

A STUDY OF THE INFLUENCE OF ADDITIVES ON THE PROCESS OF FORMATION AND CORROSIVE PROPERTIES OF TRIPOLYPHOSPHATE COATINGS ON STEEL

O. Vlasova

PhD, Associate Professor
Department of Coating, Composite Materials and Metal Protection from Corrosion
National Metallurgical Academy of Ukraine
Gagarina ave., 4, Dnipro, Ukraine, 49600

V. Kovalenko

PhD, Associate Professor
Department of Analytical Chemistry and Food Additives and Cosmetics*
Department of Technologies of Inorganic Substances and Electrochemical Manufacturing**

V. Kotok

PhD, Associate Professor
Department of Processes, Apparatus and General Chemical Technology*
Department of Technologies of Inorganic Substances and Electrochemical Manufacturing**
E-mail: valeriykotok@gmail.com

S. Vlasov

Doctor of technical sciences, Professor
Department of underground mining
National Mining University
Yavornytskoho ave., 19, Dnipro, Ukraine, 49005
Department of building manufacture**

K. Sukhyy

Doctor of Technical Sciences, Professor
Department of Plastics Processing and Photo, Nano and Printing Materials*
*Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005
**Vyatka State University
Moskovskaya str., 36, Kirov, Russian Federation, 610000

Методом зняття потенціо-динамічних поляризаційних кривих вивчено вплив добавок на анодну поведінку низьковуглецевої сталі (ст05кп) у водному розчині натрію триполіфосфату. Встановлено, що введення гідроксиду алюмінію, гліцерину і особливо бури прискорює процес ступеневого формування у водному розчині натрію триполіфосфату покриттів із захисними властивостями. Присутність гідроксиду алюмінію також сприяє поліпшенню захисних властивостей покриттів

Ключові слова: натрію триполіфосфат, добавки, анодна крива, пасиваційне покриття, захисні властивості, гідроксид алюмінію, гліцерин, бура

Методом снятия потенциодинамических поляризационных кривых изучено влияние добавок на анодное поведение низкоуглеродистой стали (ст05кп) в водном растворе триполифосфата натрия. Установлено, что введение гидроксида алюминия, глицерина и особенно буры ускоряет процесс ступенчатого формирования в водном растворе триполифосфата натрия покрытий с защитными свойствами. Присутствие гидроксида алюминия также способствует улучшению защитных свойств покрытий

Ключевые слова: триполифосфат натрия, добавки, анодная кривая, пассивационное покрытие, защитные свойства, гидроксид алюминия, глицерин, бура

1. Introduction

Conversion coatings are the most economically viable method for protecting metals against corrosion, which is used in various fields, including automobile and aerospace industries [1–7].

Currently, metal goods manufacturers aim to decrease usage of toxic chromates and nitrites conversion coatings for corrosion protection during in-between operation and long-term storage.

Development of new non-toxic, effective and relatively cheap compositions is a relevant problem in the field of metal corrosion inhibition.

Polyphosphates are of particular interest for such compositions. In comparison to other compounds, the main advantage of polyphosphates is their low toxicity. Polyphosphates are able to inhibit corrosion and salt deposition even at low concentrations.

Polyphosphates are widely used in municipal water transport systems for protecting of heat power equipment [8, 9].

They are also used as additives to solutions for degreasing and passivation of metal wares [10]. The addition of polyphosphate additives to zinc-phosphate solutions ensures the obtaining of fine crystalline coatings [9, 11] and an increase of their protective properties [12, 13].

Sodium tripolyphosphate (STPP) has a special place among industrially used polyphosphates, owing to its good solubility and low toxicity. An aqueous solution of STPP is stable, non-volatile, cheap and industrially available. STPP inhibits corrosion of iron in neutral and acidic media [14]. In comparison to traditional phosphatizing compositions (aqueous solution of phosphate salts), aqueous STPP solutions are easy to use and are more ecologically friendly. Solutions containing STPP ions form conversion coatings on the steel surface, despite the sodium cation not taking part in coat formation. Research results [14] have demonstrated the possibility of complex formation between Fe^{+2} and $\text{P}_3\text{O}_{10}^{5-}$, in the 1 M HCl solution.

It has been established that aqueous STPP solutions form the tripolyphosphate coat on the surface of the low-carbon steel. The coat has hydrophilic and protective properties. [15]. Under atmospheric conditions, low-carbon steel st08kp coated with tripolyphosphate films shows first signs of corrosion only after 20 days. For comparison, this is 2 times longer than for the steel coated with the nitrite film and 20 times longer than for bare steel [16].

All of this allows considering the use of STPP in the anticorrosion protection practice as promising for application of conversion coatings onto steel wares.

