This is due to the presence in such bodies of seams, gaps, as well as hollow elements (spars, amplifiers, thresholds), which create favorable conditions for the occurrence and development of corrosion processes. A decisive role in this process is played by aggressive pollution of the road surface. The study of samples of the road surface of the highway has showed that they mainly include the following components: ammonium ions NH_4^+, sulphates SO_4^{2-}, chlorides Cl^-, nitrates NO_3^-. When assessing the corrosivity of the road surface pollution, comparative studies were carried out with sodium chloride solution, which showed that the road simulating environment (RSE) is equivalent in corrosivity to 5 % aqueous solution of sodium chloride. Experimental data on the dependence of steel corrosion in selected media on the duration of exposure and aeration of solutions are presented. Aeration of solutions increases corrosion losses of steel by 37.50 % in sodium chloride solution and by 64.20 % in RSE. Kinetic equations for the dependence of the corrosion rate on time are derived. A hypothesis has been put forward that it is possible to effectively protect vehicle bodies from corrosion with the help of inhibitors with the addition of nanoparticles (NPs). In this regard, potassium monoborate (PMB) and PMB + titanium dioxide nanoparticles were studied as a corrosion inhibitor in RSE. It has been experimentally proven that PMB reduces the corrosivity of RSE, and titanium dioxide NPs enhance this effect. This composite can be recommended as an effective anti-corrosion additive.

1 Introduction

One of the main factors determining the lifetime of a modern vehicle is corrosion resistance, including its body, which depends on the design features, body material, properties of the anti-corrosion coatings used, road surface pollution, etc. [1].

The body in terms of corrosion is more vulnerable than other components, assemblies and parts of the vehicle, since it has many elements that are inaccessible for anti-corrosion

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treatment. These conditions expose the body to mechanical stress from the impact of various particles ejected by wheels (gravel, sand, crushed stone, soil), which destroy the integrity of protective films, contributing to the appearance of corrosion spots.

At present, the most common support framework of cars does not have a separate frame. The frame of such a body is one-piece, as its elements are assembled using various types of welding, and bears the load from the car's own weight, passengers and cargo.

The presence in the body structure of a large number of welds, slots, gaps, as well as hollow elements (spars, amplifiers, thresholds) creates favourable conditions for the occurrence and development of corrosion processes [2]. A special role in the destruction of the vehicle body, especially its bottom, belongs to aggressive road pollution and chemicals used as de-icing agents in the autumn-winter period of road operation [3, 4]. Coatings [5] and the introduction of metal corrosion inhibitors into de-icing compositions can be one of the ways to reduce the corrosive activity of road surface contamination [6, 7, 8].

In connection with the foregoing, the study of the impact of components of road surface pollution on body corrosion, as well as the development of effective corrosion inhibitors to protect the body under operational conditions, are relevant.

The purpose of the work is to reduce the corrosive activity of road surface contamination, including de-icing agents, which helps to increase the lifetime of vehicle bodies.

2 Materials and methods

2.1 The study of the corrosivity of road surface pollution

In order to study the process of body corrosion under the conditions of the vehicle operation, samples of road surface pollution were examined, taken at the 586th km of the M7 highway in the autumn-winter period from November to March, 2019-2020 and 2020-2021, which showed that the components of the main pollution were: anions of chlorides Cl^-, sulfates SO_4^{2-}, nitrates NO_3^- and ammonium cation NH_4^+ at the following concentrations: 22.00-26.00; 5.18-5.82; 5.00-7.00; 0.25-0.55 mg-eq/l, respectively (average values).

When studying the corrosive aggressiveness of road surface contamination, comparative determinations were made with 1, 3, 5 and 7.5 % aqueous solutions of sodium chloride (NaCl). The solution for road simulating environment (RSE) was prepared, based on the values of the concentration of active ions of the pollution components. To obtain RSE the following substances were dissolved in 1 liter of distilled water: 1.404 g of sodium chloride; 0.0068 g of ammonia water; 0.051 g of sodium nitrate; 0.3905 g of sodium sulfate, which were calculated from the condition of their maximum content in road pollution.

