

**M. V. Zhuravleva**, PhD student (BSTU);  
**N. P Ivanova**, PhD (Chemistry), assistant professor (BSTU);  
**T. A Zharskaya**, PhD (Engineering), assistant professor (BSTU);  
**E. T Krut'ko**, D. Sc.(Engineering), professor (BSTU)

### PROTECTIVE PROPERTIES OF MODIFIED EPOXY COATINGS

Article is devoted to the development and research of new film materials based on epoxy resins with improved properties. Evaluation of protective properties is determined by electrochemical and physico-mechanical methods of research that provides the most complete picture of the corrosion processes occurring under the paint film. These studies allowed to adjust the coating composition to the individual applications in order to achieve a high degree of protection of metal surfaces.

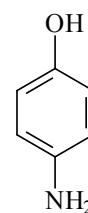
**Introduction.** Epoxy materials have superior performance properties, so they have been used to produce high quality coatings. Coating materials based on epoxy oligomers are used to prepare responsible coatings for various purposes, chemical-resistant, water-resistant, heat-resistant and insulating coatings. They are characterized by high adhesion to metallic and non-metallic surfaces, resistance to water, alkalis, acids, ionizing radiation, low porosity, small moisture absorbability and high dielectric properties [1]. However, there are a number of outstanding issues to improve the barrier properties of paints based on epoxy resins, which limit their wider use in aeronautical engineering as well as in engineering and shipbuilding [2]. Chemical structure of epoxy resins provides ample opportunities to control their properties by introducing modifying additives, to achieve maximum compliance with the requirements of the resulting material.

**Main part.** The aim of this study was to develop and research new film materials based on epoxy diene resin with improved barrier properties.

The object of the study was commercially produced epoxy resin E-41 in solution (-41 r) (TU 6-10-607-78), which is a solution of the resin E-41 with a wt fraction ( $66 \pm 2$ ) % in xylene (GOST 9410-78, GOST 9949-76) with acetone (GOST 2768-84) at a ratio of 4 : 3 by weight. Resin solution E-41 in a mixture of xylene and acetone (resin E-41 r) is used for the manufacture of paints for various purposes. Resin E-41 r refers to medium molecular weight (MW 900–2000) epoxy diene resin. Its density is 1.03–1.06 g/m<sup>3</sup>. Product of copolycondensation of low molecular epoxy resin E-40 with difenilol propane is represented by the formula shown in scheme 1.

Physico – chemical characteristics of the resin E-41 r are shown in Table 1.

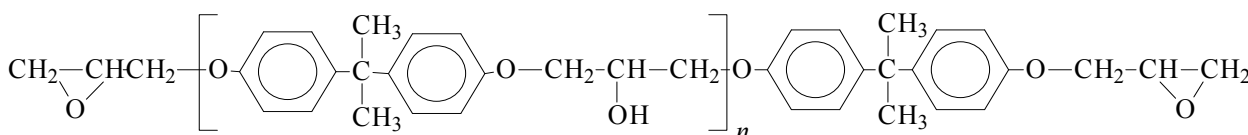
As a modifying component n-aminophenol (CFA) was used:



It is known that aminophenols are corrosion inhibitors. The presence of the aromatic ring and the amide and hydroxyl functional groups in the molecule of p-aminophenol dictates the fundamental possibility of using of this compound as a modifier of epoxy oligomer, allowing to increase the corrosion resistance of the coating.

The film-forming composition was prepared by introducing into E-41 r 10 % solution of aminophenol in dimethylformamide at a concentration range of 0.5–5.0 wt. %, followed by stirring until smooth. Hardener of brand E-45(TU 6-10-1429-79 with cheating. № 2) – low molecular weight polyamide resin solution in xylene – in the amount of 14% by weight of resin solids was used. Films on various substrates were cast from the above solutions. Curing of modified epoxy diene compositions were carried out at a temperature of 110°C for 140 min.

Adhesive strength of the formed coatings were determined by the standard method in accordance with ISO 2409 and GOST 15140-78 by the cross-cut incision with the kickback. The essence of the method in the application of cross-cut incisions on the finished coatings with the tool “Adhesion RN” and a visual assessment of the condition of the coatings after the impact action of the device “Kick – Tester” exerted on the opposite side of the plate at the site of incision. Coating condition is compared with standard classification and measured in points.