At the same time, it should be noted that in addition to hydrophilicity, tripolyphosphate coats also tend to crack upon drying [17]. Additionally, the presence of 1 mm thick layer of water on the coat surface (simulation of full submersion in the electrolyte) can cause intense washing out of STPP corrosion inhibitor from the coat [18]. This would lead to exposure of structural defects and decrease its protective properties. Significant disadvantages of tripolyphosphate coatings limit the effective applicability of aqueous STPP solutions as non-toxic compositions for metal wares preservation during transportation and storage under open-air conditions.

Therefore, improving the protecting properties of tripolyphosphate coatings by eliminating their disadvantages and structural defects is a relevant problem.

2. Literature review and problem statement

One way to eliminate structural disadvantages of tripolyphosphate coats is the usage of additives to the STPP solution that would alter the structure and properties of the forming coat.

It is known [1, 19] that various additives have been developed and used in traditional phosphate processes for many years. Their main purpose is to accelerate the treatment rate, and also to alter the structure and improve protective properties of phosphate coats. The additives vary in mechanism, nature, properties and effectiveness [1, 7]. The most important group of additives are chemical accelerators. The group encompasses inorganic oxidizers (nitrites, nitrates, permanganates, persulfates, chlorates, fluorides: [1, 7, 19], and also metals that are nobler than iron (Cu, Ni, etc.) and their compounds [20, 21]. Sulfides, phosphoric acid and its salts are used as reducers. The addition of nitrogen-containing

and other compounds (aniline, pyridine, benzaldehyde, etc.) to phosphate baths has also been described and papers proposing them are still being published. Particularly, studies on the influence of triazole compounds [7] and ethanolamine [22] additives to phosphate baths on the corrosion resistance of the metal substrate have been carried out. According to [23, 24], the use of pure silica in combination with cationic surfactants based on triethylamine and long-chain alkyl halides led to the formation of the highly-porous small-grain coat with good adhesion. The nano-SiO₂ additive that improves the microstructure and corrosion resistance of coats is viewed as a replacement for nitrites. Controlled addition of inorganic nanoparticles: TiO₂, SiO₂, Al₂O₃, ZrO₂, SiC, ZnO, CeO₂, MoS₂, diamond and graphite to treatment baths is viewed as a good alternative to existing toxic additives [25].

Analysis of literature sources [1, 19, 20] has shown that the use of additives with the aim to improve the structure and properties of conversion coats is a rather developed and effective method. The amount of data characterizing the influence of additives on the structure and properties of composite deposits and coats, particularly tripolyphosphate, is not sufficient.

With regard to composite coats and deposits of similar structure, this knowledge is limited to studies on the influence of polyvinyl alcohol (PVA) [26–28] and a number of metals [29] on the properties of nickel hydroxide. Studies on tripolyphosphate composite coats [30] have proven the presence of films on the surface of low-carbon steels, which were formed in STPP-based aqueous solutions with various additives. Modified tripolyphosphate coats [30] appear as thin, non-porous layers with high adhesion to the steel substrate and possess protective properties under conditions of atmospheric corrosion.

However, there is no clear image of the formation process and mechanism of such coats. There are no data regarding the influence of any compounds on the anodic dissolution of iron in the aqueous STPP solution. This complicates the choice of additives and control over the formation of coats with them. In turn, this narrows the range of effective practical application of tripolyphosphate coats.

3. The aim and objectives of the study

The aim of the work is to study the influence of additives on the anodic dissolution of steel in the aqueous STPP solution and properties of the formed tripolyphosphate coats.

In order to achieve the set aim, it is necessary to:

- propose additives to the aqueous STPP solution;
- study the behavior of low-carbon cold-rolled steel in the aqueous STPP solution containing additives, by recording anodic polarization curves;
- deposit the coats on the surface of steel samples the aqueous STPP solution containing additives and study their properties;
- conduct comparative analyses of samples' characteristics and determine which additives enable the formation of coats with high protective properties.

4. Materials and methods of research

The behavior of low-carbon cold-rolled steel in the 12 % aqueous STPP solution containing various additives was

studied by recording anodic potentiodynamic curves. All experiments were carried out at room temperature 20–26 °C. Working electrode samples were prepared out of steel st05kp with 0.3 mm thickness. Electrode dimensions are presented in Fig.1. Before the experiment, the electrode was polished with sandpaper of different grit, washed with distilled water, dried and wiped with alcohol. Electrochemical measurements were recorded in a glass cell, the schematic of which is presented in Fig.2.

