Досліджено склад, структуру та властивості покриттів на оцинкованій сталі. Встановлено, що з підвищенням концентрації водного розчину натрію триполіфосфату (ТПФН) питома маса і кристалічність покриттів збільшуються, захисні властивості знижуються. У складі покриттів з низькими захисними властивостями поряд з безводними фосфатами цинку присутні кристалогідрати. Структура таких покриттів представлена товстими пухкими шарами з наявністю мікротріщин

Ключові слова: оцинкований прокат, захисні властивості, склад та структура покриттів, натрію триполіфосфат, водний розчин

Исследованы состав, структура и свойства триполифосфатных покрытий на оцинкованной стали. Установлено, что с повышением концентрации водного раствора триполифосфата натрия (ТПФН) удельная масса и кристалличность покрытий увеличиваются, защитные свойства снижаются. В составе покрытий с низкими защитными свойствами наряду с безводными фосфатами цинка обнаружены кристаллогидраты. Структура таких покрытий представлена толстыми рыхлыми слоями с наличием микротрещин

Ключевые слова: оцинкованный прокат, защитные свойства, состав и структура покрытий, триполифосфат натрия, водный раствор

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INVESTIGATION OF PHYSICAL AND CHEMICAL PROPERTIES AND STRUCTURE OF TRIPOLYPHOSPHATE COATINGS ON ZINC PLATED STEEL

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1. Introduction

Metal corrosion causes significant damage to the economy, ecology, country's industry in general. Thus, the corrosion protection of metal and metalware is an actual problem of practical and scientific interest.

At present, paint coating (PC) is the most widespread method of corrosion protection. In order to improve adhesion and reduce porosity, the PC process includes phosphating as a pre-treatment process. Painting with phosphating is mainly applied to low-carbon, carbon, low-alloy steels, pig iron, aluminum, zinc, cadmium copper [1–4].

It is known [1, 4–8] that the majority of traditional zinc phosphating compositions are acidic aggressive solutions. When they are used for treatment of metalware with a thin layer of zinc, there is an increased danger of partial dissolution. In addition, most solutions are ecologically unsafe, because they contain various toxic substances and nitrogen-containing compounds [4–6]. Therefore, constant development of new innovative compositions that are more ecologically safe and provide better surface pre-treatment is being carried out [5–8].

Toughening of ecological and economical requirements for choosing a solution composition that is able to effectively replace toxic chromates while possessing a functional connection to production technology creates elevated interest to polyphosphates.

Polyphosphates possess low toxicity and provide metal corrosion resistance at low concentrations. Additionally, polyphosphates do not interfere with enamels and paint coating. In comparison to traditional phosphating compositions of aqueous phosphoric acid salt solutions, aqueous solutions of polyphosphates are easy to use and are more ecological. Despite that, the widespread application is hindered by insufficient knowledge of this question. Lack of knowledge in this field limits the possibility of effective practical application of aqueous STPP solution as non-toxic agents for pre-treatment of zinc plated steel before painting.

2. Literature review and problem statement

Literature analysis regarding practical application of polyphosphates in most complete form is presented in the papers [9, 10], devoted to the formation, structural features and properties of tripolyphosphate coatings on low-carbon steel.

For metal phosphating, the polyphosphates have found widespread application as additives to phosphating solutions for the preparation of chemical, [5, 11] and electrochemical [12, 13] small-crystalline, highly-protective zinc-phosphate coats.

One of the most perspective methods for phosphating of coiled steel is plaforization. The technology is represented by phosphating in non-aqueous solutions. The process is based on application of polyphosphate in organic solvents. The main advantage of this technology is the ability to combine at room temperatures both metal degreasing and phosphating into a single operation [14].

A number of modern studies are devoted to the prospect of using aluminum [15, 16], calcium [17], calcium magnesium [18, 19], zinc [15] polyphosphates as anti-corrosion paint pigments.