Scheme 1

Table 1

**Physico- chemical characteristics of resin E- 41r.**

Index name	Norm on the highest quality category
Appearance of the resin solution	Homogeneous transparent liquid
Appearance of the film	Poured on glass is clean. Slight rash
Color on iodometric scale, mg I <sub>2</sub> /100 cm <sup>3</sup> , not darker than	30
Viscosity by viscometer VZ-246 (OT -4) with a nozzle diameter of 4 mm at a temperature of (20.0 ± 0.5)°C, c	80–130
Volume of solids, %	66 ± 2
Mass fraction of epoxy groups in terms of dry resin	6.8–8.3
Mass fraction of chloride ion ( in terms of dry resin ), %, not more than	0.0045
Mass fraction of saponifiable chlorine (in terms of dry resin), %, not more than	0.25

Impact resistance of coating samples were evaluated using the device “Kick – Tester” in accordance with ISO 6272 and GOST 4765-73.

Method for determining the impact strength of films (measured in centimetres) is based on the instantaneous deformation of the metal plate coated with the paint by the free fall of load on the sample and is realized through the device “Impact Tester” which is intended to control the impact strength of the polymer, powder and paint coatings.

The hardness of paint coatings was determined with a pendulum device (ISO 1522). The essence of the method consists in determining the decay time (number of oscillations) of the pendulum in its contact with the painted coating. Hardness is determined by the ratio of the number of oscillations of the coated sample to the number of oscillations of the sample without coating.

Flexural strength of the coatings was determined by a device SHG1 (ISO 1519 GOST 6806-73) by bending of the coated sample around test cylinders since larger diameters at an angle of 180°.

On one of the cylinder diameters coating either cracks or breaks or peels. In this case, the paint has an elasticity of previous diameter test cylinder of the device in which it is not destroyed. Viewed count is in the radii of curvature in millimeters.

As can be seen from Table 2 at a curing temperature of 110°C of the obtained modified compositions with the modifier content of 0.5 to 2.0 % hardness of the coating and adhesion is improving and impact strength is increasing.

Protective properties of coatings are determined by the sum of physical and chemical properties, which can be reduced to four basic characteristics:

- Electrochemical and insulation properties of coatings;
- The ability of films to retard diffusion and carrying corrosive agents to a metal surface;
- The ability of coatings containing a film-forming, pigments or inhibitors, passivate or electrochemically protect metal;
- Adhesion and mechanical properties of the coatings.

Table 2

**Adhesion and strength properties of epoxydiane coatings on steel substrates (warming to 110 °C, 140 min)**

FFA content, %	Hardness, rel. u.	Adhesion to steel, points	Tensile impact, cm
0.0	0.66	1	2.5
0.5	0.69	0	5.0
1.0	0.73	0	10.5
2.0	0.70	0	7.5
3.0	0.67	1	3.0
4.0	0.63	2	6.0
5.0	0.47	2	1.0

All these properties are interrelated and influence each other mutually. Deterioration of properties of the film as a diffusion barrier will immediately lead to a reduction in adhesion due to the development of the corrosion process under the film. Therefore, adhesion itself, how high it may be, cannot provide long-lasting protection from corrosion. Likewise coatings with high diffusion limitations, but with poor adhesion cannot provide long-lasting protection [3].

Paint application is one of the most common and reliable ways to protect metal surfaces from corrosion and give a decorative surface finish. It is known that the testing of protective properties of the coating in an operational environment takes a lot of time, that does not comply with any developers or manufacturers. Rapid tests provide information about the resistance of the coating under its compulsory destruction simulating natural mechanism of aging in a short trial time. Electrochemical methods are used as these accelerated test methods.

Electrochemical methods are based on measurement of electrical parameters of the electrochemical phenomena occurring in test solution. This measurement was performed using an electrochemical cell which is a container with the test solution in which electrodes are placed. Electrochemical processes are accompanied by the appearance in the solution or changing of the potential difference between the electrodes or changing of the magnitude of current flowing through a solution [4].

To assess the protective properties and select the modifier concentration in the polymer coating the study of the time dependence of the stationary potential of the metal – coating and removal of the anodic polarization curves was used. Potential Measurement of the metal – coating was being performed in 0.5 % HCl at a temperature of  $(20 \pm 2)^\circ\text{C}$  in the scale of silver chloride reference electrode for 24 hours, then values were converted to a scale of the standard hydrogen electrode.

