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# INVESTIGATION OF COMPOSITION AND STRUCTURE OF TRIPOLIPHOSPHATE COATING ON LOW CARBON STEEL

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*Експериментально підтверджено гіпотезу матричної будови триполіфосфатних покриттів на низьковуглецевій сталі. Хімічним методом показано, що матрицеутворювачем є феррум (III) триполіфосфату. Гравіметричним методом з промиванням встановлено, що покриття вміщує в якості наповнювача 79,66–82,56 % натрію триполіфосфату. Методом рентгеноспектрального мікроаналізу виявлено наявність на поверхні матриці шару натрію триполіфосфату. Запропоновано хімічний механізм захисту сталі триполіфосфатним покриттям в атмосферних умовах*

*Ключові слова: триполіфосфат натрію, феррум (III) триполіфосфат, триполіфосфатне покриття, захисні властивості, матрична будова*

*Экспериментально подтверждена гипотеза матричного строения триполифосфатных покрытий на низкоуглеродистой стали. Химическим методом показано, что матрицеобразователем является феррум (III) триполифосфат. Гравиметрическим методом с промывкой установлено, что в качестве наполнителя покрытие содержит 79,66–82,56 % триполифосфата натрия. Методом рентгеноспектрального микроанализа выявлено наличие на поверхности матрицы слоя триполифосфата натрия. Предложен химический механизм защиты стали триполифосфатным покрытием в атмосферных условиях*

*Ключевые слова: триполифосфат натрия, феррум (III) триполифосфат, триполифисфатное покрытие, защитные свойства, матричное строение*

## 1. Introduction

The phosphating process is widely used in industry for steelwares because of high performance, low cost and ease of deposition of phosphate coatings.

Owing to multifunctionality and a wide range of practical applications of phosphate conversion coatings, the requirements to their quality and deposition techniques, including economical and ecological aspects, have increased significantly in recent years.

One of the priority directions of improving the phosphating process is the reduction of the ecological hazard of technological processes [1].

An example of such project is the replacement of traditional acidic phosphating solutions with aqueous solutions of polyphosphates.

Among the most commonly used polyphosphates, a particular place is taken by sodium tripolyphosphate (STPP). Being non-toxic inorganic polymeric compound with good solubility, the STTP is not expensive and is available on an industrial scale. An aqueous STPP solution is basic electrolyte of phosphate nature, stable in time and non-volatile at elevated temperature. This allows for it to be considered promising for the development of a more ecologically safe technology for deposition of phosphate-based coatings.

Despite that, the scientific and industrial concept of specifics of physico-chemical and technological properties of tripolyphosphate coatings on steel and their structure is not developed sufficiently. The development of tripolyphosphate coating technology requires additional research and review of acquired results on a new level.

## 2. Literature review and problem statement

Presently polyphosphates of various compositions find their use in various fields of science and technology. This is because listed objects have a number of unique properties, which draw attention to them from scientists, researchers and technologists.

The most commonly polyphosphates are used in metallurgical production as additives to solutions for cleaning, degreasing, passivation of metal wares [2, 3], and additives to technological lubricants [4]. The addition of polyphosphates to zinc-phosphate solutions lowers crystallinity and increases protective properties of coatings prepared using chemical [1, 5] and electrochemical methods [6, 7]. The introduction of such additives into ceramic suspensions changes rheological properties of these systems [8]. After carrying out the synthesis and study on the structure, chemical and electrochemical properties of polyphosphate $LiFe_2P_3O_{10}$, the authors [9] view it as a promising material for application in lithium-ion accumulators.

Sodium tripolyphosphate and hexametaphosphate are widely used in water supply and cooling systems for protection of heat equipment from corrosion and deposition of salts [2, 10]. Owing to its inhibiting properties, sodium tripolyphosphate is used in cement pastes [11]. Tripolyphosphates of zinc [12], aluminum [13], calcium [14] are used as anti-corrosion pigments in paints. In papers [15, 16], polyphosphates of magnesium and calcium were studied as a pigment in comparison to zinc pigment in 3.5 % NaCl and a mixture of acids and rainwater. It has been established that polyphosphate is an effective corrosion inhibitor with mixed action type.

Review of literature dedicated to studying the role of polyphosphate ions in inhibition of metal substrate has shown that it is about inhibition of carbon steel [10, 15], metallic zinc in neutral media [16], artificial acids [15, 16]. In particular, the STPP is widely known as a corrosion inhibitor of iron in neural media of mixed nature [2, 10]. Research results [17, 18] support its capability of inhibiting pitting and hydrochloric acid corrosion of steel.

It is known that the protection mechanism of phosphates and polyphosphates on steel substrates assumes the potential shift of the protected metal to more positive values. This is achieved by the formation of a protection passivation film with a thickness of several micrometers and [1, 7] and of different composition [19, 20].

