Лакофарбові покриття широко використовуються в світі як для надання декоративних властивостей, так і для захисту металевих виробів від корозії. Однак звичайні лакофарбові покриття мають тільки пасивним типом захисту металу. Для створення активного типу протикорозійного захисту у лакофарбові покриття вводять окремі антикорозійні добавки. В результаті аналізу даних в якості бі-функціонального (одночасно кольорового і протикорозійного) пігмента теоретично був сконструйований монофазний Zn-Al-триполіфосфатний ПШГ загальної формули $Zn_{0.8}Al_{0.2}(P_3O_{10})_{0.04}$. В даному СДГ Zn^{2+} я катіон-«хазяїн» і Al^{3+} як катіон-«гість» відповідають за білий колір пігменту, а інтеркальвоний триполіфосфат-аніон –інгібитор корозії. В якості методу отримання був обраний безперервний синтез при рівноважному pH при температурі 70 °C. Даним методом отримано зразок сконструйованого теоретично пігменту. Кристалічна структура зразку вивчена методом рентгенофазового аналізу, морфологія і розмір часток методом скануючої електронної мікроскопії, термічні властивості методом термогравіметрії. Характеристики кольору були отримані за допомогою компаратору кольору, протикорозійні властивості вивчені електрохімічно методом зняття анодних поляризаційних кривих сталі 08Кп в 5 % (масс.) розчині Na_2SO_4 з екстрактом пігменту та без екстракту. Методом рентгенофазового аналізу встановлено формування бі-фазного продукту, що складається із сконструйованого ПШГ (із структурою $Zn(OH)_2$) та Zn-Al ПШО (із структурою ZnO). Це вказує на частковий розпад ПШГ в момент отримання, причина розпаду не виявлена. Методом СЕМ показано формування однакових часток, які є агломератами більш мілких часток, та мають високорозвинену поверхню. Вивчення характеристик кольору виявило, що отриманий пігмент має високу ступінь білого (коефіцієнт дифузного відбиття більше 90 %, чистота кольору менше 1 %, світлота більше 96 %). Це обумовлено кольором як ПШГ-фази, так і ПШО-фази. Методом зняття анодних поляризаційних кривих показано зниження швидкості корозії сталі в присутності водного екстракту пігмента в 5,36 рази (густина струму корозії знижується з 5.63 мА/см² до 1.03 мА/см²). Все це чітко доводить, що синтезовано бі-функціональний «розумний» пігмент, що має високі пігментні властивості, високу ступінь білого та високі корозійно-захисні властивості

Ключові слова: лакофарбові покриття, Zn-Al ПШГ, «розумний» бі-функціональний пігмент, триполіфосфат, інгібітор

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"SMART" ANTI-CORROSION PIGMENT BASED ON LAYERED DOUBLE HYDROXIDE: CONSTRUCTION AND CHARACTERISATION

V. Kovalenko
PhD, Associate Professor
Department of Analytical Chemistry and Chemical Technologies of Food Additives and Cosmetics*
E-mail: vadimchem@gmail.com
PhD, Senior Researcher
Competence center
"Ecological technologies and systems"**
V. Kotok
PhD, Associate Professor
Department of Processes, Apparatus and General Chemical Technology*
E-mail: valeriykotok@gmail.com
PhD, Senior Researcher
Competence center
"Ecological technologies and systems"**
*Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005
**Vyatka State University
Moskovskaya str., 36, Kirov, Russian Federation, 610000

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1. Introduction

Paint coatings are widely used in the modern world. On the one hand, they are applied as a decorative surface finish. On the other hand, they can also have specific functionality. One of such properties is corrosion protection. Paint is applied to metallic surfaces that are in contact with the environment in order to protect them from corrosion. Common paint coats provide corrosion protection according to two mechanisms:

1) mechanical: isolation of painted metal surface from the corrosive environment (atmosphere);

2) adhesive: the coat strongly adheres to the metal surface, impeding the diffusion of corrosion agents and formation of corrosion products.