Removal of anodic polarization curves in a 0.5 % HCl was being performed using a potentiostat 50 PI -1, and a driving voltage programmer 8 in potentiostatic mode. Tests were carried out in a three-electrode electrochemical cell. Before removing the anode polarization curve value of the equilibrium potential of the metal – cover was being measured for 5 minutes. Anodic polarization was carried out in potentiostatic mode at a potential step change in 20 mV with delayed current at each potential for 1 min.

By the slope of the Tafel plot of the polarization curve in the coordinates  $E-\lg i$  value of the coefficient  $b$  was determined [5]:

$$b = \frac{2.303 \cdot R \cdot T}{\alpha \cdot n \cdot F}$$

Corrosion current density in the metal – coating was determined graphically by the intersection of stationary potential measured for 24 h (E24), and the straight portion of the anode polarization curve, which if necessary was extrapolated. Dependences on the capacity of the stationary metal – coating system for 24 h are shown in Fig. 1. Offset values of stationary potential of corrosive base – covering systems in electronegative side over time may be due to relief of the anode ionization of the metal due to the coating moisture permeability and increase of its conductivity.

For samples with an epoxy polymer coating stationary potential takes more electropositive value compared to carbon steel. With increasing concentration of modifying additive in the p- aminophenol coating displacement capacity reaches 30 mV.

Results on the anodic behavior of the investigated steel painted polymer in a solution of 0.5 % HCl are shown in Fig. 2. For samples with LCP with modifier content of 0.5–5.0 % in the potential range  $-0.2$ – $-0.3$  b Tafel slopes of all areas of the anode curves are approximately the same (Table 3). This suggests that the mechanism of active dissolution of iron in the pores of the polymer coating does not change, and inhibition is due to the decrease of the effective surface of the dissolving metal.

Organic modifier n-aminophenol introduced into the coating has two functional groups of atoms containing lone pairs, facilitating its adsorption on iron, which applies to transition metals with a free d-orbitals. The presence of n-aminophenol in the polymer coating decreases the effective surface of the dissolving metal and inhibites the anodic process.

Extrapolation of the linear portions of the polarization curves (Fig. 3) to the measured stationary capacity allows to determine the corrosion rate.

Table 3 shows the stationary potentials and the corrosion rate of the metal – covering systems.

From these data one can conclude that the polymer coatings inhibit corrosion of carbon steel 08 kp, which corrodes in 0.5 % HCl at a speed of  $1.95 \text{ mA/cm}^2$ . Application of epoxy polymer coating containing modifier of n-aminophenol 0.5–5.0 % reduces the corrosion rate of steel in 1.1–2.2 times.

With increasing concentration of n- aminophenol modifier in the polymer coating corrosion resistance at the system increases whereas the corrosion current density decreases (Fig. 4), and the polarization curves are shifted to lower currents. Basing on the obtained results it can be concluded that the polymer coatings based on epoxy resins inhibit corrosion of carbon steel.