A number of researches on corrosion inhibition of carbon steel [10, 15], metallic zinc in neutral media [16] and artificial acids [15, 16], using paints containing polyphosphates have shown that inorganic phosphates are a group of promising non-toxic phosphate paint inhibitors. The protective mechanism is presumably related to the formation of a protective passivation film. However, the amount of data regarding the properties, structure, formation mechanism of protective films on the surface of inhibited metal in solutions containing polyphosphate ions is insufficient.

STPP had been studied as a mixed-type corrosion inhibitor for iron in neutral media [13], an inhibitor of pitting [20] and hydrochloric acid [21] corrosion of alloyed and low-carbon steel.

From a chemical perspective, treatment with aqueous STPP solutions is a process of forming a water-insoluble layer of phosphate compounds on the metal surface. A feature of phosphating using STPP-based solutions is that sodium doesn't contribute to the coat formation. However, with such phosphating method, the metal substrate-based coat is also formed.

A possible formation mechanism and properties of such coat had been proposed in the paper [15]. It's been noted that the tripolyphosphate anion reacts with iron ions that are formed on the surface of anodic regions. This results in the formation of the coat of insoluble complex composition that mainly contains iron tripolyphosphate. The coats possess high adhesive and protective properties.

During the investigation [9], the multi-stage electrochemical formation mechanism has been established and protective properties of the tripolyphosphate passivation film on low-carbon steel have been studied. In addition, the influence of potentiostatic and potentiodynamic pre-treatment on the structure and properties of the tripolyphosphate coat has been investigated. As a result of complex [10, 22] and metallographic studies [23], it had been experimentally proven that in aqueous STPP solution, a complex coat of composite structure is chemically deposited on the surface of low-carbon steel. The coat matrix is iron tripolyphosphate with STPP filler. Being a corrosion inhibitor in neutral media, the STPP residing inside the matrix and as an additional surface layer provides the chemical protection mechanism under atmospheric conditions [10, 21].

At the same time, the data regarding the physicochemical features, technological properties and structure of tripolyphosphate coats on the surface of zinc-plated steel is almost absent.

When developing the optimal technology of tripolyphosphate coats on the zinc-plated surface from STPP solutions, it is necessary to take into account the difficulties of the coat formation. According to phosphating principles [1, 2], phosphate coats are formed as a result of simultaneously occurring chemical, electrochemical, crystalochemical, topochemical, and physical processes on the heterogeneous surface. During treatment of steel samples with constant composition, rates of these processes should be regulated by composition (concentration of components) of the solution and temperature [2, 4]. It should be noted that at early stages of phosphating iron, steel, zinc and zinc alloys, the same phosphating compositions were recommended. However, this practice has been discontinued. During investigations, significant differences and features in phosphating of zinc and alloys had been discovered [24]. Thus, it is not rational to use these works [25] because they describe patterns in the influence of the tripolyphosphate solution concentration on the coat formation on low-carbon steel. For zinc plated steel, new additional knowledge can only be acquired when conducting the corresponding studies.

3. The aim and objectives of the study

The aim of the works is to study the influence of the concentration of aqueous STPP solution on the physicochemical properties, structure and phase composition of tripolyphosphate coats on zinc-plated steel.

To achieve the set-out aim, the following objectives have been stated:

– to chemically deposit tripolyphosphate coats on zinc-plated steel samples from aqueous STPP solution;

– to determine the specific mass, protective properties, structure and phase composition of prepared tripolyphosphate coats;

– to conduct a comparative analysis of the data characterizing the specific mass, protective properties, composition and structure of prepared tripolyphosphate coats.

4. Methods and methodology for investigating the properties and structure of tripolyphosphate coats

Coat deposition method

The study was conducted on 30×40 mm samples of hot-dip galvanized steel. The coats were deposited by dipping the samples into aqueous STPP solutions (2 %, 4 %, 6 %, 10 %, 12 %, 14 %) at 70 °C for 3 minutes. The coated samples were dried for a day and were used to determine the specific mass, protective properties and to study the composition and structure of tripolyphosphate coats. The experiments were conducted on three samples with the identical coat.