Despite that this mechanism is interpreted from general views, the role of polyphosphates and STPP, in particular, as a steel inhibitor is not clear entirely. There is not enough data in the literature regarding properties and structure of passivation protective films that are formed on the surface of inhibited metal in solutions containing polyphosphate ions.

The results of experimental researches on the formation mechanism of tripolyphosphate coatings on steel have revealed that the films are hydrophilic [21] and non-porous [22–24], while their protective properties are higher than those of alkali metal phosphate coatings and are comparable to the properties of sodium nitrite coatings [23].

This leads to the idea that the structure of this coating is different from that of usual salt coatings on metal. The formation process is likely similar to the formation of polyvalent metal hydroxides, in particular, nickel hydroxide $Ni(OH)_2$ [25, 26].

It is known that kinetic laws of $Ni(OH)_2$ precipitation are such that the rate of particle formation is significantly higher than the rate of crystallization. This results in the formation of the hydrophilic precipitate composed of amorphous $Ni(OH)_2$ particles that are aggregated with each other and contain large amounts of mother liquor. Thus, nickel hydroxide actually is a matrix structure that in the freshly precipitated state consists of a matrix forming agent (nickel hydroxide) and large amounts of mother liquor microvolumes [25]. Upon drying of the vacuum-filtered nickel hydroxide precipitate, the layer thickness decreases by 6–8 times while the layer itself cracks. In addition, it is known that it is almost impossible to completely wash the filtered wet $Ni(OH)_2$ precipitate from side products (mother liquor salts) of synthesis. Thus, for complete removal a two-stage drying procedure is employed: first drying → grinding → washing from salts → second drying.

Experimental data confirms the hydrophilic nature of the tripolyphosphate coating indicating that macrostructures of the tripolyphosphate coating on the steel surface and nickel hydroxide precipitate are similar. This allows proposing a hypothesis about the presence of a special matrix structure in tripolyphosphate precipitates. If the proposed hypothesis is true, then during the formation of a coating or precipitate on the surface of steel the formation rate of iron tripolyphosphate (Fe STPP) particles is significantly higher than the rate of their crystallization. Thus, the freshly prepared precipitate or tripolyphosphate coating would include microvolumes of the mother liquor containing STPP. Upon drying of the mother liquor and water evaporation, the STPP particles would remain in the precipitate or coating. Additionally, the precipitate volume or coating thickness should decrease significantly. Taking into account the drying mechanism of porous materials, it can be assumed that STPP can not only be inside a matrix structure as a filler, but can also form an additional layer on the surface of the coating or precipitate. Because STPP also inhibits corrosion of iron in neutral media [2, 10], the tripolyphosphate coating can also possess an active (chemical) character of metal protection from atmospheric corrosion.

In order to prove the proposed hypothesis and stated assumptions, it is necessary to compare and analyze the data that characterize the composition and structure of washed and non-washed tripolyphosphate coatings on steel and iron tripolyphosphate precipitates. The washing would allow removing the water-soluble filler, which would lower protective properties of the whole coating.

## 3. Aim and objectives

The aim of the work is to experimentally prove the hypothesis on a matrix structure of the tripolyphosphate coating.

To achieve the set goal, it is necessary to:

– chemically synthesize iron (II) and iron (III) tripolyphosphate precipitates, to deposit tripolyphosphate coatings on the surface of steel samples;

– study protective properties, structure, phase composition of washed and non-washed iron (III) tripolyphosphate precipitate samples and tripolyphosphate coatings on steel;

– conduct a comparative analysis of the data characterizing protective properties, composition, and structure of washed and non-washed iron tripolyphosphate precipitates and tripolyphosphate coatings on steel;

– determine where sodium tripolyphosphate is situated in the structure of tripolyphosphate coatings and to justify the mechanism of steel protection in atmospheric conditions.

## 4. Materials and methods for studying the composition and structure of tripolyphosphate coatings

### 4. 1. Preparation and analysis methods of tripolyphosphate coatings on steel

*Coating deposition.* The coatings were chemically deposited on a surface of rectangular st05kp steel samples. The samples were submerged in the 12 % aqueous STPP solution at 80 °C for 5 min and were dried during a day.

*Study of composition and properties of samples.* The composition analysis was carried out using the gravimetric method with washing. The washing was carried out simultaneously with gravimetrical control on all stages. After drying, the samples were submerged in distilled water for 1, 3, 10 min and 24 h. After washing, the samples were dried in air. During the experiments, the following gravimetric attributes were measured:

$m_0$ – the mass of the sample before deposition;

$m_1$ – the mass of the sample with the freshly deposited coating;

$m_2$ – the mass of the sample with the coating after drying;

$m_3$ – the mass of the sample with the coating after washing with water (at different washing duration) and drying.