2.2 Determining the possibility of using TiO_2 nanoparticles as a corrosion inhibitor

The possibility of using TiO2 nanoparticles mixed with potassium monoborate as a corrosion inhibitor was evaluated. The working area was "Center for Nanomaterials and Nanotechnologies for the Agro-Industrial Complex of the Russian Federation" at Federal State Budgetary Educational Institution of Higher Education "Ryazan State Agrotechnological University Named after P.A. Kostychev". Titanium dioxide in the form of nanoparticles was obtained by precipitation of metal hydroxides from salt solutions in the presence of surfactants, followed by their low-temperature reduction in a hydrogen flow. The physical-chemical characteristics of nanoparticles were determined by such indicators as specific surface area (m2/g), phase composition (%), and size distributions of nanoparticles [9, 10, 11]. The active specific surface area was determined by BET low-temperature nitrogen

adsorption using a Quantachrome NOVA 1200e analyzer and was 77.3 m2/g (25–50 nm) for TiO2. The phase composition of the nanoparticles was studied using X-ray phase analysis (XPA). The nanoparticles had a shape close to spherical. The aggregation resistance of the dioxide was high.

Weighed portions of the studied samples of nanocrystalline titanium dioxide were placed in a given volume of distilled water, considering the concentrations of the solutions, and treated in an ultrasonic bath for at least 10 min at maximum power to increase the grinding of samples [12, 13].

2.3 The method for determining the corrosion rate

Studies to determine the corrosion rate were carried out according to the standard method given in the scientific literature [14, 15, 16]. To do this, unpainted samples of steel 08 kp with dimensions of 30×100×0.8 mm were placed in a sodium chloride solution and in RSE. The choice of sample material was justified by the fact that steel sheets 08 kp, 0.5-1.5 mm thick are used for vehicle bodies.

Corrosion mass loss of samples per year (corrosion rate) K was calculated by the following formula:

$$K = \frac{M_1 - M_2}{S \cdot T}, \text{ g/m}^2 \cdot \text{year} \tag{1}$$

where M_1 is the sample mass before testing, g; M_2 is the sample mass after testing, g; S is the sample area, cm^2; T is the test duration, h.

The duration of laboratory studies to determine the dependence of the corrosion mass loss of steel samples in selected media on the duration of exposure was 10 days, and the removal of samples and assessment of the corrosion loss of steel were carried out after 24, 72, 120, 168 and 240 hours.

To increase the corrosion resistance of steel, potassium monoborate (PMB) (KBO_2), known as an effective anticorrosion additive and TiO_2 NPs, was added to aqueous solutions of sodium chloride and RSE. Research options are presented in Table 1.

Table 1. Research options

Sodium chloride solution		Simulating environment	
Options	Concentration, %	Options	Concentration, % of maximum *
1	1	1	25
2	3	2	50
3	5	3	75
4	1 + 5 g/l PMB	4	25 + 5 g/l PMB
5	3 + 5 g/l PMB	5	50 + 5 g/l PMB
6	5 + 5 g/l PMB	6	75 + 5 g/l PMB
7	1 + 5 g/l PMB + 5·10^{-3} g/l TiO$_2$	7	25 + 5 g/l PMB + 5·10^{-3} g/l TiO$_2$
8	3 + 5 g/l PMB + 5·10^{-3} g/l TiO$_2$	8	50 + 5 g/l PMB + 5·10^{-3} g/l TiO$_2$
9	5 + 5 g/l PMB + 5·10^{-3} g/l TiO$_2$	9	75 + 5 g/l PMB + 5·10^{-3} g/l TiO$_2$

* The concentrations of the electrolyte, calculated from the highest values of the ingredients of the simulating medium, were obtained by diluting it with distilled water.

Studies of the effect of inhibitors on the corrosion resistance of steel were carried out by the gravimetric method by changing the mass of samples in an artificial environment according to [17, 18, 19].

The corrosion rate (K) was calculated by formula (1).

The inhibitory effect was determined by the following formula:

$$\gamma = \frac{K_0}{K} \qquad (2)$$

The degree of protection is, %

$$Z = \frac{K_0 - K}{K_0} \cdot 100 \qquad (3)$$

where K and K_0 are corrosion rates with and without inhibitor addition.

3 Results

Experimental data on determining the corrosion mass loss of samples made of steel 08 kp in solutions of sodium chloride and RSE at various concentrations showed that the maximum concentration, in terms of corrosion aggressiveness of RSE, was equivalent to 5 % aqueous solution of sodium chloride, therefore, this concentration was adopted for subsequent studies. According to preliminary corrosion tests, the optimal concentration for corrosion protection was 5 g/l PMB. When conducting corrosion tests, the thickness of the samples was c = 0.8 mm = 0.08 cm and test duration was 48 hours. The test conditions included room with a capacity of 800 ml, filled with solutions up to 750 ml. The level of solutions was maintained constantly.

