OPTIMIZATION OF THE FORMATION TECHNOLOGY OF TRIPOLYPHOSPHATE COATING ON MILD STEEL

Tripolyphosphate conversion coatings are promising due to the active type of anti-corrosion protection. However, to be introduced into production, it is necessary to optimize the technology of tripolyphosphate coating deposition. Coatings were deposited to samples of st05kp cold-rolled sheet steel (analogs G10050, G10060, 1CR, 2CR, D6-2, DG-2) from aqueous solutions of sodium tripolyphosphate (4 %, 6 %, 10 %, 12 %, 14 %) at t=80 °C by dip coating and sputtering. The specific weight and morphology of the coating were determined. The corrosion-protective capability was studied in the G-4 climatic chamber at 90 °C and 100 % humidity using Akimov's test.

The prospects of the dip coating and sputtering methods were shown. It was revealed that in the dip coating method, the specific weight of the coating was 1–4 g/m^2 and increased linearly at a rate of 0.3–0.35 g m^2 by 1 % (wt.) Na$_5$P$_3$O$_{10}$. For the sputtering coating method, it was revealed that at 4–8 % Na$_5$P$_3$O$_{10}$, the growth rate of the specific weight was 0.2 g/m^2 by 1 % Na$_5$P$_3$O$_{10}$ and the specific weight exceeded that of the coating obtained by the dip coating method, due to accelerated oxygen access and increased coating formation rate. At 10–14 % Na$_5$P$_3$O$_{10}$, the growth rate of the specific weight was 0.55–0.65 g/m^2 by 1 % Na$_5$P$_3$O$_{10}$. However, the specific weight was lower than that of the coating obtained by the dip coating method, due to the self-compaction of the iron tripolyphosphate matrix and decreased mass of the Na$_5$P$_3$O$_{10}$ filler.

Using accelerated corrosion testing methods, the optimum Na$_5$P$_3$O$_{10}$ concentration to obtain a coating with the highest corrosion-protective capability was 6 %–10 % (wt.). The correlation of the protective capability of the coating samples with the coating defects and cracks was revealed

Keywords: sodium tripolyphosphate, conversion coating, corrosion-protective properties, phosphating, tripolyphosphate coating

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1. Introduction

Conversion coatings are the most economically viable method of protecting metal from corrosion used in various fields of the national economy, including automotive and aerospace [1, 2].

At enterprises producing metal products, they tend not to use toxic chromates in the formation of conversion coatings and nitrites for interoperative protection and long-term conservation. As a conversion coating, phosphate coatings on the surface of zinked steel [3], Zn, and Mg alloys [4, 5] are widely used, including using special additives (for example, sodium dodecyl sulfate [6] or benzotriazole [7]).

Alkali metal polyphosphates are the most promising for obtaining conversion corrosion-protective coatings. The main advantage of polyphosphates over other substances is their low toxicity. In addition, they have the ability, even in small concentrations, to inhibit steel corrosion and scale deposition.

2. Literature review and problem statement

In practice, polyphosphates are widely used in household water communications to protect heat and power equipment [8, 9]. Polyphosphates are used as additives in solutions for cleaning, degreasing, and passivation of metal products. The introduction of polyphosphate additives into zinc-phosphate solutions provides fine crystalline coatings [9, 10] and improves their protective properties [11, 12]. Polyphosphates are used as inhibitors in cement [13]. Metal tripolyphosphates are used as corrosion-protective pigments [14]. Tripolyphosphates of Al [15], Ca [16, 17], Ca-Mg [18], as well as tripolyphosphate-intercalated Zn-Al layered double hydroxide [19], are used as such pigments.