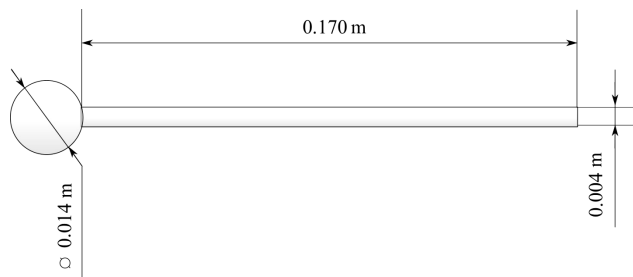


Fig. 1. Sketch of the working electrode

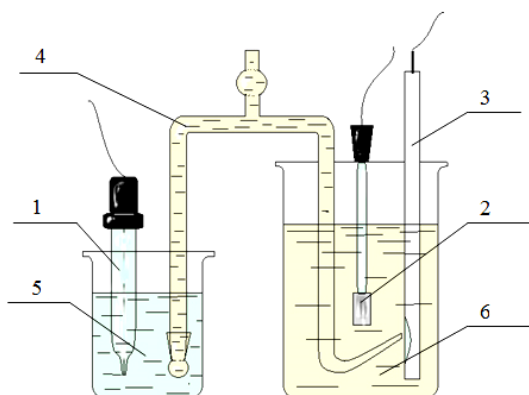


Fig. 2. Schematic of the electrochemical cell: 1 – Ag/AgCl electrode; 2 – platinum counter-electrode; 3 – working electrode in a cassette; 4 – electrolytic bridge; 5 – saturated KCl solution; 6 – studied STPP solution

The experiments were repeated 2–3 times. As can be seen from Fig. 2, Ag/AgCl was used as a reference electrode. Platinum was used as a counter-electrode. The Ag/AgCl electrode was placed in a glass with a saturated KCl solution. Working and counter electrodes were placed in another glass containing the studied STPP composition. The working electrode was placed in a rectangular Teflon cassette, composed of two parts, one of which had a round hole 0.012 m in diameter. The contact between two glasses was established with the salt bridge, filled with the studied solution, with its Luggin-Haber capillary pointing at the working electrode surface.

Glycerin, aluminum hydroxide ($\text{Al}(\text{OH})_3$) and borax ($\text{Na}_2\text{B}_4\text{O}_7$) were used as additives. Composition and pH of the studied solutions are listed in Table 1. Based on the presented data, the studied solutions are alkaline electrolytes.

The additives were chosen based on literature data: [19, 20, 30].

When studying the influence of the solution composition on the anodic behavior of low-carbon steel, the anodic polarization curves were recorded using the PI-50-1 potentiostat with the programmer PR-8 (USSR).

Table 1

Chemical properties of the studied tripolyphosphate solutions

Composition of aqueous solution	pH
12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +0.5 % glycerin	8.78
12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Al}(\text{OH})_3$	8.81
12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Na}_2\text{B}_4\text{O}_7$	9.44

Potentiostat measurements were passed to a personal computer through the analog-to-digital converter ACP E-154 (Russia), and current vs potential curves of the working electrode were recorded. Potential scan rate from the equilibrium value to 2V was 1 mV/s.

The curves were recorded using the software LGraph version 2.27 and processed using Excel and Origin.

Corrosion properties of the coats were studied by recording anodic potentiodynamic curves in the 0.1 N Na_2SO_4 solution; to model atmospheric corrosion conditions.

Coats on the surface of electrode samples were formed electrochemically in solutions (Table 1) under potentiodynamic conditions at $E=+920$ mV (vs NHE). This potential corresponds to the passivation region of low-carbon steel in 12 % aqueous STPP solutions. The obtained samples were further used to study protective properties of tripolyphosphate coats.

After corrosion tests, the appearance of the coats was examined using the optical microscope Neofot – 21 (GDR).

5. Results of studying the influence of additives on the properties of tripolyphosphate coats

5. 1. Study of the anodic behavior of low-carbon steel in the aqueous STPP solution with different additives

Fig. 3–5 show anodic polarization curves that characterize the corrosion behavior of steel st05kp in aqueous STPP solutions with different additives.