Table 2. Average corrosion mass loss of steel 08 kp samples in 5 % aqueous solutions of sodium chloride, sodium chloride with the addition of 0.5 g/l PMB and TiO_2 NPs in the amount of $5 \cdot 10^{-3}$ g/l.

S, m^2	Corrosion weight loss of samples, g/m^2·year in 5 % sodium chloride solution	Corrosion weight loss of samples, g/m^2·year in 5 % sodium chloride solution + 0.5 g/l PMB	Corrosion weight loss of samples, g/m^2·year in 5 % sodium chloride solution + 0.5 g/l PMB + $5 \cdot 10^{-3}$ g/l TiO_2 NPs
30.05±0.02	1,490.64± 21.3	1,379.29±19.14	360.88±17.22

Table 3. Average corrosion mass loss of steel 08 kp samples in solutions of RSE, RSE with the addition of 0.5 g/l PMB and TiO_2 NPs in the amount of $5 \cdot 10^{-3}$ g/l.

S, m^2	Corrosion weight loss of samples, g/m^2·year in RSE solution	Corrosion weight loss of samples, g/m^2·year in RSE solution + 0.5 g/l PMB	Corrosion weight loss of samples, g/m^2·year in RSE solution + 0.5 g/l PMB + $5 \cdot 10^{-3}$ g/l TiO_2 NPs
30.05±0.02	956.69±12.21	463.19±11.01	232±9.8

4 Discussion

The experimental results can be approximated by dependence y=f(x). Graphs of the dependence of corrosion mass loss of steel samples on the concentration of sodium chloride solution, road surface contamination with and without PMB are shown in Figures 1, 2.
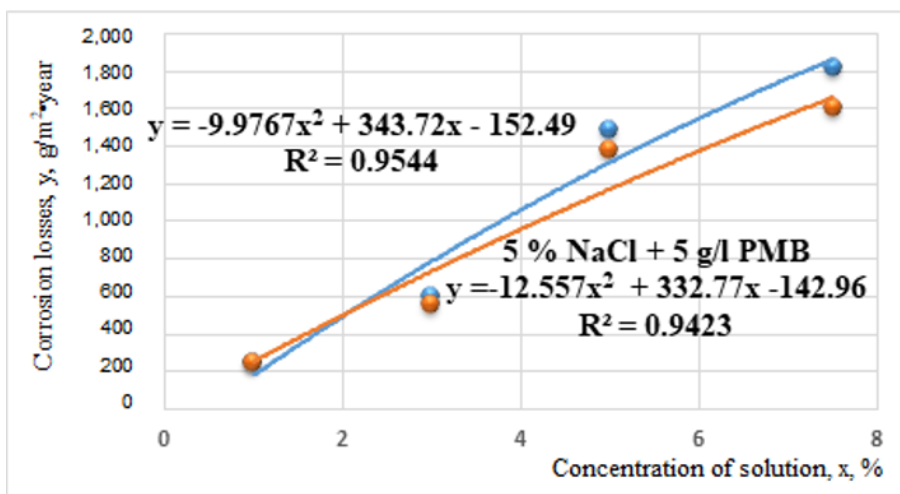
Fig. 1. The graph of the dependence of corrosion mass loss of 08 kp steel samples on the concentration of sodium chloride in an aqueous solution with and without 5 g/l PMB.
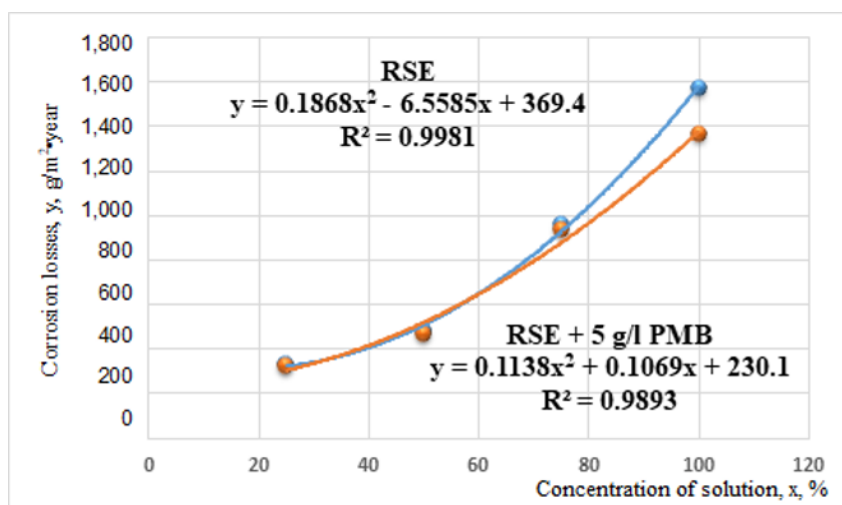
Fig. 2. The graph of the dependence of corrosion mass loss of 08 kp steel samples on the concentration of RSE in an aqueous solution with and without 5 g/l PMB.