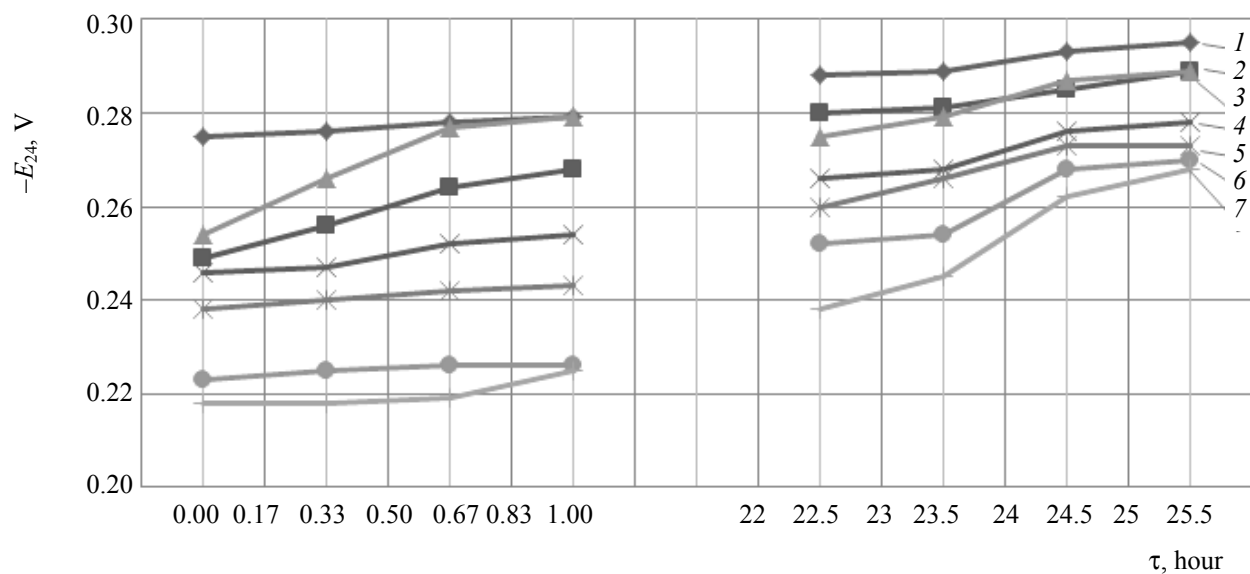


Fig. 1. Dependences on the capacity of the stationary base - covering system in 0.5% HCl:  
 1 – Carbon Steel 08 kp; 2 – Carbon Steel 08 kp – LPC + 0.5% modifier;  
 3 – Carbon Steel 08kp – LPC + 1% modifier; 4 – carbon steel 08kp – LPC + 2% modifier;  
 5 – carbon steel 08kp – LPC + 3% modifier; 6 – Carbon Steel 08kp – LPC + 4% modifier;  
 7 – Carbon Steel 08kp – LPC + 5% modifier

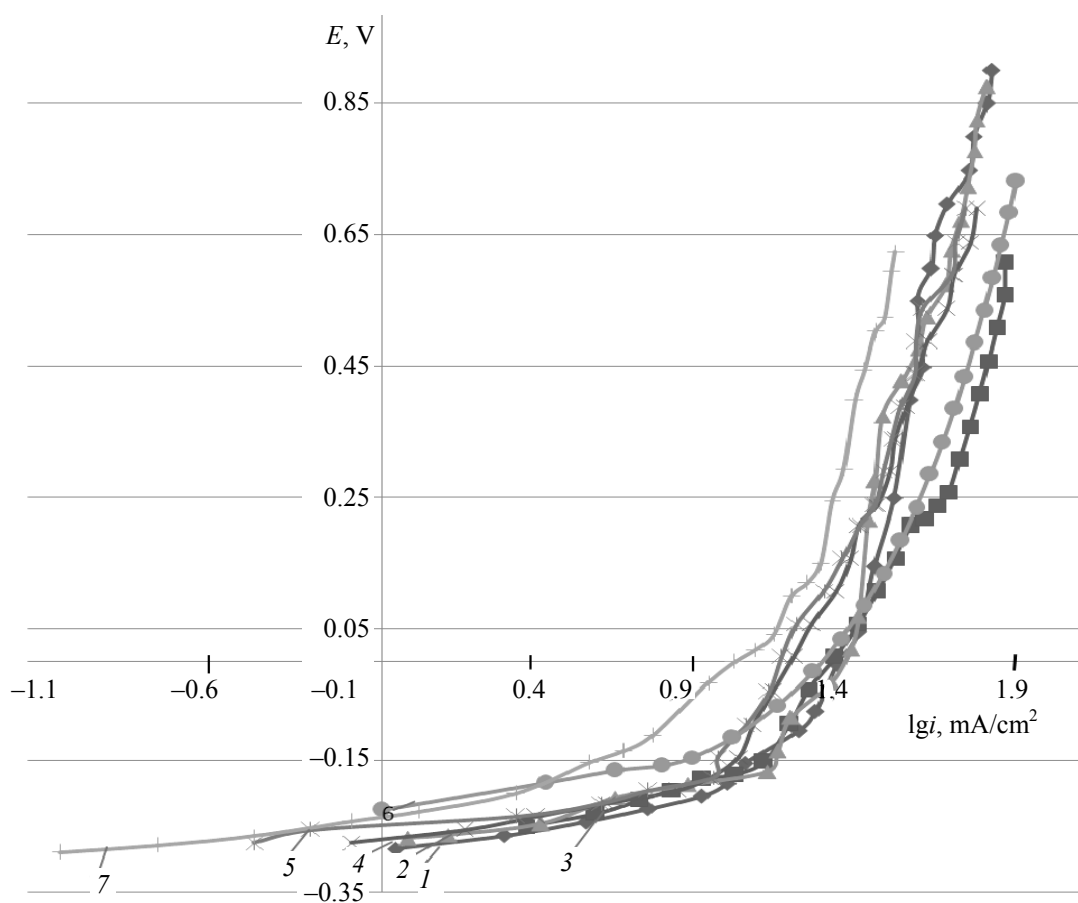
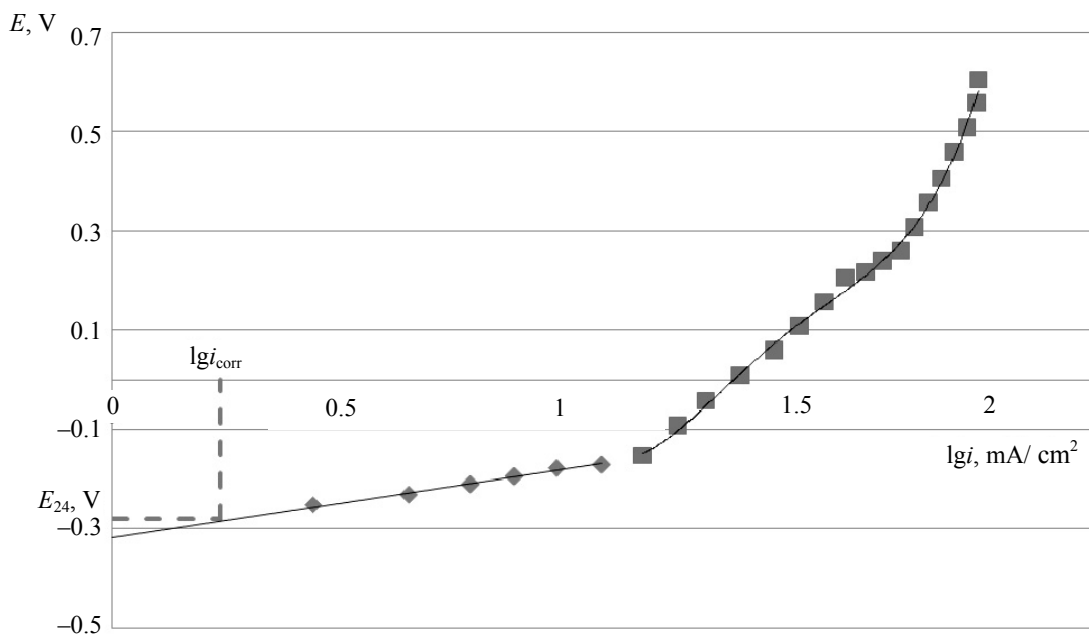