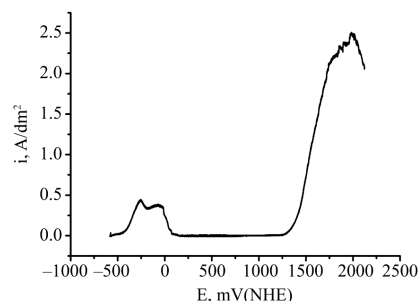


Fig. 3. Anodic polarization curve of steel st05kp recorded in an aqueous solution containing 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Al}(\text{OH})_3$

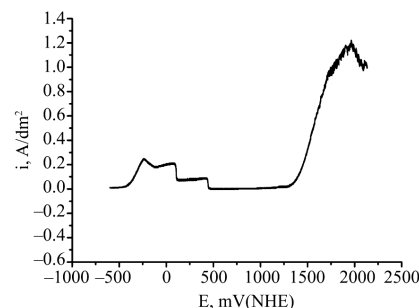


Fig. 4. Anodic polarization curve of steel st05kp recorded in an aqueous solution containing 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +0.5 % glycerin

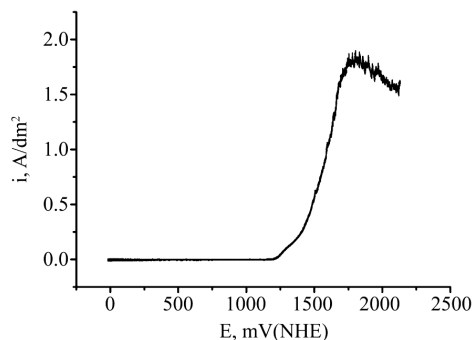


Fig. 5. Anodic polarization curve of steel st05kp recorded in an aqueous solution containing 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Na}_2\text{B}_4\text{O}_7$

As can be seen from Fig. 3, the anodic polarization curve of steel st05kp in 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Al}(\text{OH})_3$ (Fig. 3) shows three passivation plateaus. The first passivation plateau (Fig. 3) lies between - 625 and - 250 mV. The current density of anodic dissolution in the range of the passivation plateau rises from 0.07 A/dm² to 0.45 A/dm². In the potential window from - 210 mV to 0.0 mV, there is a sharp drop of anodic current density to 0.38 A/dm², which corresponds to the second passivation plateau (Fig. 3). In the potential window from +0.0 to +1250 mV, the third passivation plateau is observed. This is an effective plateau of complete passivation, because the anodic current density equals to zero. Metal dissolution along with oxygen evolution occurs at potentials above +1250 mV (Fig. 3).

The anodic curve recorded in the aqueous STPP solution with the addition of 0.5 % glycerin (Fig. 4) also shows three passivation plateaus. The complete passivation plateau lies in the narrow potential window: +1500÷+1700 mV. Additionally, the potential at which the passivation plateau is established is shifted toward negative values by about 150 mV (Fig. 4).

Upon addition of 2 % $\text{Na}_2\text{B}_4\text{O}_7$ (borax) to the 12 % aqueous STPP solution (Fig. 5), there is only one complete passivation plateau. Anodic dissolution of metal cannot be observed in the potential window from zero to 1,250 mV.

5. 2. Study of protective properties of the coats formed in the 12% aqueous STPP solution with additives

Fig. 6–8 show anodic polarization curves recorded in the 0.1 N Na_2SO_4 solution, which characterize corrosion properties of steel st05kp with the coats formed in the 12 % aqueous STPP solutions with additives.

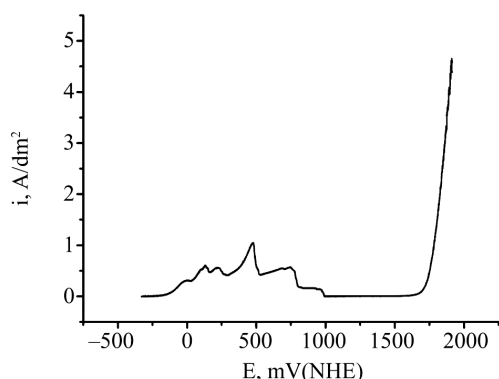


Fig. 6. Anodic polarization curve recorded in the 0.1 N Na_2SO_4 solution, for the sample with the coat formed in an aqueous solution containing 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Al}(\text{OH})_3$

For the coat formed in the 12 % aqueous STPP solution containing 2 % $\text{Al}(\text{OH})_3$ (Fig. 6), the complete passivation is observed at potentials +900÷+1,700 mV.

For the coat formed in a solution containing 0.5 % glycerin (Fig. 7), the complete passivation plateau is observed in a significantly narrower potential window: +1,500÷+1,700 mV.

