



New anti-corrosion pigment based on natural aluminosilicate with a layered structure

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Received: 15 April 2026; Revised 28 April 2026; Accept: 15 May 2026

Abstract

Eco-friendly anti-corrosion pigments based on the natural ion-exchange montmorillonite mineral with a layered structure was obtained by mechanochemical modification. It is shown that due to modification with zinc monophosphate, montmorillonite is enriched with zinc cations and phosphate anions. According to scanning electron microscopy results the montmorillonite particles are in the form of curved plates that tend to agglomerate. Using EDX analysis, it was established that the initial montmorillonite was Ca, Mg – form of montmorillonite. Due to the mechanochemical modification of montmorillonite, intercalation of Zn^{2+} cations into the layered structure of natural montmorillonite occurred, and phosphate anions were able to form surface adsorption complexes with positively charged edge surfaces of montmorillonite through the acidic environment of the crystal hydrate of the salt $Zn(H_2PO_4)_2 \cdot 2H_2O$, while the content of zinc and phosphorus is ~ 5 wt. % and ~ 4 wt. %, respectively. It was established that the obtained pigment based on mechanochemically modified montmorillonite increases the corrosion resistance of the aluminium alloy in an acid rain environment with $pH = 4.5$ by potentiodynamic polarization and electrochemical impedance spectroscopy methods. The inhibitory effect of mechanochemically modified montmorillonite consists in the release of Zn^{2+} cations from montmorillonite containers, which, interacting with OH^- anions, form zinc hydroxides at the cathode sites, and the slowing down of electrochemical corrosion occurs due to the formation of phosphates at the anode sites of the aluminium alloy. It was established that the protection degree of the aluminium alloy in the acid rain environment with mechanochemically modified montmorillonite was above 90 %. Thus, montmorillonite, an aluminosilicate mineral of natural origin, is a promising material for obtaining new eco-friendly anti-corrosion pigments in paint and varnish coatings to ensure long-term protection of metal products.

Key words: corrosion, montmorillonite, ion-exchange minerals, anti-corrosion pigment, clay, aluminium alloy.

Introduction

One of the most common and effective methods of protecting metallic materials is the use of paint coatings. However, during use, the protective properties of paint coatings diminish under the influence of the environment, which eventually leads to the formation of an active corrosion cell beneath the coating. Therefore, the long-term effectiveness of such coatings can be enhanced by the adding of anti-corrosion pigments [1, 2]. Chromate-based compounds are the most widely used and effective pigments. However, their harmful effects limit their use in paint and varnish coatings [3]. This necessitates the search for environmentally friendly alternatives that also exhibit high inhibitory effectiveness. Such alternatives include the use of natural minerals with ion-exchange properties, for example, sepiolite, galuzite or bentonite [4–6], etc. Bentonite consists mainly of montmorillonite, which possesses cation-exchange properties, and is therefore a promising natural ion-exchange material for anti-corrosion pigments [7]. Montmorillonite is a 2:1-layered hydrated aluminium silicate with a composition similar to the formula: $(\frac{1}{2}Ca,Na)(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4 \cdot nH_2O$. It consists of a central layer of aluminium oxide octahedra, which is sandwiched between two layers of silicon oxide tetrahedra [8, 9]. It can be used as a container for the intercalation of corrosion inhibitors [10]. Anti-corrosion pigments based on ion-exchange minerals can be obtained by mechanochemical modification. Therefore, the aim of this work is to obtain an environmentally friendly anti-corrosion pigment based on montmorillonite through mechanochemical



modification, and to evaluate its inhibitory effectiveness for improving the corrosion resistance of the aluminium alloy in an acid rain environment.