The values of these attributes were used to calculate the following parameters:

$\Delta m_1$ – the difference between masses before and after coating deposition, which corresponds to the mass of the freshly deposited coating;

$\Delta m_2$ – the difference between masses before and after drying, which corresponds to the mass of water in the coating;

$\Delta m_3$ – the difference between masses before and after washing, which corresponds to the mass of STPP.

$$\Delta m_1 = m_0 - m_1, \tag{1}$$

$$\Delta m_2 = m_1 - m_2, \tag{2}$$

$$\Delta m_3 = m_2 - m_3, \tag{3}$$

$$\Delta m^{sp} = \Delta m_i / S. \tag{4}$$

During corrosion tests with increased washing time, the presence of corrosion products in the form of rust spots was monitored visually. The strength of corrosion was evaluated by the increased area of the corroded region and the number of corrosion products.

The coating composition was studied using Scanning Electron Microscope JSM 6360LA equipped with Energy-Dispersive X-ray analyzer JED 2200, JEOL (Japan). The analysis was conducted at an accelerating voltage of 10 kV with 4 nm probe in diameter, with a diameter of the X-ray excitement of about 1 μm. The determination of phase composition was realized by using the non-etalon method to calculate the fundamental parameters: calculation of corrective coefficients for the probe electron reflection, absorption of characteristic X-ray emission and fluorescence. Black and white images of the sample surface were obtained in secondary electrons. The distribution of chemical elements was obtained using the mapping method as color maps with a more intense color corresponding to a higher content of a chemical element. The determination of chemical composition was carried out in the regions marked by squares and crosses, for which characteristic X-ray spectra and (or) approximate composition are presented.

*Preparation and synthesis methods of iron tripolyphosphate precipitates.* On par with coating deposition, the experiments, including synthesis and gravimetric studies with the washing of the tripolyphosphate precipitate, which was prepared chemically by mixing solutions of STPP and iron salt were conducted. The polyvalency of iron was taken into account for the precipitate synthesis, and it was assumed that it is possible to prepare it as iron (II) tripolyphosphate and iron (III) tripolyphosphate. The equivalent amounts of STPP and iron (II) chloride (or iron (III) chloride) solutions were mixed at 20 °C and 80 °C. After synthesis, the precipitates were aged for 1.5 h, vacuum filtered, washed with distilled water 5–6 times and dried at room temperature during a day.

In order to determine the composition, the precipitate was weighted before and after washing with distilled water. The calculations were carried out according to the following formulas:

$$m_2^{oc} = m_0^{oc} - m_1^{oc}, \tag{5}$$

$$m_3^{oc} = \frac{m_2^{oc}}{0{,}12}, \tag{6}$$

$$\omega_{\%\text{TPF Fe}}^{\text{dry}} = \frac{m_1^{oc}}{m_0^{oc}}, \tag{7}$$

$$\omega_{\%\text{TPF Fe}}^{\text{with solution}} = \frac{m_1^{oc}}{m_3^{oc}}, \tag{8}$$

where $m_0^{oc}$ is the mass of the precipitate; $m_1^{oc}$ is the mass of the precipitate after washing; $m_2^{oc}$ is the difference between masses before and after washing, corresponding to the mass of STPP; $m_3^{oc}$ is the mass of the solution, 0.12 is the STPP content by weight.

Coating deposition and precipitate synthesis experiments were duplicated. Then the results of the gravimetric analysis are presented as an average of 3 experiments.

## 5. Experimental results of studying the composition and structure of iron tripolyphosphate precipitates and tripolyphosphate coatings

*Results of iron tripolyphosphate synthesis.* It had been established that at both synthesis temperatures, the precipitate of iron (II) tripolyphosphate does not form. This signifies the solubility of iron (II) tripolyphosphate in water. Upon mixing the solutions of STPP and $FeCl_3$, the iron (III) tripolyphosphate precipitate forms, which has a white color at a synthesis temperature of 20 °C, and light-yellow color at a synthesis temperature of 80 °C.

*Results of gravimetric studies.* The results of calculating the composition of dried and freshly precipitated iron (III) tripolyphosphate precipitated at different temperatures by means of gravimetric analysis with washing are presented in Fig. 1.

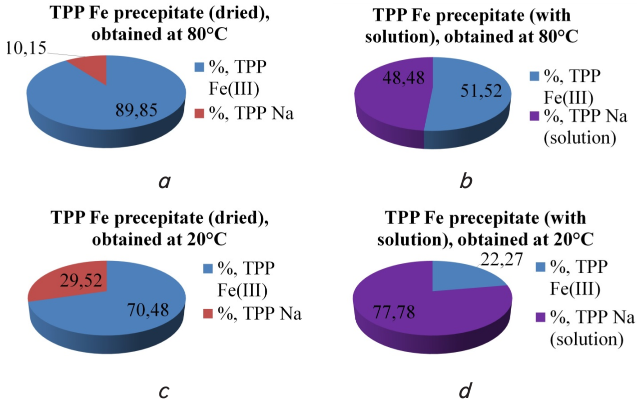


Fig. 1. Composition of iron (III) tripolyphosphate precipitate: *a* — dried, $t_{precipitation}$=80 °C; *b* — freshly precipitated, $t_{precipitation}$=80 °C; *c* — dried, $t_{precipitation}$=20 °C; *d* — freshly precipitated, $t_{precipitation}$=20 °C

It has been demonstrated that the dried iron tripolyphosphate precipitate synthesized at 80 °C contains 85–89 % of $Fe^{3+}$ TPP and approximately 11–15 % of a filler in the form of water-soluble STPP. With lowering the synthesis temperature to 20 °C, the STPP content increases to 29.52 %.