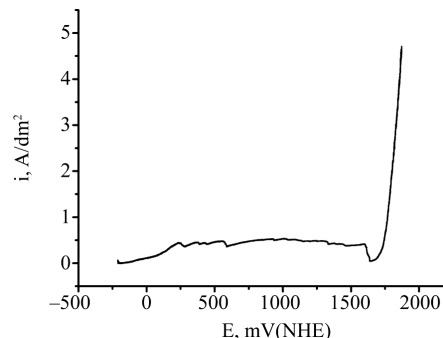


Fig. 7. Anodic polarization curve recorded in the 0.1 N Na_2SO_4 solution, for the sample with the coat formed in an aqueous solution containing 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +0.5 % glycerin

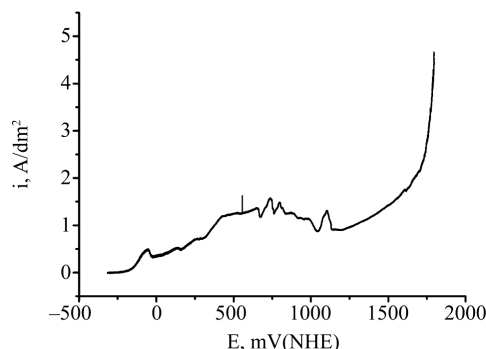


Fig. 8. Anodic polarization curve recorded in the 0.1 N Na_2SO_4 solution, for the sample with the coat formed in an aqueous solution containing 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Na}_2\text{B}_4\text{O}_7$

For the coat formed in the presence of 2 % $\text{Na}_2\text{B}_4\text{O}_7$ (borax), the polarization curve (Fig. 8) shows a broad passivation plateau from +750 to 1,750 mV. However, the passivation is not complete and the passivation current rises at potentials above +1,250 mV.

Fig. 9 shows a photograph of the working electrode of steel st05kp with the coat formed in the STPP solution with the borax additive, after corrosion tests (recording of anodic curves in the 0.1 N Na_2SO_4 solution).

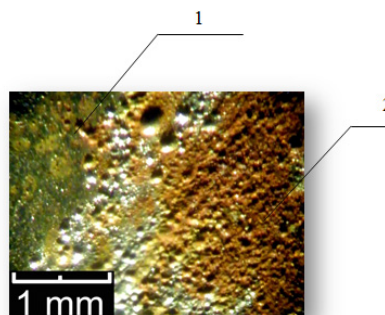


Fig. 9. Steel with the coat from 12 % $\text{Na}_5\text{P}_3\text{O}_{10}$ +2 % $\text{Na}_2\text{B}_4\text{O}_7$, 10 days since recording of the anodic curve in 0.1 N Na_2SO_4 : 1 – conversion coat; 2 – steel st05kp with rust

The electrode surface is non-uniform. The photograph shows surface regions where metal dissolution occurred and regions with a protective conversion coating.

6. Discussion of the results of studying the influence of additives on the formation and properties of tripolyphosphate coats

6.1. Anodic behavior of low-carbon steel in the aqueous STPP solution with different additives

Analysis of the curves characterizing the anodic behavior of steel st05kp in the aqueous STPP solution with additives was conducted in comparison to previous studies without additives [15]. According to it, the anodic polarization curve in the 12 % STPP solution without additives [15] shows three passivation plateaus. Table 2 shows their characteristics.

Table 2

Characteristics of passivation plateaus on the anodic polarization curve of steel st05kp in the 12 % aqueous STPP solution without additives [15]

Passivation plateau, No.	Potential, mV	Current density, A/dm ²
1	-210–+250	0.2–0.3
2	+250–+530	0.07
3	+530–+1250	0.00

Anodic curves presented in Fig. 3–5 clearly demonstrate the realization of step-wise formation of the tripolyphosphate coat in the aqueous STPP solution without additives. It can be seen that the addition of Al(OH)₃ (Fig. 3) and glycerin (Fig. 4) to 12 % STPP doesn't have a major effect on the formation mechanism (three passivation plateaus are observed on the anodic curves). Therefore, the coat formation in the STPP solution with the addition of Al(OH)₃ or glycerin occurs step-wise, similar to the formation of the protective coat in the solution without additives (Table 2). At the same time, the addition of 2 % Al(OH)₃ (Fig. 3) leads to a narrowing of the first two passivation plateaus. The complete passivation plateau is observed at potential values from 0 to 1250 mV. The obtained data show that passivation occurs earlier in the solution with the additive. Passivation measurements are more stable. Glycerin shifts the potential of passivation plateau formation toward negative potentials by about 150 mV (Fig. 4). The obtained results indicate the formation of coats with high protective properties.

The addition of borax changes the picture somewhat. In this case, the number of passivation plateaus on the anodic curve (Fig. 3, 5) is lower. However, this shouldn't affect the possibility of the coat with high protective properties to form. Additionally, no anodic dissolution of metal was observed during the coat formation in a solution with the borax additive (Fig. 5). However, given the chemical composition of the studied solution and coat formation, the complete absence of dissolution is unlikely. It should be noted that before recording polarization curves, the electrode was kept in a solution until a constant value of compromise potential. It is possible that the conversion coat was formed before the start of the experiment. It can be assumed; that the conversion coating with the borax additive would also have high protective properties. The absence of the first two passivation

plateaus on the anodic curves describing the coat formation in the STPP solution with the borax additive; indicated that the formation of such coat occurs at the highest rate.