Among polyphosphates, sodium tripolyphosphate (STPP), a non-toxic inorganic, highly soluble compound, is most often used in industry. An aqueous solution of STPP is stable over time, non-volatile at elevated temperatures, inexpensive and available. STPP is an inhibitor of iron corrosion in neutral and acidic media [20]. Compared to conventional phosphating compositions (aqueous solutions of phosphate salts [21]), aqueous solutions of STPP are easy to use and more environmentally friendly. Conversion coatings are formed on the steel surface in solutions containing STPP ions, even though the sodium cation does not participate in the coating formation. The results of studies [20] showed the possibility of forming a complex between the Fe^{+2} cation and P$_3$O$_{10}^{5-}$, anion in a 1 M HCl solution.

It was found that a tripolyphosphate coating with hydrophilic and protective properties is formed on the surface of mild steel [22] and zinked steel [23] in an aqueous solution of STPP. The introduction of some additives improves the coating characteristics [24]. At the same time, under atmospheric conditions, for samples of mild steel st05kp (analogs G10050, G10060, 1CR, 2CR, D6-2, DG-2) with a tripolyphosphate coating, the time of appearance of the first corrosion zones is 20 days. For comparison, this is 2.0 times more than for nitrite-coated steel and almost 20 times more than for uncoated steel [25].

It was shown [26] that the conversion tripolyphosphate coating is composite, like organic-organic [27] or inorganic-inorganic [28] composites. The matrix-forming agent in the coating is iron (III) tripolyphosphate, and the filler is sodium tripolyphosphate [26]. Such a coating structure is formed by a mechanism similar to the mechanism of formation of bivalent metal hydroxides, in particular nickel hydroxide [29, 30] and layered double hydroxides based on them [31].

However, it should be noted that the formation of the tripolyphosphate conversion coating was carried out at one concentration and only by the dip coating method. However, coatings of this type can also be deposited by sputtering. In addition, to convert the laboratory method into technology, it is necessary to optimize the parameters, including the concentration of STPP in the solution.

3. The aim and objectives of the study

The study aims to determine the optimum concentration of sodium tripolyphosphate and to evaluate the efficiency of using the dip coating and sputtering methods to form a conversion tripolyphosphate coating with high corrosion-protective properties on mild steel.

To achieve the aim, the following objectives were set:

– to form samples of conversion tripolyphosphate coatings by dip coating and by sputtering using sodium tripolyphosphate solutions of various concentrations and to study the characteristics of the samples;

– to study the protective properties of the conversion tripolyphosphate coating obtained from STPP solutions of various concentrations by accelerated corrosion tests.

4. Research materials and methods

Method of deposition of coating samples. For the study, we used 30×40 mm samples made of st05kp cold-rolled sheet steel (analogs G10050, G10060, 1CR, 2CR, D6-2, DG-2). For coating, we used aqueous solutions of sodium tripolyphosphate with a mass concentration of 4 %, 6 %, 10 %, 12 %, 14 % and a temperature of 80 °C. The coating was formed using a 3-minute dip coating method and the sputtering method using an automatic household sprayer (sputtering time 3 minutes). After the coating was deposited, the samples were dried in a suspended state in the air at room temperature for one day.

Method of studying the characteristics of coating samples. The most important characteristics of an anti-corrosion coating are adhesion to the substrate and protective capability. However, the works [22, 23] revealed a very high adhesion of the coating to the substrate. Therefore, the target optimization function was chosen to be the protective capability, which is largely determined by the specific weight of the coating, including inhibitor (sodium tripolyphosphate), and coating defectiveness. The specific weight of the coating was determined gravimetrically as the mass difference of the sample after and before deposition. The morphology (including defectiveness) of the coating samples was studied using an I-106 scanning electron microscope (SEM) (SELMI, Ukraine). Corrosion-protective properties of the coating samples were studied by accelerated testing methods. As the first accelerated corrosion test, we used Akimov's test [26]: a drop of a solution containing HCl and $CuSO_4$ was put onto the coating surface and the time of color change in the solution drop from blue to brown was recorded. The second accelerated corrosion test was carried out in a G-4 climatic chamber (USSR) at 100 % humidity and a temperature of 90 °C. An uncoated sample was used as a control one. After 53 days, the samples were removed from the chamber. The percentage of the sample surface (%) affected by corrosion was used as a criterion.