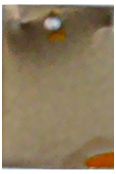
The compositions of freshly prepared and dried tripolyphosphate coatings are presented in Fig. 2.

Calculation results presented in Fig. 2 have shown that the freshly prepared tripolyphosphate contains: water – 56.30–60.56 %; STPP – 19.4–32.06 %, Fe(3+) TPP – 11.6–17.0 %. Analysis of the tripolyphosphate coating composition histograms (Fig. 2) has shown that at different washing duration, the dried coating contains 17.5–20.33 % of Fe(3+) TPP and 79.6–80.7 % of STPP, with the Fe(3+) TPP content being almost constant with increasing the washing duration.

*Results of corrosion tests for tripolyphosphate coatings.* Table 1 shows the results of corrosion tests for tripolyphosphate coatings on steel samples.

Table 1

Images of samples with tripolyphosphate coatings at different washing duration

| Washing | Duration, s | | | |
|---|---|---|---|---|
| | 60 | 180 | 600 | 86400 |
| Images of steel samples with tripolyphosphate coating after washing and drying |  |  |  |  |

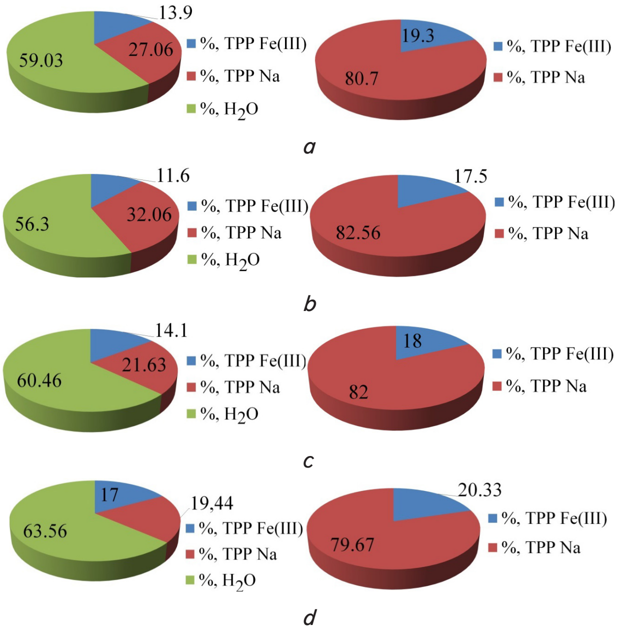
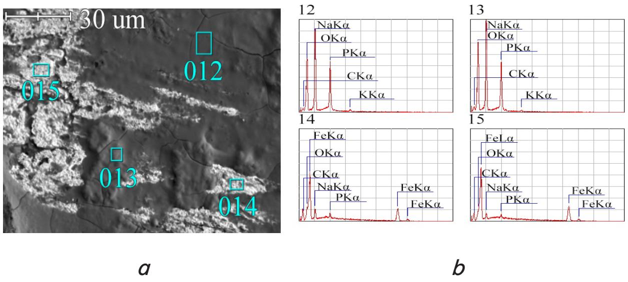


Fig. 2. Composition of freshly prepared (left) and dried (right) tripolyphosphate coating that has been preliminary washed for: *a* — 1 min; *b* — 3 min; *c* — 10 min; *d* — 24 h

The visual examination of the samples with the tripolyphosphate coating with different washing duration has revealed that with increasing the washing duration the degree of corrosion attack increases.

*Results of Energy-dispersive X-ray spectroscopy (EDX).* Fig. 3 shows the results of the EDX analysis of the tripolyphosphate coating surface, deposited from the 12 % aqueous STPP solution on st05kp steel at 80 °C.