6.2. Protective properties of the coats formed in the 12 % aqueous STPP solution with additives

According to [15], the tripolyphosphate coat formed under conditions of complete passivation at $E=+920$ mV has high protective properties. The anodic curve of steel st05kp with such coat in 0.1 N Na₂SO₄ is characterized by a complete passivation plateau at potential values from +1300 to +1500 mV. The addition of 2 % Al(OH)₃ to the 12 % Na₅P₃O₁₀ solution, (Fig. 6), resulted in the coat with high protective properties, which is indicated by the complete passivation plateau at +900–+1,700 mV.

Upon addition of 0.5 % glycerin (Fig. 7), the complete passivation plateau is observed in the narrower potential window: +1,500–+1,700 mV.

The addition of 2 % Na₂B₄O₇ (borax) leads to the appearance of the passivation plateau within the potentials from +750 to +1,750 mV. However, the passivation is not complete, because the passivation current increases at potentials above +1,250 mV (Fig. 8). Thus, the borax additive, while not much, decreases protective properties of the tripolyphosphate coat.

There is some contradiction between the anodic behavior of steel st05kp in the 12 % Na₅P₃O₁₀+2 % Na₂B₄O₇ solution and protective properties of the coat formed from this solution, which is likely related to non-uniform coat formation. This is supported by the microphotograph of the working electrode surface (Fig. 9). The electrode surface is characterized by non-uniformity: there is a region with metallic shine surface and transparent film – conversion coat, and the brown-colored region – dissolved steel and rust. The photograph was taken after 10 days after corrosion tests were conducted.

Thus, the obtained results have revealed that the introduction of the studied additives accelerates the formation of protective coats in the aqueous sodium tripolyphosphate solution. The highest acceleration took place with the addition of borax. Additionally, the introduction of additives causes improvement in protective properties of forming tripolyphosphate coats. The most positive effect on protective properties was caused by aluminum hydroxide and, possibly, borax.

The conducted study is an important preliminary step in the development of effective additives for the formation of modified tripolyphosphate coats with improved protective properties. Research involving the studied additives will be continued. The obtained data are the theoretical and practical basis for further studies on improving the methodology of choosing effective additives, formation methods for modified tripolyphosphate coats and methodology of studying their properties.

7. Conclusions

1. As a result of the analysis, it is proposed to study the influence of aluminum hydroxide, borax, glycerin on the formation of tripolyphosphate coats on steel in the aqueous STPP solution, with high protective properties.

2. It was established that the formation of coats in the STPP solution with additives; occurs step-wise. Potentio-

dynamic curves that characterize the anodic behavior of steel st05kp samples during the coat formation show up to three passivation plateaus and the complete passivation plateau with an anodic current density equal to zero. It was revealed that in STPP solutions with the addition of aluminum hydroxide, glycerin and especially borax, steel passivation occurs earlier than in the solution without additives. This is indicated by the following facts. With the addition of 2 % Al(OH)₃, a narrowing of the first two passivation plateaus is observed. The addition of glycerin shifts the potential of passivation plateaus formation toward negative values, by about 150 mV. This signifies the acceleration of the coat formation process when additives

are used. The absence of the first two passivation plateaus on the anodic curve that characterizes the coat formation in the STPP solution with the borax additive; indicated that coat formation occurs at the highest rate.

3. It was revealed that all the studied additives provide the formation of protective coats in the aqueous sodium tripolyphosphate solution: the most positive effect on protective properties was caused by aluminum hydroxide.

4. Based on the results of combined studies, it was established that aluminum hydroxide can be recommended as the most effective additive for improving protective properties of tripolyphosphate coats. Borax can be recommended as an additive that accelerates coat formation.