5. Results of studying the characteristics of conversion tripolyphosphate coatings

5. 1. Results of studying the characteristics of the coatings formed by the dip coating and sputtering methods

Fig. 1 shows histograms of the specific weight of the tripolyphosphate coatings obtained by the dip coating and sputtering methods using STPP solutions of various concentrations. For the coatings obtained by dip coating, the specific weight increased linearly with an increase in the STPP concentration: the specific weight increased by $0.6–0.8\ g/m^2$ with an increase in concentration by 2 % (wt.). The same trend was observed for the coatings obtained by the sputtering methods. However, when the STPP concentration was changed from 8 % to 10 %, the specific weight values underwent a break. It should be indicated that for the sputtering method, two series of specific weight dependences on the STPP concentration were revealed. In the series of STPP concentrations "4 % – 6 % – 8 %", the specific weight of the coating increased by $0.4\ g/m^2$ with an increase in concentration by 2 % (wt.). In this case, the specific weight of the coating was higher than that of the coating obtained by the dip coating method. At the same time, in the series of STPP concentrations "10 % – 12 % – 14 %", the specific weight of the coating increased by $1.1–1.3\ g/m^2$ with an increase in concentration by 2 % (wt.). However, the specific weight of the coating was significantly lower than that of the coating obtained by the dip coating method.
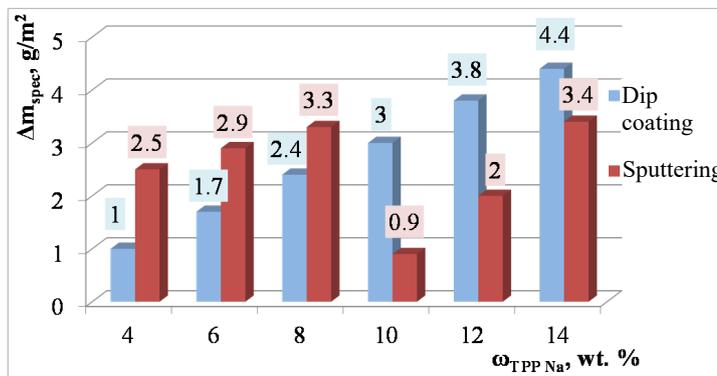

Fig. 1. Specific weight of the tripolyphosphate coating obtained by various methods at different STPP concentrations

Fig. 2 shows SEM images of the surface of coating samples obtained by the dip coating method using STPP solutions of various concentrations.
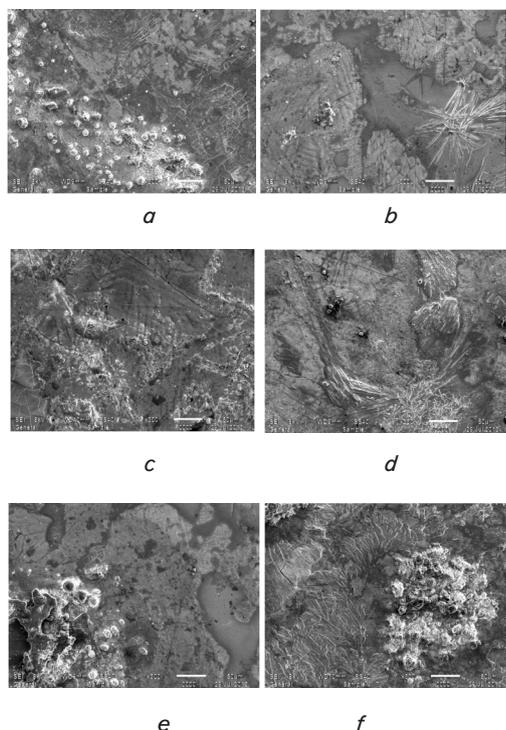

Fig. 2. SEM images of the tripolyphosphate coating on steel, formed by the dip coating method from STPP solutions with different concentrations:
$a-4\,\%;\ b-6\,\%;\ c-8\,\%;\ d-10\,\%;$
$e-12\,\%;\ f-14\,\%$

It should be noted that with the increase in sodium tripolyphosphate concentration, the coating surface became more relief, the number of coating cracks and defects increased. For the coating samples obtained from 4 %, 12 %, 14 % STPP solutions, the SEM images revealed zones with grouped light rounded objects.

