UDC 691.57 DOI: 10.31650/2786-6696-2023-4-49-55

CORROSION RESISTANCE OF POWDER COATING WITH USE OF FERRITIZATION WASTE

[1]**Gots V.I.,** D.Sc., Professor,
Gots.volodymyr@gmail.com, ORCID: 0000-0001-7103-1234
[1]**Kochetov G.V.,** D.Sc., Professor,
gkochetov@gmail.com, ORCID: 0000-0003-0041-7335
[1]**Lastivka O.V.,** PhD., Assistant Professor,
oles.lastivka@gmail.com, ORCID: 0000-0002-7499-4744
[1]**Samchenko D.M.,** PhD, Senior Researcher,
sama30071988@gmail.com, ORCID: 0000-0003-3305-8180
[1]**Mehet V.S.**, graduate student,
ss9164669@gmail.com, ORCID: 0000-0002-2830-9419
[1]*Kyiv National University of Construction and Architecture*
Povitroflotskyi prospect 31, Kyiv 03037, Ukraine

Abstract. Aspects for increasing the corrosion resistance of powder coating materials as a result of the involvement of the latest technologies for cleaning electroplating production waste are considered. The results of the effect of ferritization waste on the formation of corrosion resistance of coatings based on powder coating are shown.

The introduction of the obtained ferritization waste into the composition of powder coating systems has a different effect on the formation of corrosion resistance of coatings was found. Thus, the control composition of the powder coating using a filler in the form of barium sulfate during 480 hours of exposure in the salt fog chamber is characterized by peeling of the coating at the level of 7.5 mm. The average width of metal corrosion is 5.5 mm. The category of corrosion resistance of the coating corresponds to class C3 (average) with the provision of an average durability class (M) from 7 to 15 years. Examples of typical environments (according to DSTU ISO 12944-2:2019) where the resulting coatings can be used are urban and industrial atmospheres, moderate sulfur dioxide pollution, coastal areas with low salinity.

The use of galvanic waste sediments in general contributes to increasing the corrosion resistance of the powder coating. The efficiency of their use depends on the chemical composition of ferritization waste. Among the studied samples, the most effective is the introduction of waste in the form of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ and $Zn_{0.5}Cu_{0.5}Fe_2O_4$ into the composition of powder systems, which helps to reduce the width of coating peeling by 65...79 %, as well as the width of metal corrosion by 75...80 % compared to the control composition.

The least effective among the studied samples is the use of waste in the form of $Ni_{0.5}Zn_{0.5}Al_{0.15}Fe_{1.85}O_4$ and $CrFe_2O_4$ due to a significant decrease in the corrosion resistance of the powder coating

Powder coating systems were obtained using ferritization waste, the category of corrosion resistance of which corresponds to class C4 (high) with a high durability class (H) from 15 to 25 years. In general, the use of ferritization waste provides better corrosion resistance of coatings compared to traditional systems based on barium sulfate, which in turn gives reason to consider such systems as an alternative for corrosion protection of construction metal products and structures.

Keywords: powder coating, ferritization waste, peeling, width of metal corrosion, class corrosion.

Introduction. Generation, storage, disposal, decontamination and removal of steel waste have become one of the biggest challenges for developed countries, with the environmental condition depending on their priority solution [1, 2]. As a result of large amounts of plating wastewaters as one of the prevailing types of industrial liquid wastes, the said problem has become particularly acute. If stored in the territory of enterprises, such wastes could cause irreversible environmental pollution [3].

Depending on the source of generation and physical state, plating wastes are divided into the following types: spent concentrated process solutions; hutch water; galvanic waste [4]. Plating wastes contain a high concentration of toxic substances; therefore, these substances are referred to one of the most hazardous types of industrial waste. Among the main pollutants of plating waste are ions of heavy metals, inorganic acids, alkalis, etc. In metal plating, only 30-80 % of metals, 5-20 % of acids and 2-3 % of water are useful, meaning that large quantities of valuable raw materials are wasted and, even more, cause the environmental pollution with toxic substances. They must be recycled, for the environment to be protected against such hazardous solutions [5, 6].

Current requirements for application of plating waste disposal technologies are aimed at creating environmentally safe and resource-saving production, where the waste from one industry will be fully or partially used as raw materials for another [7].

One of the most effective methods of plating waste disposal is to apply ferritization technology [8]. Heavy metals are removed from working solutions and converted into a chemically-stable crystal structure during this process, but ferritization is performed at temperatures above 75 ºC, so its application is quite energy-consuming.