References

1. Tamilselvi, M. Progress in Zinc Phosphate Conversion Coatings: A Review [Text] / M. Tamilselvi, P. Kamaraj, M. Arthanareswari, S. Devikala, J. A. Selvi // International Journal of Advanced Chemical Science and Applications (IJACSA). – 2015. – Vol. 3, Issue 1. – P. 25–41.
2. Zeng, R. C. Progress of Chemical Conversion Coatings on Magnesium Alloys [Text] / R. C. Zeng, Z. D. Lan, J. Chen, X. H. Mo, E. H. Han // Transactions of Nonferrous Metal Society of China. – 2009. – Vol. 19. – P. 397–404.
3. Lin, B. Growth and corrosion resistance of molybdate modified zinc phosphate conversion coatings on hot-dip galvanized steel [Text] / B. Lin, J. Lu, G. Kong, J. Liu // Transactions of Nonferrous Metals Society of China. – 2007. – Vol. 17, Issue 4. – P. 755–761. doi: 10.1016/s1003-6326(07)60169-1
4. Weng, D. Corrosion and protection characteristics of zinc and manganese phosphate coatings [Text] / D. Weng, P. Jokiel, A. Uebleis, H. Boehni // Surface and Coatings Technology. – 1997. – Vol. 1-3. – P. 147–156. doi: 10.1016/s0257-8972(96)02860-5
5. Sankara Narayanan, T. S. N. Surface pretreatment by phosphate conversion coatings [Text] / T. S. N. Narayanan // Rev. Adv. Mater. Sci. – 2005. – Issue 9. – P. 130–177.
6. Amini, R. The corrosion properties of phosphate coating on AZ31 magnesium alloy: The effect of sodium dodecyl sulfate (SDS) as an eco-friendly accelerating agent [Text] / R. Amini, A. A. Sarabi // Applied Surface Science. – 2011. – Vol. 257, Issue 16. – P. 7134–7139. doi: 10.1016/j.apsusc.2011.03.072
7. Banczek, E. P. Investigation on the effect of benzotriazole on the phosphating of carbon steel [Text] / E. P. Banczek, P. R. P. Rodrigues, I. Costa // Surface and Coatings Technology. – 2006. – Vol. 201, Issue 6. – P. 3701–3708. doi: 10.1016/j.surfcoat.2006.09.003
8. Gomelya, N. D. Issledovanie processov korrozii stali v vode [Text] / N. D. Gomelya, V. M. Radovenchik, G. L. Shut'ko // Ekotekhnologii i resusoberezhenie. – 1996. – Issue 1. – P. 36–40.
9. Kuznecov, Yu. I. Ingibitory korrozii v konversionnyh pokrytyah III [Text] / Yu. I. Kuznecov // Zashchita metallov ot korrozii. – 2001. – Vol. 37, Issue 2. – P. 119–125.
10. Lipkin, Ya. N. Himicheskaya i elektrohimicheskaya obrabotka stal'nyh trub [Text] / Ya. N. Lipkin, V. M. Shtan'ko. – Moscow: Metallurgiya, 1974. – 216 p.
11. Burokas, V. The influence of hexametaphosphate on formation of zinc phosphate coatings for deep drawing of steel tubes [Text] / V. Burokas, A. Martušienė, G. Bikulčius // Surface and Coatings Technology. – 1998. – Vol. 102, Issue 3. – P. 233–236. doi: 10.1016/s0257-8972(98)00359-4
12. Lee, S.-J. Performance Improvement of Phosphate Coating on Carbon Steel by Cathodic Electrochemical Method [Text] / S.-J. Lee, D. L. H. Toan, Y.-H. Chen, H.-C. Peng // International Journal of Electrochemical Science. – 2016. – Vol. 11. – P. 2306–2316.
13. Tumbaleva, Y. Effect of the P₂O₅:NO₃ – retio on the zink phosphate coating formation [Text] / Y. Tumbaleva, D. Ivanova, L. Fachikov // Journal of the University of Chemical Technology and Metallurgy. – 2011. – Vol. 46, Issue 4. – P. 357–362.
14. Fahim, I. Sodium tripolyphosphate (STPP) as a novel corrosion inhibitor for mild steel in 1M HCL [Text] / I. Fahim, A. Kheiredine, S. Belaouad // Journal of optoelectronics and advanced materials. – 2013. – Vol. 15, Issue 5-6. – P. 451–456.
15. Vlasova, E. Research of the mechanism of formation and properties of tripolyphosphate coating on the steel basis [Text] / E. Vlasova, V. Kovalenko, V. Kotok, S. Vlasov // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 5, Issue 5 (83). – P. 33–39. doi: 10.15587/1729-4061.2016.79559
16. Vlasova, E. V. Issledovanie pokrytiy, poluchennyh iz vodnyh rastvorov fosfatov [Text] / E. V. Vlasova, T. L. Karasik // Metallurgicheskaya i gornorudnaya promyshlennost'. – 2010. – Issue 5. – P. 89–91.