Research materials and methodology

To prepare the anti-corrosion pigment, montmorillonite obtained from bentonite from the Ilnytske deposit in Zakarpattia Oblast (Ukraine), supplied by Lignit+ LLC, was used. The montmorillonite was obtained from the bentonite by sedimentation of the coarse-particle phase. Mechanochemical modification of natural montmorillonite was carried out using zinc monophosphate $Zn(H_2PO_4)_2 \cdot 2H_2O$ in a ball mill for 15 minutes at ambient temperature. The elemental composition and surface morphology of the initial and mechanochemically modified montmorillonite were studied using Zeiss MA10 scanning electron microscope equipped with an AztecLive energy-dispersive microanalysis system (EDX) based on an X Max 50 detector. The aluminium alloy, with the chemical composition (wt.%): Si \leq 0.5; Cr \leq 0.1; Mn 0.3–0.9; Cu 3.8–4.9; Mg 1.2–1.8; Fe \leq 0.5; Ti \leq 0.15; balance Al, was used in the study. The corrosion resistance of the aluminium alloy was investigated in a model acid rain solution [11] with and without montmorillonite pigments (both in their initial form and after mechanochemical modification), as well as with the addition of zinc monophosphate (at a concentration of 2 g/l) at room temperature using methods of potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS). The Versa STAT 3 frequency response potentiostat was used. The potential scanning rate during potentiodynamic polarisation was 2 mV/s. The three-electrode cell contained an Ag/AgCl reference electrode, a platinum auxiliary electrode and a working electrode made of the aluminium alloy. EIS measurements were performed in the frequency range 10,000–0.01 Hz with an applied signal amplitude of 10 mV. Equivalent circuits are shown in Fig. 1 (R_s , R_c , R_{ct} , CPE_c , and CPE_{dl} – solution resistance, protective film resistance, charge transfer resistance, constant phase element of the protective film and the double layer, respectively), which was used for fitting the EIS data of the aluminium alloy samples after 48 hours of exposure in an acid rain environment. ZView® software was used to fit the EIS data. The inhibitory efficiency (IE, %) was determined using the following formulas [12].

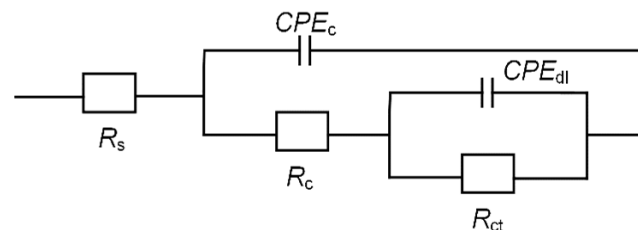


Fig. 1. Equivalent circuits for EIS data fitting after 48 hours of exposure in an acid rain environment without and with anti-corrosion pigment

Research results and discussion

An analysis of the morphology and dispersibility of the initial and mechanochemically modified montmorillonites (Fig. 2) showed that their particles are agglomerates and have the shape of curved plates, and that the modification leads to conglomeration. Their chemical composition was determined using EDX analysis. The initial montmorillonite is the Ca, Mg form of montmorillonite, as Ca and Mg were detected in its composition. As a result of the mechanochemical modification of montmorillonite, Zn^{2+} cations are intercalated into the layered structure of natural montmorillonite, whilst phosphate anions can form surface adsorption complexes with the positively charged edge surfaces of montmorillonite via the acidic environment of the $Zn(H_2PO_4)_2 \cdot 2H_2O$ salt hydrate, with the zinc and phosphorus contents being ~ 5 wt. % and ~ 4 wt.%, respectively (Table 1).

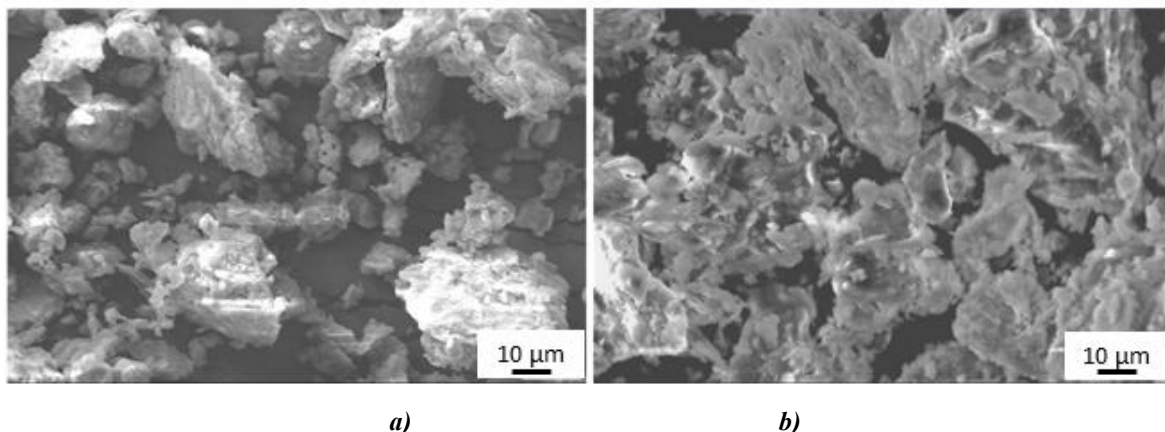


Fig. 2. SEM images of the initial (a) and mechanochemically modified (b) montmorillonites