Methodology for studying physical and chemical properties

The specific mass was determined by the gravimetric method. The protective properties were studied using the Akimov's test. Solution's color change from blue to black [5] was used as a criterion. Protective properties of the coats deposited on zinc-plated steel were studied by means of natural and accelerated atmospheric corrosion tests. The degree of corrosion during natural tests was evaluated by visual examinations. The corrosion damaging degree has been used as a corrosion parameter under acceleration tests.

Methodology for studying structure and composition of coats

The microstructure of the coats was studied by raster electron microscopy (REM) using microscope I-106 (SELMI, Ukraine). X-ray diffraction (XRD) patterns were recorded using DRON-3 diffractometer (USSR) under Cu-kα radiation.

5. Experimental results of studying the physicochemical properties and structure of tripolyphosphate coats on zinc-plated steel

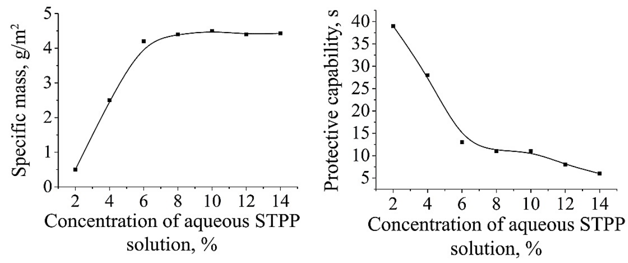
Results of studying physicochemical properties of coats. The specific mass of the coats obtained from aqueous STPP solutions of the stated concentrations on zinc-plated steel samples (Fig. 1, *a*) ranges from 0.5 to 4.5 g/m^2.

The results of studying the protective capability of the coats are presented in Fig. 1, *b*. As can be seen, with an increase of concentration, the protective capability decreases from 40 s for the samples deposited from 2 % aqueous STPP solution to 7 s for the samples deposited from 14 % aqueous STPP solution. During natural corrosion tests for 92 days, no corrosion was observed for the samples deposited from 2 % and 4 % aqueous STPP solutions. The character of observed appearance changes of the samples prepared at higher STPP concentrations (12 %, 14 %) indicates the formation of "white" zinc corrosion.

The results of accelerated corrosion tests have shown that the protection effectiveness of such zinc-plated rolled steel is 55 %.

Results of metallographic studies. General view of the microstructure of the coats prepared from aqueous STPP solution with different concentrations on zinc-plated steel is presented in Fig. 2.

It can be seen (Fig. 2, *a*, *d*) that the coat deposited from 4 % aqueous STPP solution is a thin film with an amorphous structure. The sample deposited from 6 % aqueous STPP solution (Fig. 2, *b*, *e*) possesses an amorphous-crystalline structure with crystals forming as dendrites. Increasing concentration of STPP to 12 % leads to the formation of a thick (Fig. 2, *c*, *f*), spongy film that possesses a microcrystalline structure. The surface of such coat is covered with small microcracks.



a *b*

Fig. 1. Influence of the STPP concentration on the physicochemical properties of the coats on zinc-plated steel: *a* – specific mass; *b* – protective capability