17. Vlasova, E. V. Osobennosti struktury mezhoperacionnyh tripolifosfatnyh pokrytiy metalloprokata [Text] / E. V. Vlasova // *Metallurgicheskaya i gornorudnaya promyshlennost'*. – 2015. – Issue 3. – P. 59–62.
18. Vlasova, E. Investigation of composition and structure of tripoliphosphate coating on low carbon steel [Text] / E. Vlasova, V. Kovalenko, V. Kotok, S. Vlasov, I. Sknar, A. Cheremysynova // *Eastern-European Journal of Enterprise Technologies*. – 2017. – Vol. 2, Issue 6 (86). – P. 4–10. doi: 10.15587/1729-4061.2017.96572
19. Grigoryan, N. S. Fosfatirovanie [Text]: ucheb. pos. / N. S. Grigoryan, E. F. Akimova, T. A. Vagramyan. – Moscow: Globus, 2008. – 144 p.
20. Hain, I. I. Teoriya i praktika fosfatirovaniya metallov [Text] / I. I. Hain. – Leningrad: Himiya, 1973. – 312 p.
21. Kouisni, L. Phosphate coatings on magnesium alloy AM60Part 2: Electrochemical behaviour in borate buffer solution [Text] / L. Kouisni, M. Azzi, F. Dalard, S. Maximovitch // *Surface and Coatings Technology*. – 2005. – Vol. 192, Issue 2-3. – P. 239–246. doi: 10.1016/s0257-8972(04)00432-3
22. Li, Q. The effects to the structure and electrochemical behavior of zinc phosphate conversion coatings with ethanolamine on magnesium alloy AZ91D [Text] / Q. Li, S. Xu, J. Hu, S. Zhang, X. Zhong, X. Yang // *Electrochimica Acta*. – 2010. – Vol. 55, Issue 3. – P. 887–894. doi: 10.1016/j.electacta.2009.06.048
23. Thomas, R. Environment Friendly Nano Silicon Dioxide Accelerated Zinc Phosphate Coating on Mild Steel Using a Series of Surfactants as Additives [Text] / R. Thomas, M. J. Umopathy // *Silicon*. – 2017. – Vol. 9, Issue 5. – P. 675–688. doi: 10.1007/s12633-016-9460-6
24. Sheng, M. The effects of nano-SiO₂ additive on the zinc phosphating of carbon steel [Text] / M. Sheng, Y. Wang, Q. Zhong, H. Wu, Q. Zhou, H. Lin // *Surface and Coatings Technology*. – 2011. – Vol. 205, Issue 11. – P. 3455–3460. doi: 10.1016/j.surfcoat.2010.12.011
25. Jiang, C. A review on the application of inorganic nanoparticles in chemical surface coatings on metallic substrates [Text] / C. Jiang, Y. Cao, G. Xiao, R. Zhu, Y. Lu // *RSC Adv*. – 2017. – Vol. 7, Issue 13. – P. 7531–7539. doi: 10.1039/c6ra25841g
26. Kotok, V. The electrochemical cathodic template synthesis of nickel hydroxide thin films for electrochromic devices: role of temperature [Text] / V. Kotok, V. Kovalenko // *Eastern-European Journal of Enterprise Technologies*. – 2017. – Vol. 2, Issue 11 (86). – P. 28–34. doi: 10.15587/1729-4061.2017.97371
27. Kotok, V. A. Advanced electrochromic Ni(OH)₂/PVA films formed by electrochemical template synthesis [Text] / V. A. Kotok, V. L. Kovalenko, P. V. Kovalenko, V. A. Solovov, S. Deabate, A. Mehdi, J. L. Bantignies, F. Henn // *ARPJ Journal of Engineering and Applied Sciences*. – 2017. – Vol. 12, Issue 13. – P. 3962–3977.
28. Kotok, V. The properties investigation of the faradaic supercapacitor electrode formed on foamed nickel substrate with polyvinyl alcohol using [Text] / V. Kotok, V. Kovalenko // *Eastern-European Journal of Enterprise Technologies*. – 2017. – Vol. 4, Issue 12 (88). – P. 31–37. doi: 10.15587/1729-4061.2017.108839
29. Kotok, V. Electrochromism of Ni(OH)₂ films obtained by cathode template method with addition of Al, Zn, Co ions [Text] / V. Kotok, V. Kovalenko // *Eastern-European Journal of Enterprise Technologies*. – 2017. – Vol. 3, Issue 12 (87). – P. 38–43. doi: 10.15587/1729-4061.2017.103010
30. Vlasova, E. V. Vliyanie dobavok na svoystva mezhoperacionnyh tripolifosfatnyh pokrytiy [Text] / E. V. Vlasova, E. N. Levko, V. L. Kovalenko, V. A. Kotok // *Zbirnyk naukovykh prats Natsionalnoho hirnychoho universytetu*. – 2015. – Issue 49. – P. 200–207.