For the analysis of the results, the weight contents of elements for compounds that are possibly contained in the coating were calculated. The calculated data ~~is~~ are presented in Table 2.



| Spectrum | C | O | Na | P | K | Fe | Total |
|---|---|---|---|---|---|---|---|
| 012 | 4.46 | 34.86 | 32.67 | 26.85 | 1.15 | 0 | 100 |
| 013 | 4.59 | 36.98 | 34.05 | 23.42 | 0.95 | 0 | 100 |
| 014 | 11.64 | 9.29 | 9.80 | 4.77 | 0 | 64.5 | 100 |
| 015 | 7.12 | 5.42 | 6.49 | 3.04 | 0 | 77.91 | 100 |

*c*

Fig. 3. EDX results of the tripolyphosphate coating: *a* — SEM image of the coating microstructure with marked regions for analysis, ×1000; *b* — spectra of marked regions; *c* — elemental analysis of marked regions

Table 2

Composition (weight content of the element) of compounds assumed to be in the coating

| No. | Compound | $\omega_{Fe}$, % | $\omega_{O}$, % | $\omega_{P}$, % | $\omega_{Na}$, % |
|---|---|---|---|---|---|
| 1 | $Fe_5P_3O_{10}$ | 27 | 46 | 27 | – |
| 2 | $Fe_2O_3$ | 70 | 30 | – | – |
| 3 | $Fe_3O_4$ | 72 | 28 | – | – |
| 4 | FeO | 77 | 23 | – | – |
| 5 | $Fe(OH)_3$ | 52 | 44 | – | – |
| 6 | $FePO_4$ | 37 | 43 | 20 | – |
| 7 | $Na_5P_3O_{10}$ | – | 43 | 26 | 31 |

EDX results for the analyzed region of the coating (Fig. 3, *a*) have revealed that there are two light-grey and dark regions with clearly defined boundaries in its structure. Additionally, the cracks on the surface of dark regions can also be observed.

Spectral analysis of dark areas inside the regions 012 and 013 (Fig. 3, *a*, *c*) revealed the absence of Fe. At the same time, the ratio of Na, P and O approximately corresponds to the composition of STPP (Table 2).

For light-grey areas inside the regions 014 and 015 (Fig. 3, *a*), the EDX has revealed an anomalously high content of iron at very low contents of Na and P. EDX mapping results for this region are presented in Fig. 4.

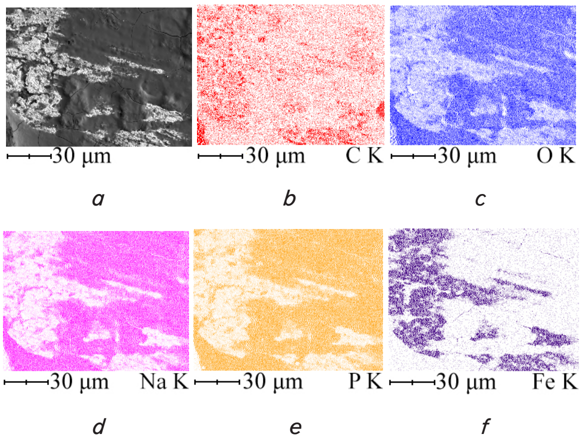


Fig. 4. Results of EDX mapping for the tripolyphosphate coating: *a* – SEM image of the coating, ×1000; *b*–*f* – maps for distribution of chemical elements inside the sampled area (C, O, Na, P, Fe correspondingly)

It can be seen that light-grey areas correspond to the highest contents of Fe and C (Fig. 4, *b*, *f*) and the lowest contents of O, Na, P (Fig. 4, *c*–*e*), while the values for dark regions are reversed.

## 6. Discussion of the results of investigating the composition and structure of the iron tripolyphosphate precipitate and tripolyphosphate coating

During the investigation, the tripolyphosphate precipitate in the form of iron (III) tripolyphosphate has been prepared chemically using solutions of sodium tripolyphosphate and iron chloride. Thus, the coating formed on the steel surface in the STPP solution is also composed of iron (III) tripolyphosphate.

The analysis of the results of carried out investigations has been conducted with an account for established facts.

The results of investigating the iron (III) tripolyphosphate precipitate using the gravimetric method with washing are presented in Fig. 1. As can be seen from the presented data, the dry precipitated prepared at 80 °C, contains 85–89 % of a matrix forming agent ($Fe^{3+}$ TPP).

Thus, the dried iron (III) tripolyphosphate precipitate has a composite (matrix) structure. Because of that, in addition to the matrix, the precipitate also contains approximately 11–15 % of a filler in the form of water-soluble STPP. It should also be noted that the filtered precipitate has been washed multiple times with distilled water. Upon decreasing the synthesis temperature to 20 °C, the STPP content has increased to 29.52 %. This can possibly be explained by decreased crystallization rate of the matrix forming agent ($Fe^{3+}$ TPP), resulting in increased content of the mother liquor in the freshly prepared precipitate.

Analysis of histograms for tripolyphosphate coating compositions (Fig. 2) has shown that with different washing duration the dried coating contains 17.5–20.33 % Fe(3+) TPP and 79.6–80.7 % STPP.