As an alternative to a traditional thermal method of ferritization, it is reasonable to use electromagnetic pulsed activation of the process saving up to 60 % of energy resources [9].

The plating waste treated by ferritization using the abovementioned methods could be reasonably used to partially replace fillers in powder coating, with subsequent powder coatings on their base. This would facilitate creating non-waste technologies and closed-loop processes for making coatings under factory conditions.

Analysis of recent studies and publications. Powder coating is one of the most promising materials for creating technical and economic, and eco-friendly protective coating for a wide selection of building products and structures. Two groups of powder coating and lacquers are distinguished by their chemical composition: on the basis of thermoplastic film forming substances and on the basis of thermoset ones [10]. The coating on the basis of thermoplastic film forming substances is made without chemical transformations due to melting of powder particles with subsequent cooling of the hot melt. In case of coatings on the basis of thermosetting resins, the cross-linking reaction of the coating system takes place in the presence of catalysts, thus making conditions for the use of polymers with significantly lower molecular mass and, respectively, a lower viscosity of the hot melt. As a result, a high content of fillers and pigments may be introduced into the system of thermoset paints and lacquers and this, in its turn, ensures a high quality of a product with a low cost ensured. At the same time, the global output of thermoset powder coatings is about 80 % of the total paints and lacquers produced, thus confirming their effectiveness [11, 12]. These materials are highly competitive as compared to coatings based on liquid paints, since they are made on the basis of film forming oligomers which, in they turn, make it possible to obtain quality coatings of 30…80 μm thick.

The prescription composition of the thermoset powder coating consists of five basic components: polymer resin, hardener, pigments, functional additions and fillers [13, 14]. Polymer resins and hardeners generally play the key role in ensuring necessary mechanical characteristics and durability of the powder coating. However, it is the correctly selected filler that contributes to regulation of functional properties of the coating, such as hardness, gloss, bending and impact strength, permeability and corrosion resistance [15, 16].

In view of high output of thermoset powder coating in the world, as well as the problem of plating waste disposal, it is reasonable to study how the sludge of plating waste of various types influences the formation of performance properties of coatings based on powder paints.

The purpose of this paper is to study the impact of plating waste sludge of different phase composition on the corrosion resistance of powder coating.

Materials and research methods. Carboxylated polyester resin Crylcoat 2618-3 made by Allnex was used as a film forming substance to perform the research. For carboxylate polyester resin it is also obligatory to use a structure-forming hardener. Primid XL-552 made by EMS-Griltech was used for this research. In order to ensure coverage of the surface of metal samples in powder systems under study, a white pigment (titanium dioxide (TiO_2)) was chosen. As a reference composition (Table 1), a powder coating system was used containing barium sulfate which is a traditional filler to obtain powder paints and lacquers.

Table 1 – Composition of powder coating

Control	Content of raw materials, %			
	Crylcoat 2618-3	HAA	TiO_2	Barium sulfate
	57	3	10	40

As a result of using ferritization treatment of waste, nine types of sludge samples were obtained, each having different phase composition: sample No. 1 – $NiFe_2O_4$; sample No. 2 – $ZnFe_2O_4$; sample No. 3 – $CuFe_2O_4$; sample No. 4 – $Ni_{0.5}$ $Zn_{0.5}Fe_2O_4$; sample No. 5 – $Ni_{0.5}Cu_{0.5}Fe_2O_4$; sample No. 6 – $Zn_{0.5}Cu_{0.5}Fe_2O_4$; sample No. 7 – $Zn_{0.5}Mn_{0.5}Fe_2O_4$; sample No. 8 – $Ni_{0.5}$ $Zn_{0.5}Al_{0.15}Fe_{1.85}O_4$; sample No. 9 – $CrFe_2O_4$. The abovementioned waste samples were used to partially replace the filler in power systems. The composition of the analysed coating systems with the use of the obtained waste was taken as follows: Crylcoat 2618-3 – 57 %, HAA – 3 %, TiO_2 – 10 %, barium sulphate – 25 %, and obtained waste sample – 15 %.

Research methods. The impact of the obtained waste treated by ferritization on the corrosion resistance of the coating based on powder coating was studied in the sequence as follows:

1. The steel plates St3 (size 150×60 mm) were covered by powder paints of different compositions. The powder paint was applied by electrostatic method according to ISO 1514:2016 using spray gun Start 50.
2. The hardening of the powder coating on sample plates took place in a curing oven at 180 ºC during 10 minutes.
3. Corrosion resistance of decorative and protective powder coating systems was tested in a salt spray chamber with 5 % condensation of saline (NaCl) on the sample surfaces during 480 hours at 35 ºC according to DSTU ISO 9227:2015 "Corrosion tests in artificial atmospheres – Salt spray tests". The average coating delamination and development of metal corrosion after the test was determined by the methods of DSTU ISO 4628-8:2012. The coating compositions were classified according to categories of atmospheric corrosion aggressiveness according to DSTU ISO 12944-2, including their durability according to DSTU ISO 12944-1.