For the realization of adhesive mechanism, paint mixture is formulated to contain high-molecular compounds such as silanes [1], alkyd or formaldehyde resins (comparable to those used in composites [2]). Both of the mentioned corrosive protection mechanisms are passive. Over time, pores and cracks develop in the paint coat. When this happens, the passive protection mechanism cannot prevent corrosion. The adhesive mechanism can insignificantly prevent the development of corrosion. But, considering that the ratio of the molar volume of corrosion products to the molar volume of steel exceeds 5, corrosion products developed a force that is sufficient to tear the paint coat off from the metal surface. This results in further acceleration of corrosion.

It is known, that more than 40 % of cast steel and iron is destroyed by corrosion. In addition, corrosion of pipes, bridges, etc. can lead to serious accidents. Therefore, in many countries, corrosion protection is an element of national security strategy. This makes the development of paint formulation with an active form of corrosion protection a relevant problem.

2. Literature review and problem statement

Active protection character is manifested in the paint upon introduction of some inorganic additives [3, 4], containing corrosion inhibitors [5, 6]. Chromates were commonly used as corrosion inhibitors, however, they are toxic and ecologically unsafe. A modern tendency is a replacement of chromates with safer anionic inhibitors: molybdates [8], dihydrophosphates [9], hypophosphates [10] and orthophosphates [7, 11]. The paper [12] described the presence of synergism between corrosion inhibition of hypophosphyte and orthophopsphate of zinc. The inhibition mechanism lies in partial solubility of the pigment and interaction of phosphate anion and steel surface, forming a passivating film [11]. The most promising pigment inhibitors are condensed phosphates [13], namely, tripolyphosphates of Zn [14, 15], Al [16, 17], Ca [18]. Combined application of zinc and calcium tripolyphosphates [19] is also effective. The listed pigments proved to be effective anti-corrosion compounds. But, aside from their function, these compounds are not colored pigments, and forming a color of the paint requires the addition of pigments.

Layered double hydroxides (LDH) are promising materials that can be used as colored and functional pigments. LDH can contain various anions [20], including anionic dyes [21, 22] or inhibitors [23, 24], intercalated into the interlayer space.

Hydroxides of divalent metals demonstrate polymorphism and exist in two forms. β-form (chemical formula $Me(OH)_2$, brucite-like structure) and α-form (chemical formula $3Me(OH)_2 \cdot 2H_2O$, hydrotalcite structure). LDH has α-form in which part of "host" metal cations is substituted by "guest" metal cations. For instance, Zn^{2+} cations are substituted with Al^{3+}. This results in the formation of excessive charge in the crystal lattice, which is compensated by intercalation of anions. For LDH based on divalent metals, the general formula is $Me1_x Me^{n+}_{1-x} (OH)_2 A^{m-}_{(n-2)/m} \cdot 0.66H_2O$, where Me1=$Ca^{2+}$, Mg^{2+}, Ni^{2+} [25, 26], Zn^{2+} [27] etc., Me2==Al^{3+} [25, 27], Fe^{3+}, Cr^{3+}, Ti^{4+} [26] etc. *A* – various anions. Under normal synthesis conditions, these anions are anions of precursor salts. However, the intercalated anions often have specific functionality. For instance, stabilizing [28] or activating [29, 30] anions are introduced to the LDH structure. LDH are promising materials to be used as nanocontainers for special anions, such as drugs [31, 32], inhibitors [24], anionic dyes [33], sensor anions [34], etc.

When preparing LDH-based pigments, the use of different cations and dye-anions can significantly broaden the color gamut: Zn-Al and Acid Yellow 17 [35], Mg-Al and o-Methyl Red [36], Ni-Fe and o-Methyl Red [37], Zn-Al and Mordant Yellow 3 [38, 39], Zn-Al and Acid Yellow 3 [40], Zn-Al and bi-anion Acid Green 28 [41].