Fig. 2. Potentiostatic polarization curves in logarithmic coordinates  
 1 – base (steel 08 kp); 2 – Steel 08kp – LPC + 0.5% modifier; 3 – Steel 08 kp – LPC + 1% modifier,  
 4 – steel 08 kp – LPC + 2% modifier; 5 – Steel 08kp – LPC + 3% modifier,  
 6 – steel 08kp – LPC + 4% modifier; 7 – Steel 08kp – LPC + 5% modifier



$E_{24} = -0,275 \text{ V}; i_{\text{corr}} = 1,62 \text{ mA/cm}^2, t = 19^\circ\text{C}.$   
 Fig. 3. Anodic polarizat – Steel 08 kp – LPC + 1% modifier

Table 3

Stationary potentials and the corrosion rate of the steel 08 kp – epoxy coating in 0.5% HCl

tested Sample	$E, \text{ B}$	$\lg i, \text{ mA/cm}^2$	$i, \text{ mA/cm}^2$	$b, \text{ B}$	Percentage of modifier
Carbon steel 08kp	-0.288	0.29	1.95	0.1346	–
Carbon steel 08kp – LPC + 0.5 M	-0.28	0.24	1.74	0.1130	0.5
Carbon steel 08kp – LPC + 1.0 M	-0.275	0.21	1.62	0.0978	1
Carbon steel 08kp – LPC + 2.0 M	-0.266	0.18	1.51	0.0911	2
Carbon steel 08kp – LPC + 3.0 M	-0.26	0.15	1.41	0.0572	3
Carbon steel 08kp – LPC + 4.0 M	-0.252	0.11	1.29	0.0434	4
Carbon steel 08kp – LPC + 5.0 M	-0.238	-0.05	0.89	0.0328	5

