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NON-TOXIC ANTI-CORROSION PIGMENT MIXTURES WITH VEGETABLE COMPONENT FOR PAINT PRIMERS

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The restriction on the use of toxic chromates necessitated the search for environmentally safe and effective anticorrosive pigments for paint and varnish primers. The aim of the study was to develop a non-toxic anti-corrosion pigment mixture of zinc phosphate (ZnPh), calcium phosphate (CaPh), and crushed walnut shells (WSh) and a predictive model describing the relationship between its composition and the effectiveness of inhibiting corrosion processes, which will allow the development of optimal formulations for water-based primers. The anticorrosive efficiency of extracts of different compositions on Q215 steel samples was assessed by massometry. Using a simplex lattice design of the experiment, a mathematical model was built that describes the dependence of the degree of protection on the composition of the mixture. By optimization, the optimal composition of the mixture was determined: 4.7 g WSh, 2.4 g CaPh, and 7.9 g ZnPh per 100 g of water, for which the calculated degree of protection was 90.06%. Experimental verification confirmed the high efficiency of the mixture, showing a degree of protection of 87.8%. The resulting model can be used to predict the anti-corrosion properties of pigment mixtures for the development of environmentally friendly water-based primers.

Keywords: paints and varnishes, anti-corrosion pigments, corrosion, walnut shell, phosphates, tannins, optimization.

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Introduction

The effectiveness of anticorrosive primers depends primarily on the chemical nature and functional activity of the pigments included in their composition. With the transition to environmentally friendly coatings, the search for effective, non-toxic pigments is relevant. The ban on hexavalent chromium compounds, which were once considered the gold standard of corrosion inhibitors due to their strong oxidizing and passivating properties, has significantly accelerated the research into alternative anticorrosive compounds. As a result, phosphate-based pigments have attracted particular interest due to their lower toxicity and ability to form protective phosphate-containing films on the steel surface. Zinc phosphate, the most common representative of this class, together with calcium phosphate, has been shown to improve the barrier properties of coatings for metal surfaces [1–4].

Despite these advantages, simple phosphate pigments generally exhibit lower inhibition efficiency compared to chromate systems, which has led to research into improving or modifying their functional characteristics. One of the most effective approaches is to create synergistic combinations of pigments. Numerous studies have confirmed that mixtures of zinc and calcium phosphates exhibit significantly improved corrosion inhibition compared to each component used separately, due to their ability to form mixed Ca/Zn-phosphate phases that are less permeable [2,3]. These phases contribute to the formation of passivating films with higher structural stability on steel surfaces. At the same time, further developments have been aimed at creating composite pigments, including phosphate-modified natural fillers, nanoengineered calcium-zinc compounds and hybrid phosphate-silicate systems. These pigments have demonstrated reduced porosity and improved adhesion and barrier properties in various resin matrices [4–10].

In parallel with these studies, there are current trends in sustainable development that point to the prospects for the use of renewable raw materials. Plant-derived components, in particular those containing polyphenolic structures, have been recognized as promising corrosion inhibitors due to their natural ability to chelate metal ions, adsorb on metal surfaces, and inhibit anodic and cathodic reactions. Walnut shells are one such promising additive, which is rich in lignocellulosic compounds and tannins. These polyphenolic compounds are known inhibitors that can form low-solubility complexes with Fe^{3+}, Zn^{2+}, and Ca^{2+} ions. Therefore, they have been successfully incorporated into synthesized pigments such as calcium and zinc tannates, which exhibit high anti-corrosion performance in organic coatings [11–15]. Previous work by the authors has also shown that walnut shell powder, when used together with mineral pigments, can significantly improve the corrosion resistance of primers, forming stable hybrid organic-inorganic films [12].

Thus, the combination of phosphate-based pigments and plant materials containing tannins is a promising research direction. Phosphate pigments form protective inorganic phases, while tannins promote the formation of metal–tannate networks, which have the ability to densify protective layers and inhibit corrosion processes. This suggests that a mixed system containing both inorganic and organic inhibitor components can outperform traditional pigments. However, finding the optimal ratio of these components requires not only experimental studies, but also mathematical modeling, taking into account nonlinear interactions that can affect the stability of protective films on metal surfaces.

In this context, the present work focuses on systematically evaluating the inhibitory efficiency of mixtures based on zinc phosphate, calcium phosphate, and finely ground walnut shells, and determining how variations in the component ratios influence the corrosion protection of steel. To achieve this, the study combines experimental assessment of aqueous extracts, statistical modeling using a simplex lattice design, and subsequent optimization of mixture composition. The purpose of the study is to determine an environmentally safe and effective anti-corrosion pigment mixture and create a predictive mathematical model that describes the relationship between the composition of the mixture and the inhibition efficiency, which allows you to choose the optimal formulation for use in water-soluble primer coatings.