It can be seen from the figures that the dependences of the corrosion mass loss of steel samples on the concentration of sodium chloride solution, road surface contamination with and without PMB have a polynomial character, since the value of reliability R^2 in this case has a maximum value. Dependence equations have been obtained that make it possible to determine the annual corrosion mass loss of steel samples at any concentration of sodium chloride, road surface contamination in their aqueous solutions with and without PMB.

The high ability to protect PMB is obviously associated with the formation of a denser passive ferrohydroxyborate film on the metal surface, which is formed during the chemisorption of borate ions.

The results of the study of the effect of PMB on the corrosion resistance of steel are presented in Table 4.

Table 4. The dependence of the corrosion rate for 30 days, the inhibitory effect and the degree of protection of 08 kp steel on the concentration of PMB in RSE.

Medium composition	$K \cdot 10^{-3}$, g/m^2·h	γ	Z, %
RSE (control)	68.12	1.00	0.00
RSE + 2 g/l PMB	14.86	4.58	78.19
RSE + 3 g/l PMB	7.96	8.56	88.31
RSE + 4 g/l PMB	3.08	22.12	95.48
RSE + 5 g/l PMB	2.16	31.54	96.83
RSE + 6 g/l PMB	4.05	28.23	94.99

Table 4 shows that the corrosion rate of steel in RSE is quite high. When PMB is added to RSE, the steel corrosion rate is rapidly reduced. In this case, the greatest inhibitory effect is achieved at PMB concentration of 5 g/l. A further increase in PMB concentration practically does not increase the degree of steel protection against corrosion.

According to [20], the reduction in steel corrosion in RSE when adding PMB is associated with the formation of protective oxide films and with the chemisorption of borates on the surface of the samples.

Thus, PMB can be recommended as an effective anti-corrosion additive in deicing mixtures. The addition of TiO$_2$ nanoparticles enhances the corrosion protection of PMB several times.

Corrosion inhibitor based on a monoborate and TiO$_2$ nanoparticles

Figures 3 and 4 show the results of electrochemical testing of steel samples treated with 5 g/l PMB and PMB with the addition of titanium dioxide nanoparticles in alkaline and acidic media, respectively, in 5 % sodium chloride solution and untreated with an inhibitor.

In an acidic (Figure 3), alkaline (Figure 4) environment, the addition of titanium dioxide nanoparticles leads to an increase in the value of the electrode potential. This indicates an increase in the corrosion resistance of steel treated with an inhibitor containing nanoparticles for the entire range of concentrations under study.