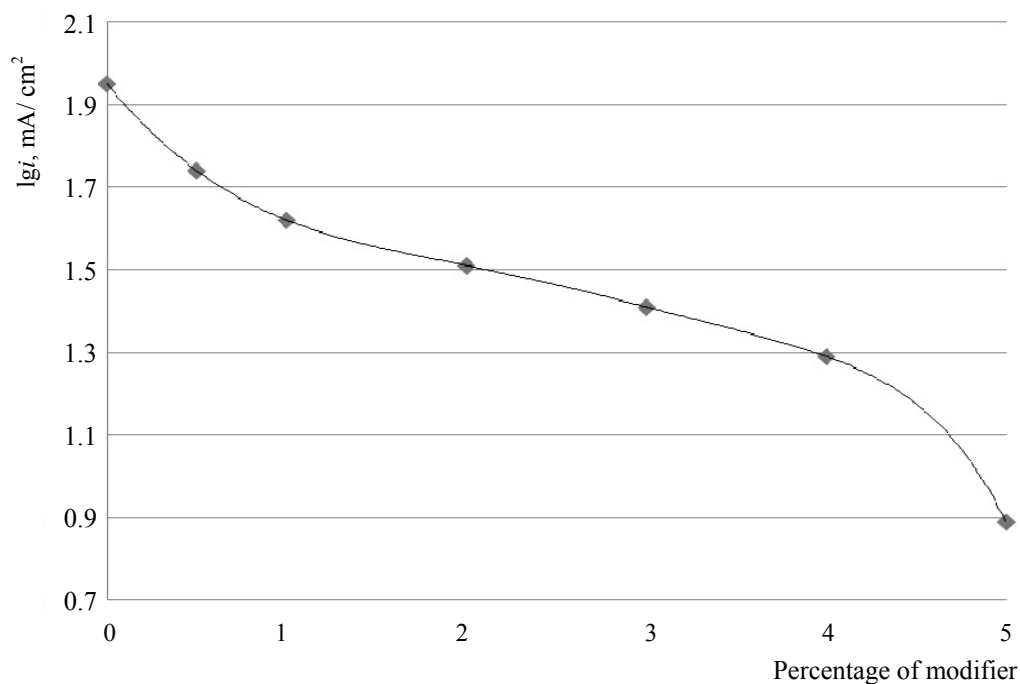


Fig. 4. The dependence of the corrosion current on the percentage of modifier

**Conclusion.** Introduction of n- aminophenol modifier at a concentration of 0.5–5.0 wt. % into a polymeric epoxy resin coating improves the corrosion resistance of the system to 0,5 % HCl, while the current density of steel corrosion 08kp decreases from 1.95 to 0.89 mA/cm<sup>2</sup> and the polarization curves are shifted to lower currents. Application of the epoxy polymer coating modifier in an amount of 5 % reduces the corrosion rate of carbon steel in 08kp 0,5 % HCl 2.2 times. Addition of 0.5–2.0 % modifier also improves physical and mechanical characteristics (improved strength, hardness and adhesion of coatings ).

Experimental studies have shown that additional evaluation of protective properties of coatings by electrochemical methods in conjunction with conventional for the paint industry methods of research yielded a better understanding of corrosion processes under cover, allowed to assess their impact on the course of the concentrations of the modifier. These studies allowed to adjust the coating composition to the individual applications

in order to achieve a high degree of protection of metal surfaces.

### References

1. Ли, Х. Справочное руководство по эпоксидным смолам / Х. Ли, К. Невилл. – М.: Энергия, 1973. – 268 с.
2. Киреева, В. Г. Лакокрасочные материалы на основе эпоксидных смол / В. Г. Киреева. – М.: НИИТЭХИМ, 1992. – 48 с. – (Обзорная информация / Сер. «Лакокрасочная промышленность»).
3. Розенфельд, И. Л. Ингибиторы коррозии / И. Л. Розенфельд. – М.: Химия, 1977. – 352 с.
4. Семенова, И. В. Коррозия и защита от коррозии / И. В. Семенова, Г. М. Флорианович, А. В. Хорошилов; под ред. И. В. Семенова. – М.: Физматлит, 2006. – 328 с.
5. Дамаскин, Б. Б. Электрохимия: учеб. пособие / Б. Б. Дамаскин, О. А. Петрий. – М.: Высшая школа, 1987. – 295 с.

*Received 27.02.2013*