Experimental

Reagents and equipment

The reagents employed in the study included zinc phosphate with the chemical formula $Zn_3P_2O_8{\cdot}xH_2O$ (ZnPh), calcium phosphate $Ca_3(PO_4)_2$ (CaPh), both procured from Shanghai Macklin Biochemical Co., Ltd., China, and finely ground walnut shell (WSh) with a particle size of 75 μm, sourced from Lingshou Fengfeng Mining Products Processing Factory, China.

Based on pigments ZnPh and CaPh, as well as walnut shell powder WSh, the corresponding extracts were prepared through ultrasonic treatment of an aqueous suspension. This suspension comprised finely ground walnut shell powder and/or aluminum phosphate powder combined with water in varying ratios. The suspension was subjected to processing using an ultrasonic homogenizer WH003 (Jiagyin Weiheng Industrial Technology Co., China). The treatment regimen encompassed a total duration of 10 minutes, during which ultrasonic treatment at a frequency of 20 kHz and a power of 1200 W was applied for every five-second interval, followed by a period of rest. Following ultrasonic treatment and resting, the suspension was filtered.

Corrosion rate studies were conducted on samples measuring 40×25×1 mm from cold-rolled steel grade Q215 (standard GBT700_2006, China). The chemical composition of Q215 steel included: carbon (C): ≤0.15%, silicon (Si): ≤0.35%, manganese (Mn): ≤1.20%, phosphorus (P): ≤0.045%, sulfur (S): ≤0.050% (grade A). Elements such as chromium (Cr), nickel (Ni), and copper (Cu) were present in trace amounts, typically not exceeding 0.30% each.

The corrosion rate was ascertained through the gravimetric method by exposing steel samples to extracts. The entire duration of the corrosion process extended to 120 hours (5 days). The variation in mass of the samples during the corrosion examinations was measured using an electronic balance with a precision of five digits.

The preparation of samples for testing encompassed the mechanical cleaning of the metal surface using P-1920 paper (PRC) with a grain size of 18 mm, followed by degreasing with ethanol, drying with hot air, and then exposure for 24 hours in a desiccator containing a moisture absorber. After one day, the mass of the samples was measured with an accuracy of 0.00001. Subsequently, following the corrosion tests, the samples were cleaned of corrosion products for a duration of 1–2 minutes in a 5% sodium thiosulfate solution, rinsed, dried, and the change in mass was subsequently determined.

Based on the results of massometric analyses, the corrosion rate (v_{cor}) and the extent of inhibition efficiency of the metal (IE_{WLM}) [13] were determined utilizing formulas (1) and (2), respectively.

$$v_{cor} = \frac{w_1 - w_2}{A \cdot t}, \quad (1)$$

$$IE_{WLM} = \frac{w_1 - w_2}{w_1} \cdot 100, \quad (2)$$

where w_1 and w_2 are the sample masses before and after testing (g); A is the area of the metal sample (m^2); t is the sample exposure time in the corrosive environment (h).

Modeling and optimization of the mixture composition of walnut powder, zinc, and calcium phosphates

To identify the most effective formulation of the mixture utilized in the production of anti-corrosion primers, a series of experimental investigations were undertaken, a mathematical model was established, and an optimization problem was articulated and resolved.

The level of inhibition efficiency of the metal IE_{WLM} (%) was chosen as the optimization criterion. Considering the selected criterion, an objective function was compiled that describes the dependence of the degree of protection (IE_{WLM}) and the composition of the mixture.

$$IE_{WLM} = f(x_1, x_2, x_3), \quad (3)$$

where x_1 is the mass fraction of walnut shell powder in the mixture; x_2 is the mass fraction of calcium phosphate; and x_3 is the mass fraction of zinc phosphate.

Subsequently, the optimization problem is reduced to determining the maximum of function (3), while adhering to the specified constraints.

$$0 \le x_i \le 1, \quad (4)$$

$$\sum_{i=1}^{3} x_i = 1, \quad (5)$$

where x_i (i=1, 3) are the mass fractions of the components of the mixture under study.