It should be noted, that characteristics of colored LDH-based pigments are well studied and many samples have been prepared. It is known that the synthesis method has a significant impact on characteristics of LDH [42]. There are many methods for preparing layered double hydroxides. LDH can be prepared by the ion-exchange method [43], for which nitrate LDH is prepared and then soaked in a solution of target anion for ion exchange. The disadvantage of this method is a long duration. LDH can also be prepared electrochemically [44, 45], however, for tripolyphosphate LDH this method is problematic to execute. LDH can also be prepared using homogeneous precipitation [46, 47]. However, this method requires large power consumption and their tripolyphosphate would have to compete with cyanate for intercalation. The most simple method is chemical precipitation at high supersaturation [47, 48]. The main disadvantage of this method is that powder is produced in batches, which can result in the invariance of powder characteristics. Continuous synthesis at constant pH does not have this disadvantage.

However, the literature review did not yield any information on the LDH-based "smart" bi-functional pigment, which under normal conditions acts as a pigment, and as an active corrosion inhibitor when the paint coat is damaged.

This doesn't account the benefit of such pigment in replacing two paint components.

3. The aim and objectives of the study

The aim of the work is to evaluate the possibility of preparing "smart" pigment that would act as a colored pigment and corrosion inhibitor and study its characteristics.

To achieve the set aim, the following objectives were formulated:

– to theoretically construct bi-functional pigment based on inhibitor-intercalated LDH by means of the reasoned choice of "host" and "guest" cations, inhibitor anion and to synthesize the constructed pigment;

– to conduct a complex study of physical, physico-chemical, color and anti-corrosive characteristics of the prepared pigment.

4. Materials and methods for constructing "smart" pigment and study of its characteristics

4. 1. Method for theoretical construction of bi-functional LDH-based pigment

According to the general LDH formula, bi-functional LDH-based pigment would include three components: "host" metal cation, "guest" metal cation and inhibitor anion. A molar ratio of "host": "guest" must be chosen. Synthesis method must also be chosen.

Selection of "host" metal cation. The aim is to prepare a colored pigment with anti-corrosion properties. The pigment should be universal and suitable for use in paints of any color. It should be mentioned that colored pigments in paint formulations are split into two groups:

1) pigments that form the main color (colored pigments);
2) bleaching pigments (white color).

The latter are used in paints of any color. Therefore, when selecting “host” and “guest” metal cations, the goal should be the whitest pigment possible.

Selection of “host”:“guest” molar ratio. When choosing a molar ratio, one should consider that lower value leads to higher inhibitor content, but the stability of LDH decreases.

Selection of intercalated inhibitor anion. The choice of anionic inhibitor should be based on the ability to form a passivating film on the metal surface, even at low concentrations.

4. 2. Synthesis of “smart” LDH-based pigment

The pigment was prepared by continuously feeding the reaction vessel with three solutions (zinc and aluminum nitrates, alkali and sodium tripolyphosphate). The compounds were taken in stoichiometric ratios, with the volume of each solution being 0.5 L. Synthesis was conducted at 70 °C with continuous stirring. After the solutions were added, the suspension was kept under the same conditions for 20 minutes. The prepared pigment precipitate was then vacuum filtered, dried at 90 °C for 24 h, ground, washed from soluble salts, filtered and dried again at the same conditions.

4. 3. Characterization of “smart” LDH-based pigment

The crystal structure of the pigment sample was studied by means of X-ray diffraction (XRD), using the DRON-3 diffractometer (Russia) (Co-Kα radiation, scan range 10–90° 2θ, scan rate 0.1 °/s).

Morphology and particle size were determined using the JEOL JSM-6510LV scanning electron microscope (“JEOL”, Japan).

Thermal properties and content of samples were investigated by DTG-60 (“Shimadzu”, Japan) in the air atmosphere under the heating rate of **5 °**C/min.