Table 1

Chemical composition (wt. %) of the initial and mechanochemically modified montmorillonites									
Element	O	Na	Mg	Al	Si	Fe	Zn	Ca	P
Initial montmorillonite	45.9	0.3	1.1	11.4	28.7	11.3	-	1.3	-
Mechanochemically modified montmorillonite	46.0	1.2	0.9	8.0	21.7	11.4	5.5	0.9	4.4

Figure 3 shows the polarization curves of the aluminium alloy after 48 hours of exposure to an acid rain environment. Electrochemical parameters obtained by the Tafel method of extrapolation of polarization curves are shown in the Table 2. Zinc monophosphate does not improve corrosion resistance due to the reduction of the environment's pH to 3.1, which promotes the dissolution of the aluminium matrix. Mechanochemically modified montmorillonite reduces the corrosion current density of the aluminium alloy by a factor of ~25 compared to the acid rain environment without it after 48 hours of exposure (Table 2), and the inhibitory effectiveness is ~96%. The protective effect of mechanochemically modified montmorillonite lies in the formation of insoluble $Zn(OH)_2$ hydroxides at the cathodic sites and aluminium phosphates at the anodic sites of the aluminium alloy. A similar inhibitory mechanism is described in [13], where the inhibitory effect of mechanochemically modified zeolite with zinc monophosphate at a 1:1 component ratio on an aluminium alloy in a chloride solution was investigated. It was found that the synthesised anti-corrosion pigment reduces the corrosion rate of the aluminium alloy in a 0.1% NaCl solution, with an inhibitory effectiveness of 83%.

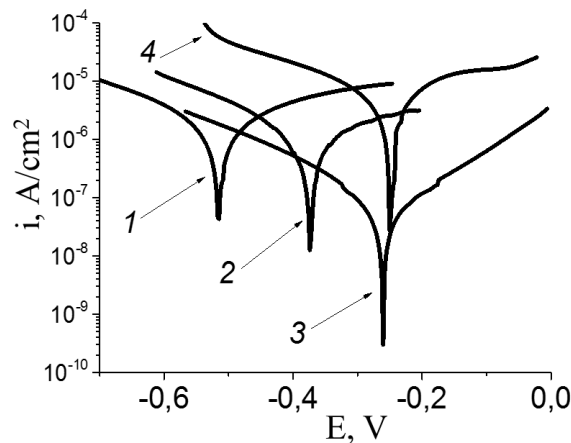


Fig. 3. Polarization curves of the aluminium alloy after 48 hours of exposure in an acid rain environment: 1 – without montmorillonite; 2 – with the initial montmorillonite; 3 – with the mechanochemically modified montmorillonite; 4 – with zinc monophosphate

Table 2

Electrochemical characteristics of the aluminium alloy after 48 hours of exposure in an acid rain environment

Environment	E_{cor} , V	i_{cor} , A/cm ²
Acid rain environment	-0.51	$9.7 \cdot 10^{-7}$
Acid rain environment + the initial montmorillonite	-0.37	$6.2 \cdot 10^{-7}$
Acid rain environment + the mechanochemically modified montmorillonite	-0.26	$3.9 \cdot 10^{-8}$
Acid rain environment + zinc monophosphate	-0.25	$3.4 \cdot 10^{-6}$

The results of the polarisation and EIS studies correlate with one another (Figs. 4 and 5, Table 3). The pigment based on montmorillonite, mechanochemically modified with zinc monophosphate, increases the charge transfer resistance of the aluminium alloy compared to samples exposed to an acid rain environment and when adding either the initial montmorillonite or zinc monophosphate. The inhibitory effectiveness, as determined by EIS results, is 94.5%. On the Bode diagram corresponding to the aluminium alloy in an acid rain solution without pigment, a peak is present in the low-frequency region, indicating the occurrence of electrochemical reactions resulting in the formation of corrosion products on the surface. The formation of a high-frequency peak following exposure when using mechanochemically modified montmorillonite indicates the formation of a protective film. The Bode plot of the aluminium alloy in an acid rain solution containing zinc monophosphate has a peak with an intensity reaching up to 60° , indicating the formation of a film on the surface; however, due to the acidic environment (pH=3.1) caused by zinc monophosphate, which promotes the dissolution of aluminium, it contains corrosion products.