5. 2. Results of studying the anticorrosive characteristics of the coatings formed from the solutions with different concentrations

Accelerated corrosion tests carried out using Akimov's test (Fig. 3) showed a high anticorrosive activity of the coatings obtained at all sodium tripolyphosphate concentrations. However, the longest time of the drop color change was typical for the coatings obtained from 6 % and 10 % STPP solutions (wt.). Thus, Akimov's test indicated that the optimum STPP concentration was 6–10 % (wt.).

Accelerated tests in the G-4 climatic chamber (Fig. 4) showed that the degree of corrosion damage to the surface of all samples coated with the tripolyphosphate coating was significantly lower than that of the control, uncoated sample (10–18 % compared to 90 %).

It should be noted that the minimum degree of corrosion damage (10 %) was typical for the tripolyphosphate coating sample formed in a 6 % STPP solution. The worst anticorrosive activity (degree of damage 18 %) was found in the coating sample formed in a 4 % solution.
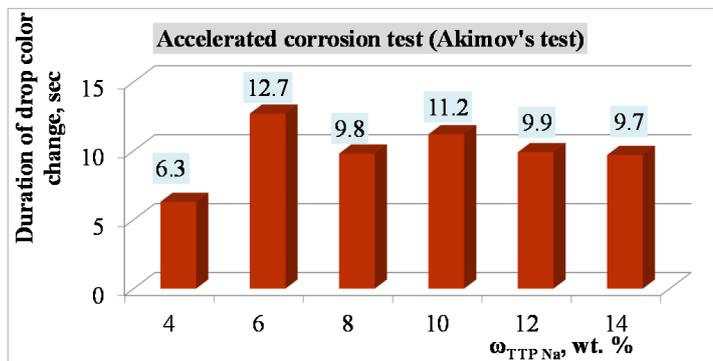

Fig. 3. Anticorrosive properties of tripolyphosphate coatings obtained using Akimov's test
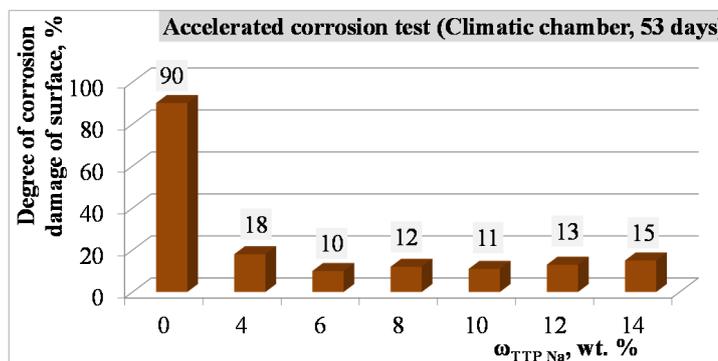

Fig. 4. Anticorrosive properties of tripolyphosphate coatings obtained by accelerated testing in the climatic chamber

6. Discussion of the results of studying the characteristics of tripolyphosphate coating samples

The specific weight of the tripolyphosphate coating is an essential criterion for anticorrosive activity. According to the composite structure of the tripolyphosphate coating proved in [23], the specific weight of the coating consists of the mass of iron (III) tripolyphosphate (coating base) and the mass of sodium tripolyphosphate (inhibitor). The results of determining the specific weight of the coatings obtained by the dip coating method (Fig. 1) showed that the specific weight increased in proportion to the STPP concentration in the solution for obtaining the coating ($0.3-0.35\,\text{g/m}^2$ with an increase in the STPP concentration by 1 % (wt.)). An increase in the sodium tripolyphosphate concentration led to an increase in the growth rate of iron (III) tripolyphosphate. In this case, the spongy, matrix structure of the coating can include a larger volume of mother liquor containing a greater amount of STPP. The work [23] showed that the unrinsed coating contained 48.9 % of mother liquor. Thus, the mass of both the matrix former and the filler increased. However, an increase in the growth rate of iron (III) tripolyphosphate led to an increase in the volume of the cavities filled with the mother liquor. When such a coating dries, more coating cracks and damage may appear, as confirmed by scanning electron microscopy images (Fig. 2). This effect is most pronounced for the coatings obtained in 10 %, 12 %, and 14 % STPP solutions (Fig. 2, $d–f$).