The structural and parametric identification of the coefficients of the objective function (3) was conducted utilizing experimental and statistical methodologies. Based on prior research by the authors [14], it was presumed that the response surface possesses a nonlinear character; consequently, a polynomial of the subsequent form was proposed as the fundamental mathematical model:

$$IE_{WLM} = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_i x_i^2 + \sum_{\substack{i,j=1 \\ j \ne i}}^{n} a_{ij} x_i x_j \quad (6)$$

Results and discussion

Results of mathematical processing of experimental data

To determine the coefficients, a simplex lattice experimental design was devised and implemented (Table 1). This design facilitates the calculation of the model's coefficients (6). In order to ensure uniform coverage of the entire mixture space, equally spaced fractions within the interval [0, 1] were selected for each component, corresponding to a standard simplex lattice design of degree m=3: 0, 1/m, 2/m, ..., m/m. It encompasses all mixture variants, where each component assumes the values 0, 1/3, 2/3, or 1, including the central point. Thus, the selected component ratios cover each edge of the simplex at equal intervals and include internal points required for evaluating interactions and for approximation using polynomial models. The total mass of the mixture components was 5 g per 100 g of water. Additionally, each experimental condition adheres to the specified design condition (5).

To achieve a more precise model, three parallel experiments were conducted for each point of the design. The average values of the initial parameter, the inhibition efficiency IE_{WLM}, are presented in Table 1.

The coefficients in equation (6) were evaluated employing the Student's *t*-test:

$$t_{jp} > t_{kp}, \quad (7)$$

where $t_{jp} = \frac{|a_j|}{s_{aj}}$ is the calculated value of the Student's *t*-test for the *j* coefficient of the equation; s_{aj} is the standard deviation of the coefficient; $t_{\kappa p}$ is the critical value of the test criterion for a significance level of *q*=0.01.

After rejecting insignificant coefficients, the subsequent equation was derived:

$$IE_{WLM}=3.9\cdot 10^{-5}-1.223\cdot x_1+6.094\cdot x_2+ \\ +7.841\cdot x_3-0.134\cdot x_1\cdot x_3-1.236\cdot x_2\cdot x_3+ \\ +0.210\cdot x_1^2+0.488\cdot x_1\cdot x_2\cdot x_3 \quad (8)$$

The adequacy of the obtained level was evaluated using the Fisher criterion, and the multiple correlation coefficients *R*, along with the standard deviation *s*, were calculated accordingly: F=11.71 ($>F_{KP}$), R=0.96, s=5.3.

The results obtained demonstrate that the model accurately represents the experimental data to a satisfactory degree. Consequently, the dependence (8) may be employed as an objective function for the resolution of the optimization problem.

Subsequently, a response surface study was undertaken. As shown in Fig. 1a, the concentration of walnut shell powder and calcium phosphate was systematically varied from 0 to 5 g per 100 g of water; the concentration of zinc phosphate was derived from condition (5). Similarly, in Fig. 1c, the concentration of walnut shell powder and zinc phosphate was varied within the same range, with the concentration of calcium phosphate calculated according to condition (5). Additionally, in Fig. 1c, as the concentrations of zinc phosphate and calcium phosphate were varied, the concentration of walnut shell powder was determined based on the corresponding condition (5).

As illustrated in Fig. 1, the response surface appears relatively smooth; however, it exhibits a nonlinear character concerning the content of WSh powder, zinc phosphate and calcium phosphate.

To determine the limits of variation in the concentrations of mixture components for the identification of the optimal region, contour diagrams were constructed. These diagrams depict the relationship between the level of anti-corrosion protection of the metal – ranging from 60% to 100% – and the concentrations of WSh powder, calcium phosphate, and zinc phosphate (Fig. 2).

It was found that the concentrations of the mixture components should be varied from 2 to 10 g/100 g of water; therefore, the search for the maximum value of the objective function (8) was conducted within these limits. The optimization problem was solved using the OPTIMIZ-M program [12]; as a result, the following values were obtained: x_1=4.7, x_2=2.4, and x_3=7.9. The calculated value of the degree of anti-corrosion protection of the metal is 90.06%.

Experimental verification of the obtained results showed that for the calculated values (x_1, x_2, x_3), the degree of anti-corrosion protection of the metal is 87.8%. The calculated and experimental values of the protection level are very similar; therefore, the model (8) can be used for forecasting purposes.

Discussion of the mechanism underlying the anti-corrosion efficacy of the mixture

The analysis of the literature sources presented above has demonstrated that the extractive component of combinations of phosphate compounds of zinc and calcium has proven effective as a synergistic anti-corrosion agent. Various studies have verified that complex mixtures of iron phosphates and mixed phosphates of zinc and calcium form on the surface of iron. The latter tend to create denser, and consequently less porous, frameworks (for example, phases such as partially amorphous Ca–Zn-phosphates or $CaZn_2(PO_4)_2$-like aggregates). These structures reduce the permeability of the protective film and contribute to the overall stabilization of the phosphate layer. This provides an explanation for the high effectiveness of calcium- and zinc-based pigment compositions in enhancing the corrosion resistance of paint and varnish coatings.