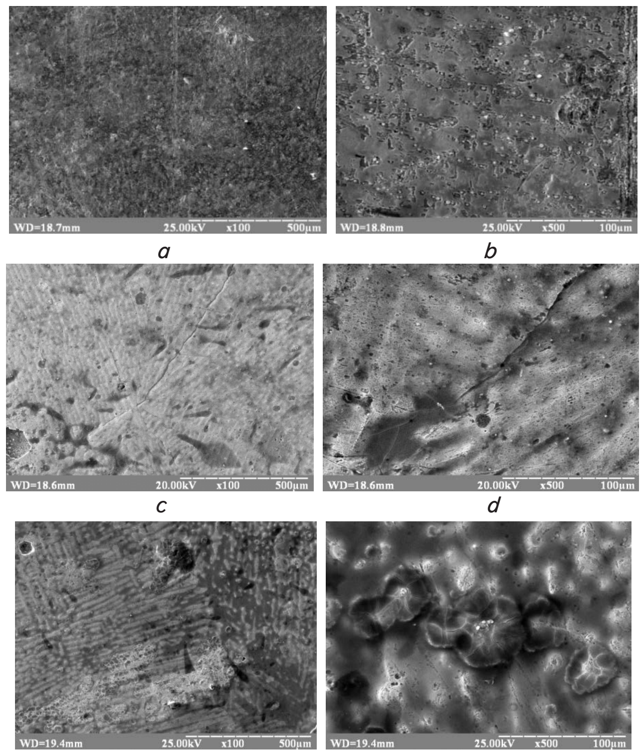


Fig. 2. Microstructure of the coats deposited on zinc-plated steel from aqueous STPP solutions, at different magnifications: *a* – 4 %, ×100; *b* – 6 %, ×100; *c* – 12 %, ×100; *d* – 4 %, ×500; *e* – 6 %, ×500; *f* – 12 %, ×500

XRD results. Fig. 3 shows the XRD pattern of the coat deposited from 4 % aqueous STPP solution.

The XRD pattern of the sample deposited from 4 % aqueous STPP solutions (Fig. 3, *a*) doesn't have any peaks of crystalline structure, which characterizes the X-ray amorphous structure. The XRD pattern of the coat deposited from 6 % aqueous STPP solutions (Fig. 3, *b*) shows peaks of zinc phosphate compounds with low crystallinity. At the same time, reflexes of the coat deposited from 12 % STPP solution look higher and narrower (Fig. 3, *c*). This indicates larger sizes of crystallites. Therefore, crystallinity increases. Additionally, unlike the coat deposited from 4 % aqueous STPP solution, the coats deposited from 6 % and 12 % solutions contain not only anhydrous zinc phosphates but also hydrated compounds.

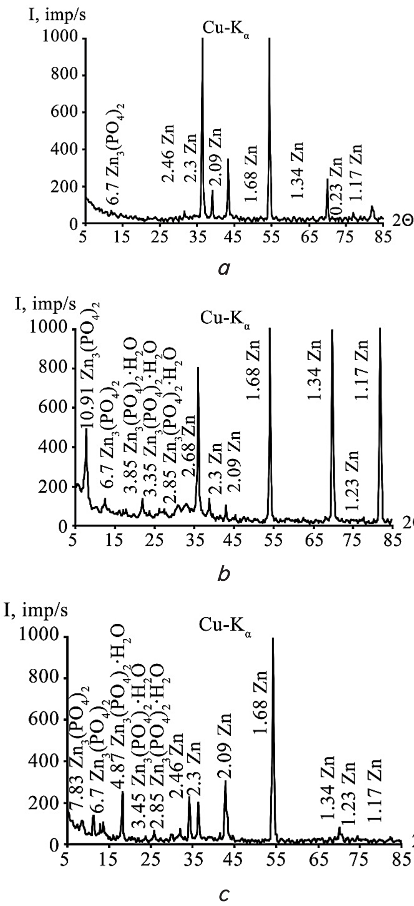


Fig. 3. XRD patterns of the coats deposited onto zinc-coated steel from aqueous STPP solutions with different concentrations: *a* – 4 %; *b* – 6 %; *c* – 12 %

6. Discussion of results of studying the properties and structure of tripolyphosphate coats on zinc-plated steel

It is known that the specific mass value is one of the important properties that define the application of such coats as adhesive coats. Thus, for the coats obtained from traditional phosphating, the specific mass value ranges from 0.1 to 50 g/m^2 [2]. According to the requirements of automobile standards, layers with a mass no more than 5 g/m^2 [2] are used for painting. The research results presented in Fig. 1, *a* showed that the specific mass of tripolyphosphate coats prepared from aqueous solutions of different concentrations ranges from 0.5 to 4.5 g/m^2. The highest increase of the specific mass of 8.4 times to 4.2 g/m^2 is observed in the concentration range of 2–6 %. With further increase of concentration, the specific mass of the coats doesn't change significantly and reaches a maximum value of 4.5 g/m^2 for the coats prepared from 10 % aqueous STPP solution. Even though the specific mass of the coats increases with increasing concentration of STPP, the protective capability decreases, as can be seen from Fig. 1, *b*. The sharpest drop is observed in the concentration range of 2–6 %. In the concentration range of 6–10 %, the value of the Akimov's tests stabilizes. Increasing STPP concentration to 14 % leads to a decrease of protective properties.