The comparison of compositions of the coating and precipitate prepared at 80 °C has shown that the precipitate contains 85–89 % of Fe(3+) TPP while the coating only 17.5–20.33 %. Such significant ifference is likely because of different formation conditions for iron tripolyphosphate during the coating deposition and precipitation. When solutions with equivalent amounts of reactants are mixed during chemical precipitation, the reaction solution would contain a sufficient amount of Fe(3+) ions. Thus, the precipitate structure and composition will be primarily determined by the kinetics of precipitate formation, i.e. the ratio between the rate of particle formation and the rate of particle crystallization. At the same time, during coating formation on steel from the STPP solution, the Fe(3+) ions participating in coating formation, are formed by the operation of a short-circuited corrosive galvanic element with oxygen depolarization, with the rate of Fe(3+) formation being limited by the reduction rate of depolarizer, i. e. oxygen. Thus, the number of iron ions for coating formation is significantly lower than during chemical precipitation, which indicates that the coating structure and composition are significantly affected by the rate of Fe(3+) formation and transport of these ions to the reaction region.

The results of investigating the tripolyphosphate coating composition using the gravimetric method with washing (Fig. 2) support the washing out of STPP from the dried coating. It should be noted that the content of Fe(3+) TPP was almost constant with increasing the washing time.

Initially, it has been assumed that longer washing time would lead to more precise determination of the Fe(3+) TPP content because of a more complete removal of water-soluble STPP and the content of Fe(3+) TPP should have been increasing with prolonged washing. The fact that it didn't happen can be explained by the increased corrosion rate of washed samples (Table 1).

Thus, the mass lost because of washed out STPP was compensated by the mass of corrosion products. Appearance analysis of the samples with tripolyphosphate coatings with different washing duration has demonstrated that with increasing the washing duration the number of corrosion products in the form of rust spots increases. Thus, the increased washing duration leads to a decrease of protective properties indirectly indicating the washing out of water-soluble STPP.

It should be noted that the removal of STPP reveals the coating defects, thus lowering its capabilities of active chemical protection of the substrate from corrosion.

EDX analysis results for the coatings prepared from 12 % STPP at 80 °C on st05kp steel are presented in Fig. 3, 4. As can be seen from the EDX map of the analyzed coating region (Fig. 3, *a*), there are two components in its structure that are represented by light-gray and dark regions with clearly defined boundaries.

Spectra analysis of the dark component in the regions 012 and 013 (Fig. 3, *a, c*) has shown a complete absence of Fe, while the ratio of Na, P and O approximately corresponds to the composition of STPP (Table 2), which allows assuming that on the surface of the coating there is a layer of pure STPP. It is likely that during drying the mother liquor contained in the coating rises to the surface, the water evaporates, while STPP present in the mother liquor forms an additional layer on the surface. The presence of cracks in this layer is related to caking during drying.

In the map regions 014 and 015, the coating microstructure is presented by the light-grey component (Fig. 3, *a*). According to the EDX results, there is an anomalously high iron content with very low contents of Na, P. Taking into account that there is not enough oxygen or phosphorus to match the iron content (Table 2), it can be concluded that iron in this region is in the form of $Fe^0$. Thusly, the regions 014 and 015 (Fig. 3, *a*) are defective regions of the coating, in which STPP crystals have formed upon drying. In this case, EDX analysis can also receive a response from the steel substrate. EDX mapping results for this region (Fig. 4) support this conclusion. As can be seen from the presented data, the areas of the light-grey coating component correspond to the highest contents of Fe and C (Fig. 4, *b, f*) and the lowest contents of O, Na, P (Fig. 4, *c–e*), while the dark component is characterized by the highest contents of Na, P, O. The established fact supports that the dark areas are a layer of STPP.

Having conducted a comparative analysis of acquired data and comparing it to the research data [27], it can be concluded that acquired results have experimentally supported the hypothesis on the matrix (composite) structure of the tripolyphosphate coating on low-carbon steel.

The results of conducted combined investigation have proved the presence of STPP in the composition of the coating, which allowed justifying its protection mechanism in atmospheric conditions.

The acquired knowledge of the composition and structure of tripolyphosphate coatings on steel significantly expand the theoretic and practical base of further investigations aimed at the development of effective ecologically-safe methods for their application for corrosion protection of metal wares.

## 7. Conclusions

1. By means of the chemical synthesis method, it has been demonstrated that the chemical basis of the coating formed on steel in the aqueous STPP solution is iron (III) tripolyphosphate.

2. The samples of iron (III) tripolyphosphate and tripolyphosphate coatings on steel have been prepared. By means of the gravimetric method with washing, it has been determined that the dried precipitate synthesized from the 12 % STPP iron (III) chloride solution is a composite material. The precipitate is composed of a matrix – iron (III) tripolyphosphate (85–89 %) and filler – the water-soluble STPP (11–15 %). The dried coating formed on the surface of st05kp steel in the 12 % STPP solution is a composite. However, the coating is composed of 17.5–20.33 % iron (III) tripolyphosphate and 79.66–82.56 % STPP filler.