In an acidic environment in the range of ZnO concentrations in suspension from 0.05 % to 0.15 %, a clear pattern is observed: the higher the content of nanoparticles is, the higher the corrosion resistance is. At TiO$_2$ concentration of 0.5 wt %, the value of the electrode potential decreases. This may be due to the fact that the steel surface is oversaturated with inhibitor molecules and particles, their adhesion on the surface deteriorates, and a part of the protective layer peels off from the surface. Thus, the optimal concentration of NPs in the inhibitor suspension is 0.05–0.15% wt. for this environment.
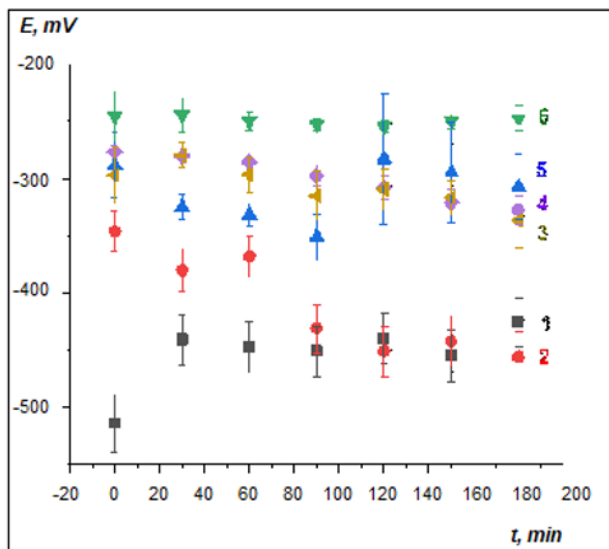
Fig. 3. Results of electrochemical tests in an acidic environment (HCl):
1 - pure 08 kp steel
2 - 08 kp steel + monoborate
3 - 08 kp steel + monoborate + TiO_2 0.05 % wt.
4 - 08 kp steel + monoborate + TiO_2 0.1 % wt.
5 - 08 kp steel + monoborate + TiO_2 0.15 % wt.
6 - 08 kp steel + monoborate + TiO_2 0.5 % wt.
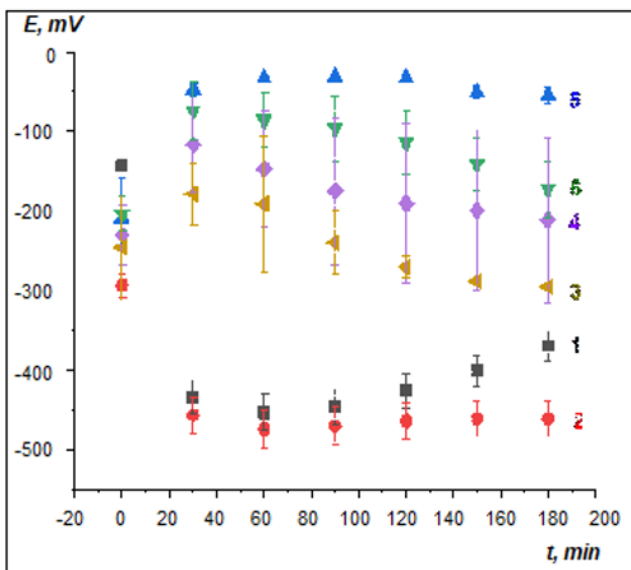
Fig. 4. Results of electrochemical tests in an alkaline environment (NaOH):
1 - pure 08 kp steel
2 - 08 kp steel + monoborate
3 - 08 kp steel + monoborate + TiO_2 0.05 % wt.
4 - 08 kp steel + monoborate + TiO_2 0.1 % wt.
5 - 08 kp steel + monoborate + TiO_2 0.15 % wt.
6 - 08 kp steel + monoborate + TiO_2 0.5 % wt.

In an alkaline environment (Figure 4), the addition of TiO_2 nanoparticles also demonstrates a pronounced tendency to improve the corrosion properties of steel (dependencies 4-6). However, in this case, at the maximum content of NPs in the suspension, no deviations are observed, as in an alkaline medium. A clear pattern is observed over the entire range of studied concentrations.

Based on the dependences obtained, one can also note a different mechanism for the formation of DES on the surface of clean steel, steel treated with a monoborate solution on the one hand (red and black markers), and samples treated with a suspension of titanium dioxide particles (patterns 3-6), on the other hand. It can be seen that the value of the electrode potential decreases significantly at the initial stage of holding the electrode in the solution for clean steel and steel treated with a monoborate solution. In the case of using TiO_2 nanoparticles, on the contrary, an increase in the electrode potential is observed at the initial stage (Figure 5). This unambiguously indicates the presence of chemical interactions at the metal-electrolyte solution interface.