Color characteristics of the prepared pigment were measured using the color comparator CC-3 with light source *A*. A thin layer of the pigment sample was placed into a polyethylene ZIP-bag, which was placed onto a flat solid base. As a result of measurements, chromaticity (*x*, *y*, *z*) and color coordinates (*X*, *Y*) were recorded. Color tone value (predominant wavelength – λ) and color purity (*P*, %) were determined from the color graph in *X*, *Y* coordinates. The color coordinates were also recalculated into CIE 1976 L*a*b*. Lightness (*L*) and color saturation (*S*) were calculated. Diffuse reflection coefficient also was measured.

Anti-corrosion properties of the samples were studied by recording anodic polarization curves. The curves were recorded in a special electrochemical cell YSE-2 (USSR), using the digital potentiostat-galvanostat Ellins P-8. Working electrode – low alloy 08KP steel, cleaned and degreased with Na_2CO_3 and ethanol. Counter-electrode – Pt, reference electrode – Ag/AgCl(KCL sat.). Electrolyte – 5 % (wt.) Na_2SO_4 solution, as a standard electrolyte for atmosphere corrosion modeling [49]. Anodic polarization curves were recorded from compromise potential to +2,000 mV, at 1 mV/s. For comparison, two anodic curves were recorded:

1) in pure 5 % (wt.) Na_2SO_4 solution;

2) in 5 % (wt.) Na_2SO_4 solution with pigment extract.

The extract was prepared by soaking of 0.5 g of pigment in 5 % (wt.) Na_2SO_4 solution for 24h, after which mother liquor was decanted.

5. Results of constructing “smart” LDH-based pigment and study of its characteristics

5. 1. Results of theoretical construction of LDH-based bi-functional pigment

Selection of “host” and “guest” cations.

To obtain the whitest pigment possible, the hydroxide of “host” metal should also be white. It is proposed to use Zn as a “host” metal. It is known, that unlike many other divalent metals, zinc hydroxide only exists in α-form, which simplifies LDH formation. In addition, ZnO has white color and is commonly used in paints as a white pigment.

Based on the formation mechanism of LDH, the “guest” metal hydroxide should have sufficiently lower formation pH than the “host” metal hydroxide. It should also be white and have a stabilizing effect on LDH. Al^{3+} matches all these requirements and was chosen as a “guest” metal cation.

The molar ratio of “host”:“guest” (Zn:Al) was chosen based on the literature data. According to the works [20, 35, 38–41], the optimal Zn:Al ratio ranges from 2:1 to 4:1. Based on the stability of Zn-Al LDH, the molar ratio of Zn:Al=4:1 was chosen.

Selection of intercalated anion-inhibitor. Chromates and phosphates are effective film-forming anionic inhibitors. However, chromates are toxic and ecologically dangerous. Therefore, various phosphates were considered. The paper [50] describes the inhibitive properties of different phosphates. It is described that polyphosphates, namely pyrophosphate and tripolyphosphate are the most effective. In previously conducted studies, sodium tripolyphosphate was found to be highly effective in inhibiting corrosion on steel [51, 52] and galvanized steel [53]. So, tripolyphosphate anion $P_3O_{10}^{5-}$ was chosen as inhibiting anion.

As a result of construction, the following LDH composition was chosen $Zn_{0.8}Al_{0.2}(P_3O_{10})_{0.04}$.

5. 2. Results of studying the prepared “smart” pigment

Visuals observation showed that a large volume of white precipitate was formed. The dried pigment also had a snow-white color. It should also be noted that during grinding, the precipitate was very soft and easily pasted onto mortar walls.

XRD analysis results (Fig. 1) revealed that the prepared sample contained $Zn(OH)_2$ and ZnO. The theoretically developed LDH $Zn_{0.8}Al_{0.2}(P_3O_{10})_{0.04}$ should have a crystal structure that of $Zn(OH)_2$. This means that the prepared sample has a bi-phase structure. ZnO peaks have a higher intensity than those of $Zn(OH)_2$ (practically LDH).