3. An assumption has been proposed that quantitative differences between the compositions of the iron (III) tripolyphosphate precipitate and tripolyphosphate coatings are related to different formation conditions. The difference is defined by the character of the limiting stage. The coating on the steel surface forms as a result of corrosion process with oxygen depolarization. The limiting stage is the formation of iron (III) ions, while the formation of iron (III) tripolyphosphate occurs in the excess of iron ions.

4. The hypothesis about the matrix (composite) structure of the tripolyphosphate coating on steel with sodium tripolyphosphate as a filler has been proven experimentally. It has been established that the composite structure of tripolyphosphate coatings is determined by the nature of iron (III) tripolyphosphate.

5. By means of EDX analysis, it has been established that as a part of the composite tripolyphosphate coating, the STPP is situated not only as a filler inside the matrix but is also situated as an additional layer on its surface.

6. The chemical (active) protection mechanism of tripolyphosphate coatings on steel in conditions of atmospheric corrosion because of the presence of sodium tripolyphosphate inhibitor has been justified. Upon the filler washing out, the corrosion rate is increased significantly.

## References

1. Grigoryan, N. S. Fosfatirovanie [Text]: uch. pos. / N. S. Grigoryan, E. F. Akimova, T. A. Vagramyan. – Moscow: Globus, 2008. – 144 p.
2. Akol'zin, A. P. Protivokorrozionnaya zashchita stali plenkoobrazova-telyami [Text] / A. P. Akol'zin. – Moscow: Metallurgiya, 1989. – 192 p.
3. Lipkin, Ya. N. Himicheskaya i ehlektrohimicheskaya obrabotka stal'nyh trub [Text] / Ya. N. Lipkin, V. M. Shtan'ko. – Moscow: Metallurgiya, 1974. – 216 p.
4. Pat. No. 94340 UA. Mastylo dlya prokatky stal'nykh bezshovnykh trub ta sposib yoho oderzhannya. MPK S 10 M 103/00, S 10 M 177/00 [Text] / Cheremysinova A. O., Panasenko S. P.; vlasnyk DVNZ UDKhTU. – No. a201001874; declareted: 22.02.2010; published: 26.04.2011, Bul. No. 8. – 3 p.
5. Abdalla, K. The Effect of pH on Zinc Phosphate Coating Morphology and its Corrosion Resistance on Mild Steel [Text] / K. Abdalla, A. Rahmat, A. Azizan // Advanced Materials Research. – 2012. – Vol. 626. – P. 569–574. doi: 10.4028/www.scientific.net/amr.626.569