For the coatings obtained by sputtering, an unusual effect was revealed – a clearly identified break and a fundamentally different specific weight for the coatings obtained

from 4–8 % solutions (wt.) and for the coatings obtained from 10–14 % solutions (wt.). For the series of STPP concentrations "4 % – 6 % – 8 %", the specific weight of the coating increased by 0.2 g/m^2 with an increase in concentration by 1 % (wt.). The specific weight of the coating obtained by sputtering was higher than that of the coating obtained by dip coating. This is due to the coating formation mechanism. On the anodic section of the metal surface, iron was oxidized according to the $Fe^0 \rightarrow Fe^{2+} \rightarrow Fe^{3+}$ scheme, after which the formed Fe^{3+} cations reacted with the tripolyphosphate anion to form iron (III) tripolyphosphate. The depolarizer was restored at the cathode section. The $Fe^{2+} \rightarrow Fe^{3+}$ reaction can occur only upon reduction of molecular oxygen at the cathode region [22]. The speed of this process is limited by the formation rate of iron tripolyphosphate as a whole. When using the dip coating method, the rate of oxygen reduction was limited by the diffusion of oxygen from the solution surface to the metal surface. When using the sputtering method, the oxygen delivery rate increased sharply, which led to a significant increase in the amount of the iron (III) tripolyphosphate matrix. In the series of STPP concentrations "10 % – 12 % – 14 %", the specific weight of the coating increased by $0.55–0.65 \text{ g/m}^2$ with an increase in the STPP concentration by 1 % (wt.). However, the specific weight of the coating was significantly lower than that of the coating obtained by dip coating. With an increase in the STPP concentration to 8 wt %, the principle of coating formation could change. It should be noted that the coating matrix (iron (III) tripolyphosphate) was formed in the bulk of the mother liquor. When using the dip coating method, there were no restrictions on the solution volume, and with an increase in the STPP concentration, the thickness of the wet and the mass of the dried coating grew. When using the sputtering method, the thickness of the wet coating was limited by the thickness of the solution film on the vertical surface of the sample. At an STPP concentration of 10 wt %, the thickness of the free-growing iron (III) tripolyphosphate matrix could reach the thickness of the solution layer. Therefore, iron (III) tripolyphosphate later began to grow inside the already formed matrix, which led to its self-compaction. In this case, the content of the mother liquor sharply decreased, and as a result, the content of sodium tripolyphosphate decreased as well. This led to a sharp decrease in the specific weight of the coating. With a further increase in the STPP concentration, the coating continued to self-compact, however, the mass of STPP in the mother liquor increased. However, this effect needs to be studied further.

In general, it should be noted that both the dip coating method and the sputtering method can be used to form a conversion tripolyphosphate coating.

The accelerated corrosion test of tripolyphosphate coating samples using Akimov's test (Fig. 3) revealed the following. The worst corrosion-protective properties were characteristic of the coating obtained from a 4 % STPP solution. This is due to the low content of the filler-inhibitor – sodium tripolyphosphate. The best protective capability was revealed by the coatings formed from 8 %, 10 %, and 12 % STPP solutions. At these concentrations, the coating contains enough active inhibitor component. It should be noted that cracking and defects of the tripolyphosphate coating upon drying were revealed [23]. It was proved that the resulting cracks were filled with sodium tripolyphosphate but this filling was not dense. With an increase in STPP concentration, the amount of mother liquor increased, and as