The Nyquist diagrams are semicircular in shape, indicating that the rate of the electrochemical process is determined by the charge transfer stage. The diameter of these semicircles depends on the presence of modified montmorillonite, which also indicates the formation of a protective film that helps inhibit corrosion.

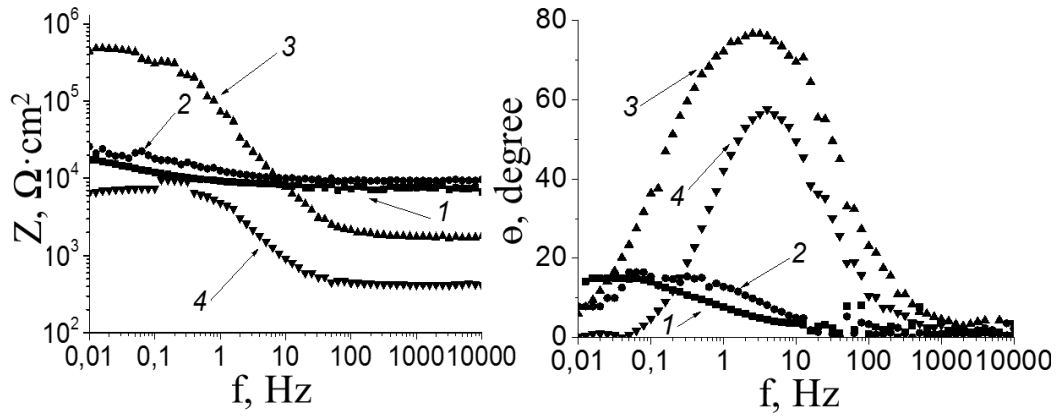


Fig. 4. Bode diagrams of the aluminium alloy after 48 hours of exposure in an acid rain environment: 1 – without montmorillonite; 2 – with the initial montmorillonite; 3 – with the mechanochemically modified montmorillonite; 4 – with zinc monophosphate

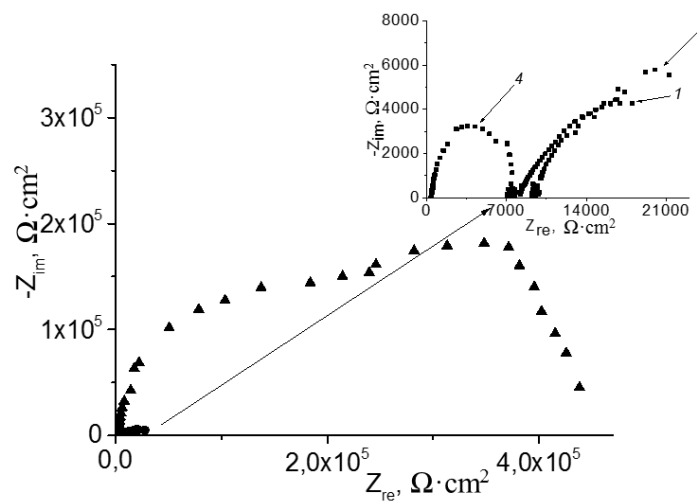


Fig. 5. Nyquist diagrams of the aluminium alloy after 48 hours of exposure in an acid rain environment: 1 – without montmorillonite; 2 – with the initial montmorillonite; 3 – with the mechanochemically modified montmorillonite; 4 – with zinc monophosphate

Table 3
EIS characteristics of the aluminium alloy after 48 hours of exposure in an acid rain environment