Conversely, walnut shells were incorporated into the examined pigment mixture, from which phenolic

Table 1

Experimental design and the degree of metal corrosion protection in the extracts

Experiment No.	Mass fraction of WSh	Mass fraction of CaPh	Mass fraction of ZnPh	Inhibition efficiency, IE_{WLM}
1	1	0	0	26.554
2	0	1	0	54.802
3	0	0	1	72.693
4	0.67	0.33	0	47.269
5	0.67	0	0.33	85.876
6	0.33	0.67	0	53.861
7	0	0.67	0.33	84.934
8	0.33	0	0.67	85.876
9	0	0.33	0.67	36.911
10	0.33	0.33	0.33	63.500

compounds were extracted into the solution, commonly referred to as tannins. These compounds are renowned for their exceptional capacity to bind iron ions generated during the corrosion process into chelate complexes with low solubility.

This is corroborated by the findings of research on the efficacy of artificially synthesized pigments of calcium tannates [14] and zinc tannates [15], which establish protective layers on metal surfaces. A comparative analysis of the anti-corrosion performance of calcium tannates versus calcium phosphates indicated that calcium tannates are more effective when incorporated into paint coatings [14]. Additionally, an examination of the compounds constituting the protective film formed on the metal surface, as evidenced in the calcium tannate extract, revealed that it contains iron tannates [14].

The probable composition of the protective film formed in the extract of a mixture of calcium/zinc phosphates and walnut shell powder is as follows.

Insoluble or sparsely soluble iron phosphates (Fe-phosphates) develop on the surface of steel – a well-established phase resulting from the reaction of phosphates with steel: $Fe^{3+}+PO_4^{3-} \rightarrow$ insoluble iron phosphates. These layers possess the capacity to passivate the anodic regions of the metal surface [9,10].

Phosphate pigments, by generating the corresponding Ca^{2+} and Zn^{2+} ions, facilitate the formation of denser and less porous mixed “frameworks,” such as phases including partially amorphous Ca–Zn-phosphates or $CaZn_2(PO_4)_2$-like aggregates. This process results in a reduction in permeability and promotes stabilization of the phosphate film.