Analysis of the corrosion tests results and determination of the Akimov's test shows the presence of correlation of acquired data when evaluating the protective properties of the coats. During natural corrosion tests for 92 days, no corrosion was observed for the samples with the coats with the higher protective capability (Fig. 1, *b*) that were prepared from 2 % and 4 % aqueous STPP solutions. The character of the observed changes in the appearance of the samples with the coats prepared from the solutions with higher STPP concentrations (12 %, 14 %) indicates the occurrence of "white" zinc corrosion. It is known [2, 7] that under conditions of constant high humidity, white products of zinc corrosion do not interfere with future corrosion.

In general, it has been established that increasing concentration of aqueous STPP solution leads to the formation of coats with lower protective properties. According to the data of accelerated corrosion tests, the protection effectiveness of such coats on zinc-plated steel decreases to 55 %.

General view of the microstructure of the coats on zinc-plated steel prepared from aqueous STPP solutions with different concentrations is presented in Fig. 2.

Microstructure analysis of the studied coats showed that the deposition of the coat from 4 % aqueous STPP solution leads to the formation of a relatively thin film (Fig. 2, *a*, *d*) that has an amorphous structure. Further increase of the STPP concentration to 6 % (Fig. 2, *b*, *e*) leads to the formation of a film of an amorphous-crystalline structure with crystals forming as dendrites. Increasing STPP concentration to 12 % leads to the formation of a thick (Fig. 2, *c*, *f*) spongy film that has a crystalline structure. The surface of such coat is covered with small microcracks.

Thus, the crystallinity of the coat formed at elevated STPP concentrations increases significantly. This is supported by the data from the XRD analysis (Fig. 3).

Fig. 3, a shows the XRD pattern of the coat deposited from 4 % STPP solution. It can be seen that the coat structure is almost X-ray amorphous. At the same time, the reflexes of the coat deposited from 6 % solution (Fig. 3, *b*) indicates the presence of zinc compounds of phosphate and hydrated nature. At the same time, the XRD pattern of the coats from 12 % STPP solution shows high and narrow peaks (Fig. 3, *c*), which indicates larger sizes of crystallites. The coats themselves are formed as thick spongy layers with the presence of microcracks. Such coats are good at accumulating and holding moisture, which promotes metal corrosion under atmospheric conditions.

Thus, the formation of the coats based on insoluble zinc phosphate compounds in aqueous STPP solution proves that STPP possesses the inhibitive properties in relation to the zinc substrate. It also has been established that increasing STPP concentration leads to an increase of the specific mass of the coats and decrease of protective properties, the coat structure changes.

7. Conclusions

1. The specific mass of the tripolyphosphate coats deposited on zinc-plated steel from 2–14 % aqueous STPP solution is 0.5–4.5 g/m^2.

2. It has been established that with increasing concentration of aqueous STPP solution, the specific mass and the coat crystallinity increase, the coat structure changes from X-ray amorphous to crystalline. However, the protective capability and protective properties decrease.

3. The coat with high protective properties is formed in 2–4 % aqueous STPP solution. Low protective properties of the coats prepared from 6–14 % aqueous STPP solutions are explained by the presence of hydrated zinc phosphates in addition to anhydrous phosphate compounds.

4. The coats with the lowest protective properties, prepared from 12–14 % aqueous STPP solutions, are formed as thick, spongy layers that accumulate and hold moisture, which promotes corrosion under atmospheric conditions.

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