a result, cracks and defects of the coating grew. This reduced the protective capability of the coating. In this study, the data of the accelerated corrosion test with Akimov's test correlated with the data of scanning electron microscopy. It follows from the SEM images that the coating samples obtained from 8 %, 10 % and 12 % STPP solutions (Fig. 2, *b–d*) had the least number of defects and cracks. These data correspond to the best anticorrosive activity of the coatings. At the same time, there were zones with group objects consisting of light spheroid elements on the SEM of the coating samples formed from 4 %, 12 %, 14 % STPP solutions (Fig. 2, *a, e, f*). According to the element-by-element analysis given in [23], the iron content increased, and the phosphorus content decreased for such objects. These objects are anodic sites, with little tripolyphosphate coating and low protective capability.

The results of the accelerated corrosion test in the G-4 climatic chamber (Fig. 4) confirmed the results of the corrosion test using Akimov's test. The lowest protective capability (18 % corrosion damage) was in the coating obtained from a 4 % STPP solution, the highest protective capability was in the coatings obtained from 8 %, 10 % and 12 % STPP solutions. Two facts should be noted. First, the degree of corrosion damage to the uncoated sample was 7.5–9.0 times higher (Fig. 4) than that of the samples with the tripolyphosphate coating formed at the optimum concentration of solutions. This indicates a very high active corrosion-protective capability of the conversion tripolyphosphate coating. Secondly, the test in the G-4 climatic chamber was carried out at 100 % air humidity. As a result, water droplets condensed on the sample surface and gradually fell into the tray. In this case, the active inhibitory component of the tripolyphosphate coating was partially rinsed out. Therefore, an increase in the corrosion damage to the samples with the coatings obtained at higher STPP concentrations is explained by the rinsing out of the inhibitor (sodium tripolyphosphate) from more defective coatings (Fig. 2, *e, f*).

Thus, we should conclude that for obtaining the most corrosion-protective coating by the dip coating method, the optimum STPP concentration lies in the range of 6–10 wt %. The optimum concentration should be clarified during full-scale tests.

Moreover, the development of this study will determine the corrosion-protective capability of the coatings obtained by the sputtering method.

7. Conclusions

1. The method of determining the specific weight showed the prospects of using the dip coating and sputtering methods to form a conversion tripolyphosphate coating. The coatings formed by the dip coating method are characterized by a linear increase in specific weight with an increase in the sodium tripolyphosphate concentration ($0.3–0.35 \text{ g/m}^2$ by 1 % (wt.)). For the coatings obtained by sputtering, the dependence of the specific weight on the sodium tripolyphosphate concentration consists of two fundamentally different sections. The specific weight of the coating at a sodium tripolyphosphate content of up to 8 % increases linearly with an increase in concentration (0.2 g/m^2 by 1 % (wt.)). However, the specific weight is higher than that of the coating obtained by dip coating, which is due to a significant acceleration of oxygen access and an increase in the coating growth rate. At a sodium tripolyphosphate concentration of 10 %, the specific weight

drops sharply and becomes lower than that of the coating obtained by dip coating, which is due to the self-compaction of the iron tripolyphosphate matrix and a decrease in the mass of the sodium tripolyphosphate filler. With a further increase in concentration, the specific weight grows at a significantly higher rate $(0.55-0.65 \text{ g/m}^2$ by 1 % (wt.)).

2. A study of the protective capability of the samples of conversion tripolyphosphate coating obtained by dip coating in sodium tripolyphosphate solutions of various concentrations, accelerated corrosion testing methods using the Aki-

mov's test, and exposure in the climatic chamber was carried out. The results of both methods revealed that the optimum sodium tripolyphosphate concentration for obtaining a coating with the highest corrosion-protective capability is in the range of 6–10 % (wt.). The correlation of the protective capability of the coating samples with the coating defects and cracks determined by scanning electron microscopy was revealed. Defects and cracks are filled with an inhibitor (sodium tripolyphosphate), which, however, is easily rinsed out if water drops or films are formed on the surface.

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