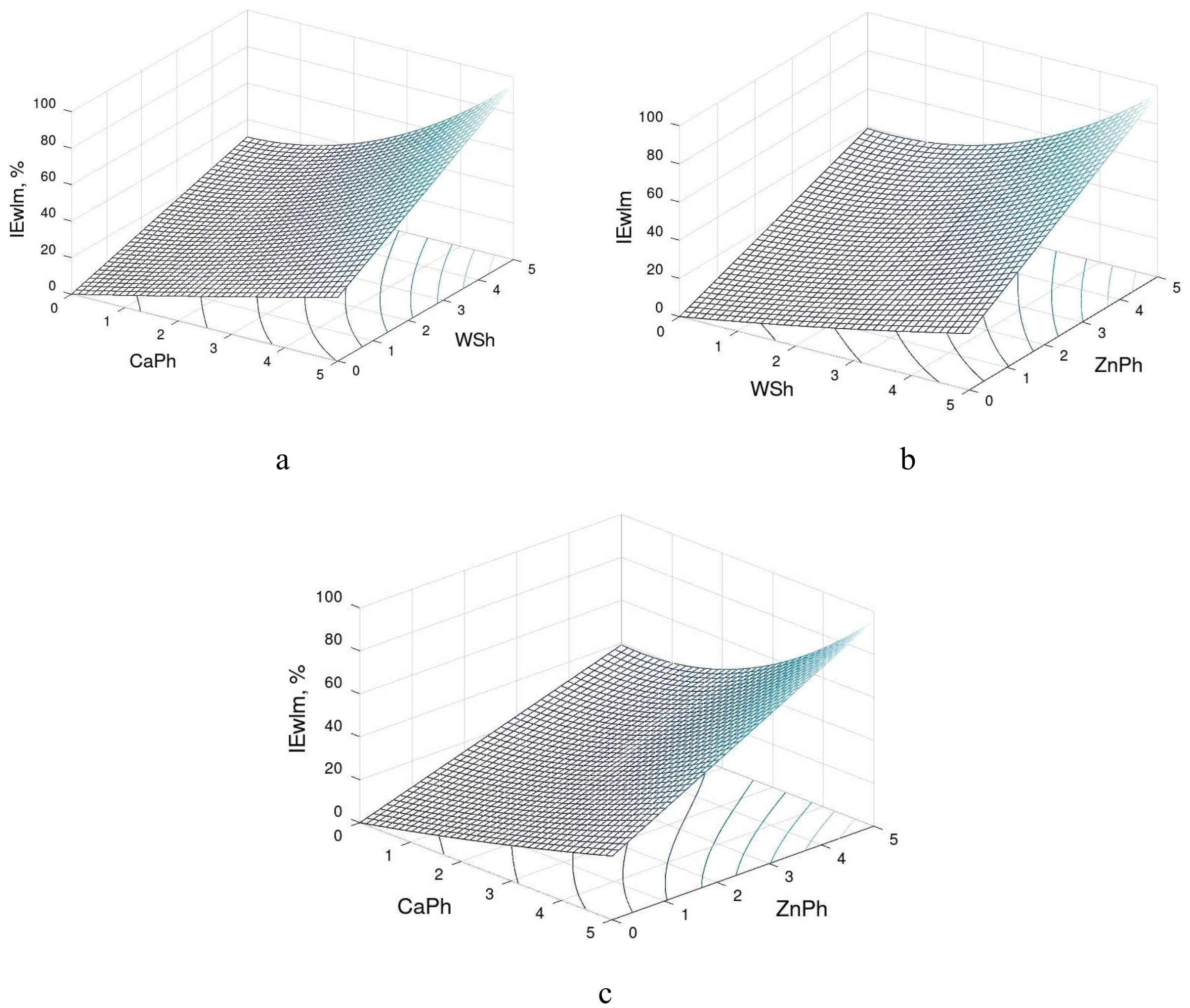

Fig. 1. Dependence of the inhibition efficiency on varying contents of components (g per 100 g of water): (a) for changes in calcium phosphate and walnut shell powder; (b) for changes in shell and zinc phosphate; (c) for changes in zinc phosphate and calcium phosphate

The phenolic constituents contained within the extracts of the pigment mixture engage in the formation of compounds with Zn^{2+}, Ca^{2+}, and Fe^{3+} ions, resulting in the creation of polymer complexes of the metal-tannate type, such as Zn-tannate, Ca-tannate, and Fe-tannate [14,15]. These tannates may serve as an organic-inorganic matrix that effectively «binds» phosphate particles.

Therefore, it can be assumed that the protective film formed on the steel surface in the extract of the pigment mixture is a multilayered partially polymerized organo-inorganic layer, where the phosphate «skeleton» (Ca/Zn/Fe–P) is bound/filled with compounds of the tannate type.

Therefore, walnut shell tannins function concurrently as a chelating agent, adsorbent or barrier, and «crosslinker» of the phosphate layer. In essence, it can be asserted that they alter the protective film. This elucidates the observed synergy within the three-component mixture, which may be attributed to the development of a film with a less porous structure, thereby providing enhanced corrosion protection.

Conclusions

Based on the results obtained in this work, the following conclusions can be drawn:

A combination of pigments derived from calcium and zinc phosphates, in addition to finely ground walnut shell powder, was examined. It was determined that the aqueous extract of this mixture offers superior anti-corrosion protection for steel compared to individual double mixtures.

The optimal ratios of the mixture components were determined through mathematical optimization. The calculated and experimental values of the corrosion protection degree at the optimal component ratio concur with an acceptable level of accuracy.

The incorporation of walnut shells into the mixture facilitated the development of a promising