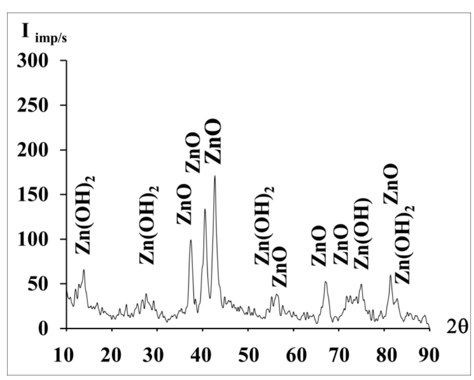

Fig. 1. XRD pattern of pigment

SEM images (Fig. 2), show that the pigment particles are agglomerates of spherical particles. The high specific surface area of the particles should also be noted.

Results of the thermogravimetric analysis are shown in Fig. 3. Two poorly-defined weight losses are observed on the TG curve. They correspond to two endothermic peaks on the DTA curves: more intense at 177 °C, and less intense and blurred at 265 °C. The first peak corresponds to the removal of structural water from LDH, and second – the collapse of the LDH lattice to layered double oxide (LDO).

Table 1 lists color coordinates of the developed and prepared pigment. It is worth to note; that the sample has a high diffuse reflection coefficient, low color purity (*P*), high lightness (*L*), low color saturation (*S*).

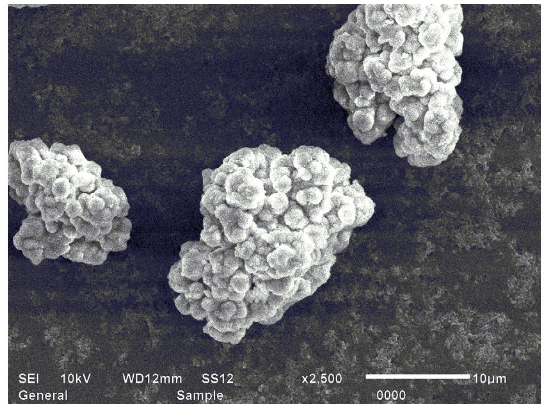

Fig. 2. SEM image of pigment particles

Table 1

Color characteristics of the developed Zn_4Al-tripolyphosphate pigment

Diffuse reflection coefficient, %				Color tone	Color purity	Chromaticity		
1	2	3	Average	λ, nm	P, %	*X*	*Y*	*Z*
90.49	89.46	90.26	90.07	560*	1	99.52	90.15	31.63
CIE Lab				Color saturation		Chromaticity coordinates of the light source		
A	*b*	*L* (Lightness)		*S*		*X*0	*Y*0	*Z*0
0.800	0.902	96.097		1.206		109.85	100	35.582

*Note: * – the pigment's point on the color graph is so close to the point of light that color tone is approximated*