For a quantitative comparison of the results obtained, the value of the steady-state equilibrium electrode potential was used (Table 5).
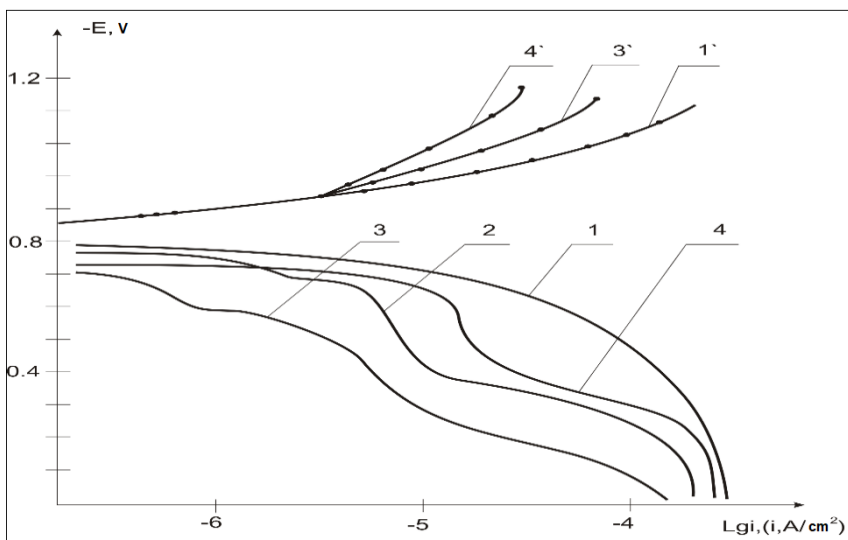
Fig. 5. Anode potentiodynamic curves (0.1V/min.) of steel in water, with addition of HCl, (pH=2, rotating electrode, 90° C): without inhibitor (1); with the addition of PMB + 0.05 % TiO2 NPs (2), PMB + 0.5 % TiO2 NPs (3), PMB (4) and cathodic potentiostatic without inhibitor (1') and with the addition of PMB (3'), PMB + 0.5% TiO2 NPs (4′)

Table 5. Equilibrium potentials of 08 kp steel (E_{eq}), mV.

Inhibitor	0.1 M HCl (pH=1)	0.1M NaOH (pH=13)
–	-426	-369
Monoborate	-456	-461
PMB + TiO_2 0.05 % wt.	-336	-295
PMB + TiO_2 0.1 % wt.	-327	-210
PMB + TiO_2 0.15 % wt.	-307	-54
PMB + TiO_2 0.5 % wt.	-247	-172

The table shows that the addition of titanium dioxide particles allows 1.72 times to increase the corrosion resistance of steel in an acidic environment and 6.8 times in an alkaline environment.

To evaluate the behavior of an inhibitor under conditions of application of an external potential difference, potentiodynamic curves of steel samples with inhibitors of various compositions were obtained. From these dependences, four parameters of corrosion processes were calculated: corrosion current, corrosion potential, equilibrium potentials of the oxidizing and reducing agents (Table 6).

Table 6. Corrosion parameters of 08 kp steel in Ringer's solution, measured in the potentiodynamic test mode.

Inhibitor	I_{cor}, µA	E_{cor}, V	E_{OX}, V	E_{RED}, V
–	7.5	-0.281	-0.346	-0.261
PMB	5.9	-0.31	-0.35	-0.288
PMB + TiO$_2$ NPs	3.4	-0.263	-0.324	-0.236

The most indicative parameter is the corrosion current. A decrease in the corrosion current is observed almost two times compared with the initial surface when adding nanoparticles. Systems with PMB allow to reduce the corrosion current only by 21 %.

When TiO$_2$ NPs are added to the solution, the sample loses less mass, and with an increase in the concentration of nanoparticles, the corrosion resistance of the metal increases. This suggests that in this case, only titanium dioxide nanoparticles, filling the pores on the metal surface, prevent the formation of corrosion.

5 Conclusion

During the autumn-winter period of road operation, the important components of road surface pollution are ammonium ions NH^{4+}, chlorides Cl^-, nitrates $NO3^-$, sulfates $SO42^-$. Corrosive contaminants are equivalent in their aggressiveness to the aggressiveness of 5 % aqueous solution of sodium chloride. The vehicle body is most susceptible to corrosion damage and it is made of 08 kp steel sheets. In this regard, the processes of 08 kp steel corrosion in RSE and sodium chloride solution at various concentrations were studied. It has been established that the corrosion rate of 08 kp steel decreases with the addition of PMB, so PMB can be recommended as an effective anti-corrosion additive in deicing mixtures, which helps to increase the lifetime of vehicle components and assemblies.

The scientific novelty of this article is that it provides for the first-time experimental data on the anticorrosive properties of road surface pollution solutions with and without a corrosion inhibitor, which is proposed as potassium monoborate with the addition of titanium dioxide nanoparticles. Titanium dioxide nanoparticles have a high adsorption activity, forming a protective film on the metal surface, filling the pores on the metal surface and preventing its destruction.

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