Environment	R_s , Ohm	R_f , Ohm · cm ²	CPE_f , s ⁿ / Ohm · cm ²	R_{ct} , Ohm · cm ²	CPE_{ct} , s ⁿ / Ohm · cm ²
Acid rain environment	6997	890	$1.93 \cdot 10^{-6}$	23096	$2.22 \cdot 10^{-4}$
Acid rain environment + the initial montmorillonite	9379	2600	$7.22 \cdot 10^{-5}$	26000	$1.50 \cdot 10^{-5}$
Acid rain environment + the mechanochemically modified montmorillonite	1722	2507	$2.40 \cdot 10^{-6}$	420500	$2.54 \cdot 10^{-7}$
Acid rain environment + zinc monophosphate	424	1611	$2.17 \cdot 10^{-5}$	5300	$7.68 \cdot 10^{-6}$

Conclusions

The use of a pigment based on mechanochemically modified montmorillonite enhances the corrosion resistance of the aluminium alloy in an acid rain environment. The inhibitory effect of mechanochemically modified montmorillonite based on the release of Zn²⁺ cations from montmorillonite containers, which, interacting with OH⁻ anions, form zinc hydroxides at the cathodic sites, and the slowing down of electrochemical corrosion occurs due to the formation of phosphates at the anodic regions of the aluminium alloy.

According to electrochemical studies, the degree of protection of the aluminium alloy in an acid rain environment with mechanochemically modified montmorillonite is over 90%. Thus, montmorillonite – a naturally occurring aluminosilicate mineral – is a promising material for the production of new, environmentally friendly anti-corrosion pigments in paint and varnish coatings to ensure long-term protection of metal products.

Acknowledgements

The authors gratefully acknowledge the financial support for this work from grant “Development of anti-corrosion pigments based on natural aluminosilicate mineral with laminar structure for polymer coatings on aluminium alloys” (Project of the National Research Foundation of Ukraine No. 2025.05/0001)

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Даниляк М.-О.М., Корній С.А. Новий протикорозійний пігмент на основі природного алюмосилікату шаруватої структури

Екологічно безпечний протикорозійний пігмент на основі природного іонообмінного мінералу монтморилоніту шаруватої структури отримано механохімічною модифікацією. Показано, що при модифікації цинк монофосфатом монтморилоніт збагачується катіонами цинку та фосфат аніонами. За результатами скануючої електронної мікроскопії показано, що частинки монтморилоніту мають вигляд вигнутих пластинок, що схильні до агломерації. За допомогою EDX-аналізу встановлено, що вихідний монтморилоніт є формою Са, Mg монтморилоніту. Показано, що внаслідок механохімічної модифікації монтморилоніту відбувається інтеркаляція катіонів Zn^{2+} у шарувату структуру природного монтморилоніту, а аніони фосфату утворюють поверхневі адсорбційні комплекси з позитивно зарядженими крайовими поверхнями монтморилоніту через кисле середовище кристалічного гідрату солі $Zn(H_2PO_4)_2 \cdot 2H_2O$, при цьому вміст цинку та фосфору становить ~ 5 мас. % та ~ 4 мас. % відповідно. За допомогою потенціодинамічної поляризації та електрохімічної імпедансної спектроскопії встановлено, що отриманий пігмент на основі механохімічно модифікованого монтморилоніту підвищує корозійну стійкість алюмінієвого сплаву в умовах кислотного дощу з $pH = 4,5$. Інгібуючий ефект механохімічно модифікованого монтморилоніту полягає у вивільненні катіонів Zn^{2+} з контейнерів монтморилоніту, які, взаємодіючи з аніонами OH^- , утворюють гідроксиди цинку в катодних ділянках, а уповільнення електрохімічної корозії відбувається завдяки утворенню фосфатів в анодних ділянках алюмінієвого сплаву. Встановлено, що ступінь захисту алюмінієвого сплаву в середовищі кислотного дощу за допомогою механохімічно модифікованого монтморилоніту перевищував 90 %. Таким чином, монтморилоніт, алюмосилікатний мінерал природного походження, є перспективним матеріалом для отримання нових екологічно безпечних протикорозійних пігментів у лакофарбових покриттях з метою забезпечення довготривалого захисту металевих виробів.

Ключові слова: корозія, монтморилоніт, іонообмінні мінерали, глина, протикорозійний пігмент, алюмінієвий сплав