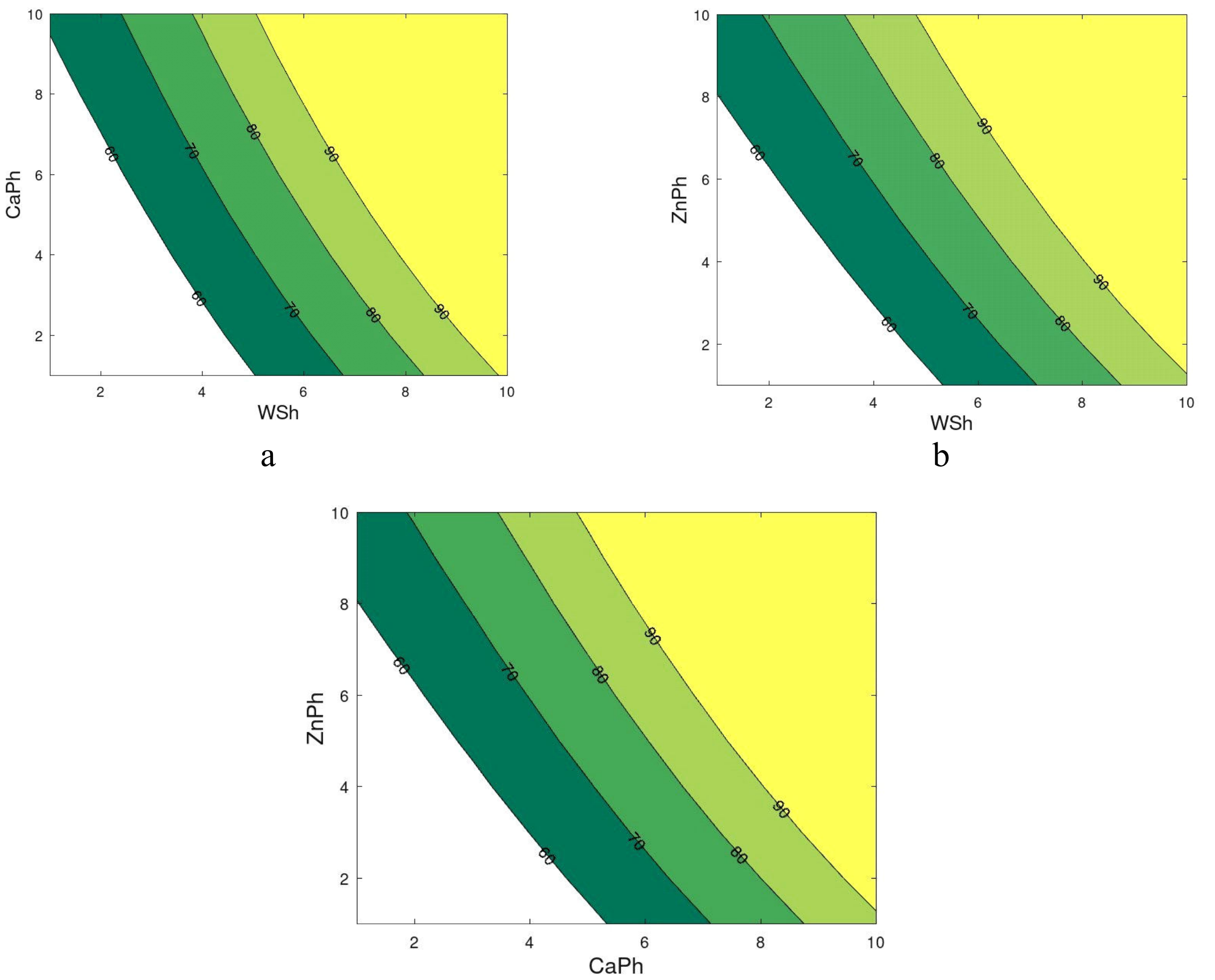

Fig. 2. Inhibition efficiency depending on component concentrations (g per 100 g of water): (a) for changes in calcium phosphate and walnut shell powder; (b) for changes in shell and zinc phosphate; (c) for changes in zinc phosphate and calcium phosphate

ecological pigment blend suitable for integration into water-based paint and varnish coatings, which exhibit high anti-corrosion properties. Tannins contained within the plant component contributed to enhancing the protective qualities of the film formed by the extract on the metallic surface, likely due to its further modification with Zn/Ca/Fe-tannates compounds via adsorption, chelation, and the inhibition of the overall metal corrosion process in a neutral environment.

REFERENCES

1. *Comparative* study on the anti-corrosive performance of zinc phosphate in powder coatings / Yang S., Huang Ji., Chen Ji., Noel J.J., Barker I., Henderson J.D., He P., Zhang H., Zhang H., Zhu J.A. // Coatings. – 2022. – Vol.12. – Art. No. 217.

2. *Synergistic* effect of phosphate and calcium-containing pigments on the corrosion resistance of galvanized steel / Pokhmurs'kyi V., Zin' I., Layon S., Bilyi L. // Mater. Sci. – 2003. – Vol.39. – No. 2. – P.153-160.

3. *Inhibition* of steel and galvanised steel corrosion by zinc and calcium ions in the presence of phosphate / Zin I., Lyon S., Pokhmurskii V., Simmonds M. // Corros. Eng. Sci. Technol. – 2004. – Vol.39. – No. 2. – P.167-173.

4. *Hydrothermal* in-situ synthesis and anti-corrosion performance of zinc oxide hydroxyapatite nanocomposite anti-corrosive pigment / Xu X., Wang H., Wu J., Chen Z., Zhang X., Li M. // Coatings. – 2022. – Vol.12 – Art. No. 420.

5. *Anticorrosion* properties of composite inhibiting pigment based on natural calcium silicate and zinc monophosphate / Khlopyk O., Zin I., Datsko B., Bilyi L., Duriagina Z., Korniy S. // Mater. Sci. – 2023. – Vol.59. – No. 2. – P.234-241.

6. *Anticorrosion* properties of composite inhibiting pigment based on natural calcium silicate and zinc monophosphate in alkyd coating on carbon steel / Khlopyk O., Zin I., Korniy S., Datsko B., Bilyi L. // Mater. Sci. – 2025. – Vol.60. – No. 5. – P.584-592.

7 *Epoxy* nanocomposite coating based on calcium zinc phosphate with dual active/barrier corrosion mitigation properties / Alibakhshi E., Haddadi S.A., Labbani Motlagha A., Ghaderi M., Ramezanzadeh B., Mahdavian M., Arjmand M., Jalili M. // Prog. Org. Coat. – 2022. – Vol.163. – Art. No. 106677.