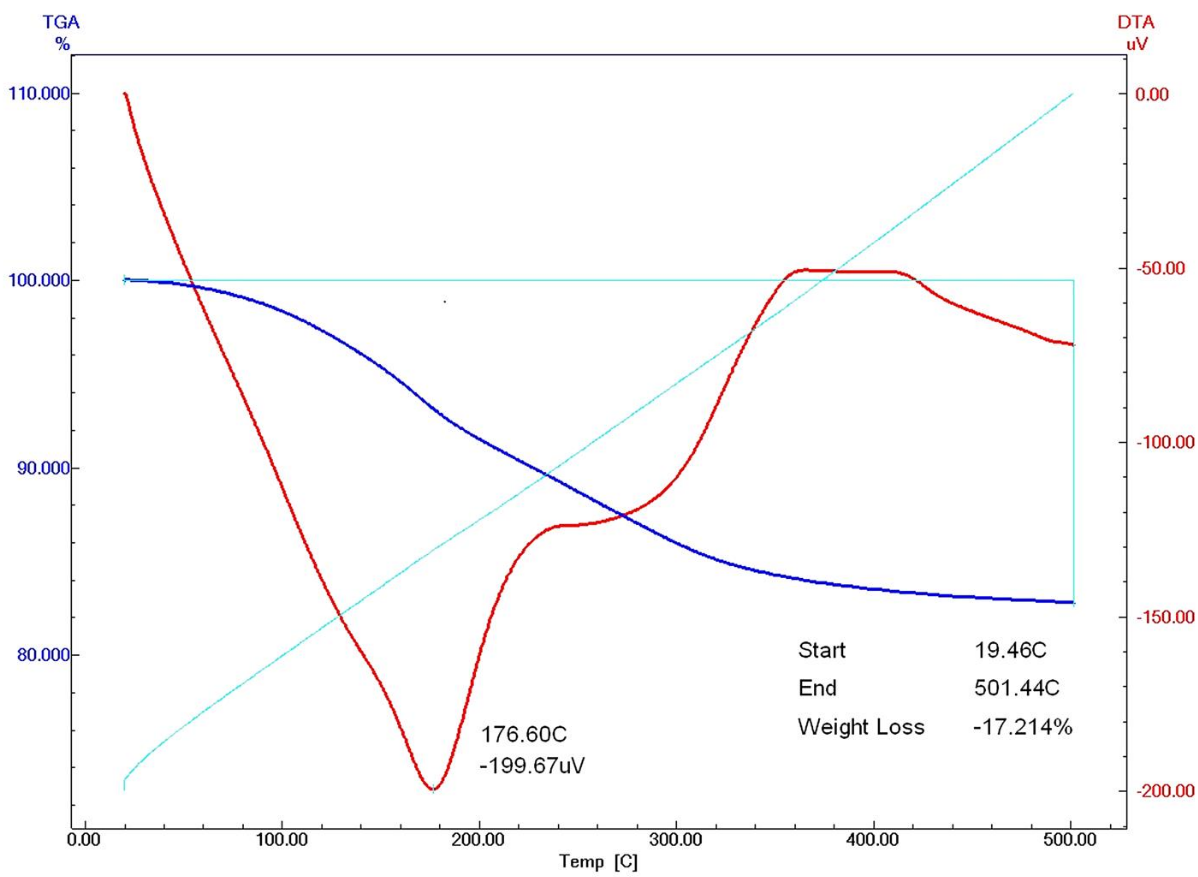

Fig. 3. DTG of pigment sample

Corrosion protection investigation.

Fig. 4 shows anodic polarization curves of 08Kp steel in pure 5 % (wt.) Na_2SO_4 solution and in 5 % (wt.) Na_2SO_4 solution with pigment extract.

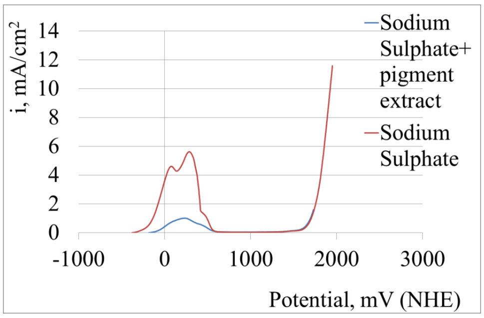

Fig. 4. Anodic polarization curves of 08KP steel in 5 % (wt.) Na_2SO_4 solution with and without pigment extract

Both curves have the shape characteristic of anodic passivation cures. The anodic curve recorded in pure 5 % (wt.) Na_2SO_4 solution has 3 peaks of anodic dissolution (corrosive oxidation). Maximum corrosion current density is 5.63 mA/cm^2. In the presence of pigment, the anodic curve flattens, and the maximum current density is lowered to 1.03 mA/cm^2.