6. Tumbaleva, Y. Effect of the $P_2O_5$:$NO_3$ – 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.
7. Kuznecov, Yu. I. Ingibitory korrozii v konversionnyh pokrytiyah II [Text] / Yu. I. Kuznecov // Zashchita metallov ot korrozii. – 2001. – Vol. 37, Issue 2. – P. 119–125.
8. Piani, L. Sodium Tripolyphosphate and Polyphosphate as Dispersing Agents for Alumina Suspensions: Rheological Characterization [Text] / L. Piani, A. Papo // Journal of Engineering. – 2013. – Vol. 2013. – P. 1–4. doi: 10.1155/2013/930832
9. Ait-Salah, A. Synthesis, Structure and Electrochemical Properties of LiFe2P3O10 Synthesized by Wet Chemistry [Text] / A. Ait-Salah, C. V. Ramana, F. Gendron, J. F. Morhange, A. Mauger, K. Zaghib, C. Julien // ECS Transactions. – 2007. – Vol. 3, Issue 36. – P. 95–100. doi: 10.1149/1.2795110
10. Rozenfel'd, I. L. Ingibitory korrozii [Text] / I. L. Rozenfel'd. – Mosocw: Himiya, 1977. – 352 p.
11. Ltifi, M. Effects of sodium tripolyphosphate addition on early-age physico-chemical properties of cement pastes [Text] / M. Ltifi, A. Guefrech, P. Mounanga // Procedia Engineering. – 2011. – Vol. 10. – P. 1457–1462. doi: 10.1016/j.proeng.2011.04.242
12. Deya, M. Performance of Anticorrosive Coatings Containing Tripolyphosphates in Aggressive Environments [Text] / M. Deya, A. R. Di Sarli, B. del Amo, R. Romagnoli // Industrial & Engineering Chemistry Research. – 2008. – Vol. 47, Issue 18. – P. 7038–7047. doi: 10.1021/ie071544d
13. Deya, M. Aluminium tripolyphosphate pigments for anticorrosive paints [Text] / M. Deya, V. F. Vetere, R. Romagnoli, B. del Amo // Pigment & Resin Technology. – 2001. – Vol. 30, Issue 1. – P. 13–24. doi: 10.1108/03699420110364129
14. Vetere, V. F. Calcium Tripolyphosphate An Anticorrosive Pigment for Paint [Text] / V. F. Vetere, M. C. Deya, R. Romagnoli, B. Amo // Journal of Coatings Technology. – 2001. – Vol. 73, Issue 6. – P. 57–63. doi: 10.1007/bf02698398
15. Yanga, Y. F. A Novel Anti-corrosion Calcium Magnesium Polyphosphate Pigment and Its Performance in Aqueous Solutions on Mild Steel [Text] / Y. F. Yanga, J. D. Scantleburya, E. Koroleva, O. Ogawab, H. Tanabeb // ECS Transactions. – 2010. – Vol. 24, Issue 1. – P. 77–85. doi: 10.1149/1.3453608
16. Yanga, Y. F. A Novel Anti-corrosion Calcium Magnesium Polyphosphate Pigment and its Performance in Aqueous Solutions on Mild Steel When Coupled to Metallic Zinc [Text] / Y. F. Yang, J. D. Scantlebury, E. Koroleva, O. Ogawa, H. Tanabe // ECS Transactions. – 2010. – Vol. 24, Issue 1. – P. 163–168. doi: 10.1149/1.3453615
17. Burlov, V. V. Lokal'naya korroziya oborudovaniya sovremennogo nefte-pererabatyvayushchego zavoda [Text] / V. V. Burlov, A. I. Al'cybeeva, T. M. Kuzikova // Izvestiya Sankt – Peterburgskogo gosudarstvennogo tekhnolo-gicheskogo universiteta (tekhnicheskogo universiteta). – 2011. – Issue 11 (37). – P. 92–96.
18. Kheireddine, A. Sodium tripolyphosphate (STPP) as a novel corrosion inhibitor for mild steel in 1M HCL [Text] / A. Kheireddine, I. Fahim // Journal of optoelectronics and advanced materials. – 2013. – Vol. 15, Issue 5-6. – P. 451–456.
19. Yohai, L. Inhibiting Steel Corrosion in Simulated Concrete with Low Phosphate to Chloride Ratios [Text] / L. Yohai, W. Schreiner, M. B. Valcarce, M. Vazquez // Journal of The Electrochemical Society. – 2016. – Vol. 163, Issue 13. – P. C729–C737. doi: 10.1149/2.0511613jes
20. 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 // Int. J. Electrochem. Sci. – 2016. – Vol. 11. – P. 2306–2316.
21. Vlasova, E. Research of the mechanism of formathion and properties of tripolyphosphate coatingon 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
22. Vlasova, E. V. Issledovanie pokrytij, poluchennyh iz vodnyh rastvorov fosfatov [Text] / E. V. Vlasova, T. L. Karasik // Metallurgicheskaya i gornorudnaya promyshlennost'. – 2010. – Issue 5. – P. 89–91.
23. Vlasova, E. V. Rolled metal products functional coatings based on alkali metals phosphates [Text] / E. V. Vlasova, T. L. Karasik, E. N. Levko, V. L. Kovalenko, A. A. Lizogub // Eastern-European Journal of Enterprise Technologies. – 2011. – Vol. 5, Issue 6 (53). – P. 30–33. – Available at: http://journals.uran.ua/eejet/article/view/1244/1146
24. Sutchenko, A. S. Issledovanie struktury i svojstv sovremennyh mezhoperacionnyh pokrytij [Text]: Mezhd. nauch. prakt. konf. / A. S. Sutchenko, E. V. Vlasova, N. V. Yaroshenko // Innovacionnyj potencial miro-voj nauki XXI stoletiya. – 2014. – P. 61–62.
25. Kovalenko, V. L. Nickel hydroxide obtained by high-temperature two-step synthesis as an effective material for supercapacitor applications [Text] / V. L. Kovalenko, V. A. Kotok, A. A. Sykchin, I. A. Mudryi, B. A. Ananchenko, A. A. Burkov et. al. // Journal of Solid State Electrochemistry. – 2016. – Vol. 21, Issue 3. – P. 683–691. doi: 10.1007/s10008-016-3405-2
26. Kovalenko, V. Definition of factors influencing on Ni(OH)2 electrochemical characteristics for supercapacitors [Text] / V. Kovalenko, V. Kotok, O. Bolotin // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 5, Issue 6 (83). – P. 17–22. doi: 10.15587/1729-4061.2016.79406
27. Burmistr, M. V. Antifriction and Construction Materials Based on Modified Phenol-Formaldehyde Resins Reinforced with Mineral and Synthetic Fibrous Fillers [Text] / M. V. Burmistr, V. S. Boiko, E. O. Lipko, K. O. Gerasimenko, Yu. P. Gomza, R. L. Vesnin et. al. // Mechanics of Composite Materials. – 2014. – Vol. 50, Issue 2. – P. 213–222. doi: 10.1007/s11029-014-9408-0