8. *Protective* properties of epoxy coatings with zeolite-phosphate anti-corrosion pigment on aluminum alloy / Datsko B., Khlopyk O., Zin I., Sobodosh N., Holovchuk M., Korniy S. // Mater. Sci. – 2024. – Vol.60. – P.85-90.

9. *Corrosion* protection of mild steel by an alkyd resin coating reinforced with calcium zinc phosphate derived phosphate sludge as green inhibitive pigment / Elmourabit M., Zarki Y., Arfoy B., Ben Seddik N., AitAghzzaf A., Chaouket F., Draoui K. // Emergent Mater. – 2025. – Vol.8. – P.2325-2343.

10 *Aluminium* alloy corrosion inhibition by composite pigment based on nanoporous synthetic zeolite and zinc dihydrogen phosphate / Korniy S., Zin I., Danyliak M.O., Khlopyk O., Datsko B., Holovchuk M. // Appl. Nanosci. – 2023. – Vol.13. – P.7257-7266.

11. *Inhibitor* properties of «green» pigments for paints / Bethencourt M., Botana F.J., Marcos M., Osuna R.M., Sanchez-Amaya J.M. // Prog. Org. Coat. – 2003. – Vol.46. – P.280-287.

12. *Optimization* of the composition of aluminium phosphate and walnut shell-based composition to increase the corrosion resistance of paint coatings / Chyhyrynets O., Sanginova O., Hu J., Wu Ye., He X. // Technology Audit and Production Reserves. – 2025. – Vol.4/3. – No. 84. – P.12-17.

13. *Plant* extracts as green corrosion inhibitor for ferrous metal alloys: a review / Salleh S.Z., Yusoff A.H., Zakaria S.K., Taib M.A.A., Abu Seman A., Masri M.N., et al. // J. Clean. Prod. – 2021. – Vol.304. – Art. No. 127030.

14. *Tannin-based* inhibitive pigment for sustainable epoxy coatings formulation / Lamprakou Z., Bi H., Weinell C.E., Dam-Johansen K. // Prog. Org. Coat. – 2022. – Vol.167. – Art. No. 106841.

15. *Zinc* tannate and magnesium tannate as anticorrosion pigments in epoxy paint formulations / Zmozinski A.V., Peres R.S., Freiberger K., Ferreira C.A., Tamborim S.M.M., Azambuja D.S. // Prog. Org. Coat. – 2018. – Vol.121. – P.23-29.

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НЕТОКСИЧНІ АНТИКОРОЗІЙНІ ПІГМЕНТНІ СУМІШІ З РОСЛИННИМ КОМПОНЕНТОМ ДЛЯ ҐРУНТУВАЛЬНИХ ПОКРИТТІВ

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Обмеження на використання токсичних хроматів зумовлює необхідність пошуку екологічно безпечних та ефективних антикорозійних пігментів для ґрунтувальних лакофарбових матеріалів. Метою дослідження було розроблення нетоксичної антикорозійної пігментної суміші фосфату цинку (ZnPh), фосфату кальцію (CaPh) і подрібненої шкаралупи волоських горіхів (WSh) та прогностичної моделі, що описує взаємозв'язок між її складом та ефективністю інгібування корозійних процесів, що дозволить розробити оптимальні рецептури для ґрунтовок на водній основі. Антикорозійну ефективність екстрактів різного складу на зразках сталі Q215 оцінювали методом масометрії. Використовуючи симплексну ґратчасту схему експерименту, було побудовано математичну модель, яка описує залежність ступеня захисту від складу суміші. Шляхом оптимізації було визначено оптимальний склад суміші: 4,7 г WSh, 2,4 г CaPh та 7,9 г ZnPh на 100 г води, для якого розрахунковий ступінь захисту становив 90,06%. Експериментальна перевірка підтвердила високу ефективність суміші, показавши ступінь захисту 87,8%. Отриману модель можна використовувати для прогнозування антикорозійних властивостей пігментних сумішей для розробки екологічно чистих ґрунтовок на водній основі.

Ключові слова: лакофарбові матеріали, антикорозійні пігменти, корозія, шкаралупа волоського горіха, фосфати, таніни, оптимізація.

NON-TOXIC ANTI-CORROSION PIGMENT MIXTURES WITH VEGETABLE COMPONENT FOR PAINT PRIMERS

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Keywords: paints and varnishes; anti-corrosion pigments; corrosion; walnut shell; phosphates; tannins; optimization.