6. Discussion of the results obtained from studying the constructed "smart" LDH-based pigment

Physico-chemical characteristics of constructed and prepared pigment. Results of XRD analysis (Fig. 1) revealed that the pigment does not have a monophase LDH structure, as it was assumed during theoretical construction. Reflexes of two phases are observed in the pigment's structure. The first phase with ZnO structure, which is likely Zn-Al layered double oxide. The second phase with $Zn(OH)_2$, which is constructed Zn-Al layered double hydroxide. It is likely that during synthesis, LDH partially decomposed with the formation of Zn-Al LDO. Analysis of thermal behavior revealed that the temperature of the first decomposition peak of the dried pigment (Fig. 3) is 177 °C. Meaning that the pigment should not decompose during synthesis, however, thermal properties of formed and dried LDH and LDH during synthesis can differ. Therefore, further studies are required to find the causes of formation of the bi-phase system.

The bi-phase nature of the final product can be disadvantageous for use as a pigment if the phases are distributed inhomogeneously. However, SEM images (Fig. 2) show that the particles of prepared pigments have the same morphology. In addition, they possess a high specific surface area. All of these indicate good pigment properties.

Color characteristics of constructed and prepared pigment. Visual observation revealed the formation of snow-white precipitate that can be ground easily. The study of color characteristics on the CC-3 color comparator reveals that the prepared pigment has a high degree of whiteness (diffuse reflection coefficient is above 90 %, color purity less than 1 %, lightness above 96 %). This data clearly indicates that this powder is suitable for use as a pigment in paint formulations. It is possible that the formation of ZN-Al LDO, with ZnO structure, increases the whiteness of the product. This can be related to the high whiteness of ZnO (zinc paint), which could be improved by the inclusion of Al^{3+}.

Corrosion inhibition properties of constructed and prepared pigment. Anodic polarization curves recorded for 08KP steel in the presence of water extract of the pigment revealed that the peak current density of corrosion dissolution of steal decreased by 5.36 times. This is explained by the fact that event at low concentration of tripolyphosphate anion that was released upon dissolution of constructed LDH, a passivating film formed. Additionally, Zn-Al LDO present in the pigment could have a synergetic effect, improving the corrosion inhibiting property of the pigment. This is in agreement with the literature data [54], which describes improved corrosion protection of the paint with ZnO added to it.

The present study revealed the formation of biphase pigment. High anti-corrosion activity of the pigment was found. Thus, the developed and synthesized pigment can be used in paint formulations for outdoor applications, painting of metal surfaces. This pigment is especially promising for paints used in renovations of hard to reach metal constructions: bridge elements, crane and other high constructs. However, the anti-corrosion properties of the pigment were studied using the accelerated method. More complete understanding of anti-corrosion characteristics and the necessary amount of pigment in the paint formulation requires preparation of paint samples and field trials. From a theoretical point of view, the synthesis of such pigments with different inhibitor anions is promising.

7. Conclusions

1. A bi-functional (colored and anti-corrosion) pigment has been theoretically constructed as monophase Zn-Al-tripolyphosphate LDH with the generalized formula $Zn_{0.8}Al_{0.2}(P_3O_{10})_{0.04}$. In this LDH, Zn^{2+} – "host" cation, Al^{3+} – "guest" cation, and tripolyphosphate – intercalated inhibitor anion. A sample of the constructed pigment was prepared.

2. By means of X-ray diffraction analysis, it was found that bi-phase precipitate, containing the constructed LDH (with $Zn(OH)_2$ structure) and Zn-Al LDO (ZnO structure) was formed. This indicated partial decomposition of LDH during synthesis, but the reason for it is unknown. By means of SEM, the formation of agglomerates of the same particles with high surface area was found. The study of color characteristics revealed that the prepared pigment has a high whiteness value (diffuse reflection coefficient above 90 %, color purity below 1 %, lightness above 96 %). This is due to the color of both LDH and LDO phases. By recording anodic polarization curves, it was found that the corrosion rate in the presence of water extract of the pigment is lower by 5.36 times. This is due to the influence of tripolyphosphate anion as an inhibition component of the pigment and synergetic effect of the Zn-Al LDO part of the pigment. All of this shows that a bi-functional pigment was prepared, which has great pigment properties, high whiteness, and high anti-corrosion properties.

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