REFERENCES

1. Yang S, Huang J, Chen J, Noel JJ, Barker I, Henderson JD, et al. Comparative study on the anti-corrosive performance of zinc phosphate in powder coatings. *Coatings.* 2022; 12: 217. doi: 10.3390/coatings12020217.

2. Pokhmurs'kyi VI, Zin' IM, Layon SB, Bilyi LM. Synergistic effect of phosphate and calcium-containing pigments on the corrosion resistance of galvanized steel. *Mater Sci.* 2003; 39: 153-160. doi: 10.1023/B:MASC.0000010264.27310.9e.

3. Zin IM, Lyon SB, Pokhmurskii VI, Simmonds MC. Inhibition of steel and galvanised steel corrosion by zinc and calcium ions in the presence of phosphate. *Corros Eng Sci Technol.* 2004; 39(2): 167-173. doi 10.1179/147842204225016967.

4. Xu X, Wang H, Wu J, Chen Z, Zhang X, Li M. Hydrothermal in-situ synthesis and anti-corrosion performance of zinc oxide hydroxyapatite nanocomposite anti-corrosive pigment. *Coatings.* 2022; 12: 420. doi: 10.3390/coatings12040420.

5. Khlopyk OP, Zin IM, Datsko BM, Bilyi LM, Duriagina ZA, Korniy SA. Anticorrosion properties of composite inhibiting pigment based on natural calcium silicate and zinc monophosphate. *Mater Sci.* 2023; 59: 234-241. doi: 10.1007/s11003-024-00768-9.

6. Khlopyk OP, Zin IM, Korniy SA, Datsko BM, Bilyi LM. Anticorrosion properties of composite inhibiting pigment based on natural calcium silicate and zinc monophosphate in alkyd coating on carbon steel. *Mater Sci.* 2025; 60: 584-592. doi: 10.1007/s11003-025-00923-w.

7 Alibakhshi E, Haddadi SA, Labbani Motlagha A, Ghaderi M, Ramezanzadeh B, Mahdavian M, et al. Epoxy nanocomposite coating based on calcium zinc phosphate with dual active/barrier corrosion mitigation properties. *Prog Org Coat.* 2022; 163: 106677. doi: 10.1016/j.porgcoat.2021.106677.

8. Datsko BM, Khlopyk OP, Zin IM, Sobodosh NYo, Holovchuk MYa, Korniy SA. Protective properties of epoxy coatings with zeolite-phosphate anti-corrosion pigment on aluminum alloy. *Mater Sci.* 2024; 60: 85-90. doi: 10.1007/s11003-024-00856-w.

9. Elmourabit M, Zarki Y, Arfoy B, Ben Seddik N, AitAghzzaf A, Chaouket F, et al. Corrosion protection of mild steel by an alkyd resin coating reinforced with calcium zinc phosphate derived phosphate sludge as green inhibitive pigment. *Emergent Mater.* 2025; 8: 2325-2343. doi: 10.1007/s42247-024-00964-y.

10 Korniy S, Zin I, Danyliak MO, Khlopyk O, Datsko B, Holovchuk M. Aluminium alloy corrosion inhibition by composite pigment based on nanoporous synthetic zeolite and zinc dihydrogen phosphate. *Appl Nanosci.* 2023; 13: 7257-7266. doi: 10.1007/s13204-023-02888-1.

11. Bethencourt M, Botana FJ, Marcos M, Osuna RM, Sanchez-Amaya JM. Inhibitor properties of «green» pigments for paints. *Prog Org Coat.* 2003; 46: 280-287. doi: 10.1016/S0300-9440(03)00013-4.

12. Chyhyrynets O, Sanginova O, Hu J, Wu Y, He X. Optimization of the composition of aluminum phosphate and walnut shell-based composition to increase the corrosion resistance of paint coatings. *Technology Audit and Production Reserves*. 2025; 4/3(84): 12-17. doi: 10.15587/2706-5448.2025.334800.

13. Salleh SZ, Yusoff AH, Zakaria SK, Taib MAA, Abu Seman A, Masri MN, et al. Plant extracts as green corrosion inhibitor for ferrous metal alloys: a review. *J Clean Prod*. 2021; 304: 127030. doi: 10.1016/j.jclepro.2021.127030.

14. Lamprakou Z, Bi H, Weinell CE, Dam-Johansen K. Tannin-based inhibitive pigment for sustainable epoxy coatings formulation. *Prog Org Coat*. 2022; 167: 106841. doi: 10.1016/j.porgcoat.2022.106841.

15. Zmozinski AV, Peres RS, Freiberger K, Ferreira CA, Tamborim SMM, Azambuja DS. Zinc tannate and magnesium tannate as anticorrosion pigments in epoxy paint formulations. *Prog Org Coat*. 2018; 121: 23-29. doi: 10.1016/j.porgcoat.2018.04.007.