Research results. It was found that introduction of obtained waste treated by ferritization into the composition of powder coating systems has different impacts on the formation of corrosion resistance of the coating (Fig. 1, Fig. 2). Thus, the reference composition of the powder coating using such filler as barium sulphate after curing during 480 hours in the salt spray chamber is characterized by the coating delamination of 7.5 mm (Fig. 1). The average width of metal corrosion is 5.5 mm (Fig. 2). The category of corrosion resistance of the coating corresponds to class *C3 (middle)* ensuring a middle class of durability (M) of 7 to 15 years. The examples of typical environments (according to DSTU ISO 12944-2:2019) where the obtained coatings may be used are urban and industrial environments, with moderate pollution of sulphur dioxide, and coastal regions with law total salt content.

In case of partial replacement of barium sulphate by the waste of phase composition $Zn_{0.5}Mn_{0.5}Fe_2O_4$ (sample No.7), one can generally observe the increased corrosion resistance of the coating. Using such waste actually results in the increase of average coating delamination from 7.5 to 8.5 mm, which is 14 % more as compared to the reference composition. However, the average width of metal corrosion is reduced by 29 % from 5.5 to 3.9 mm. This could be due to formation of a passive film on the steel surface because of introduction of the said waste, with a respective slowdown in the anode process of electrochemical corrosion. The category of corrosion corresponds to class *C4 (high),* with the middle class of *durability (M)* from 7 to 15 years ensured. The examples of typical environments where the obtained coatings may be used are industrial and coastal regions with moderate total salt content.

A similar situation is also observed after introduction of $ZnFe_2O_4$ (sample No.2) to the coating system – as compared to the reference composition, the average coating delamination is increased from 7.5 to 9.8 mm, but the average width of metal corrosion is reduced at the same time by 37 % and reaches 3.5 mm. Corrosion resistance corresponds to class C4 (high), with the medium class of durability (M) ensured from 7 to 15 years.

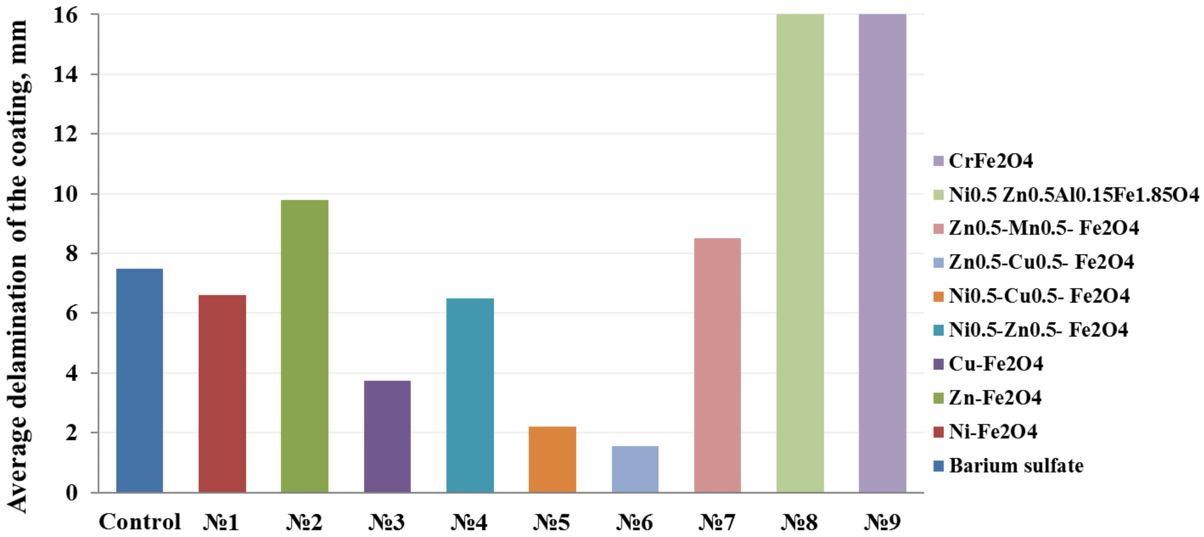

Fig. 1. Average width of coating delamination

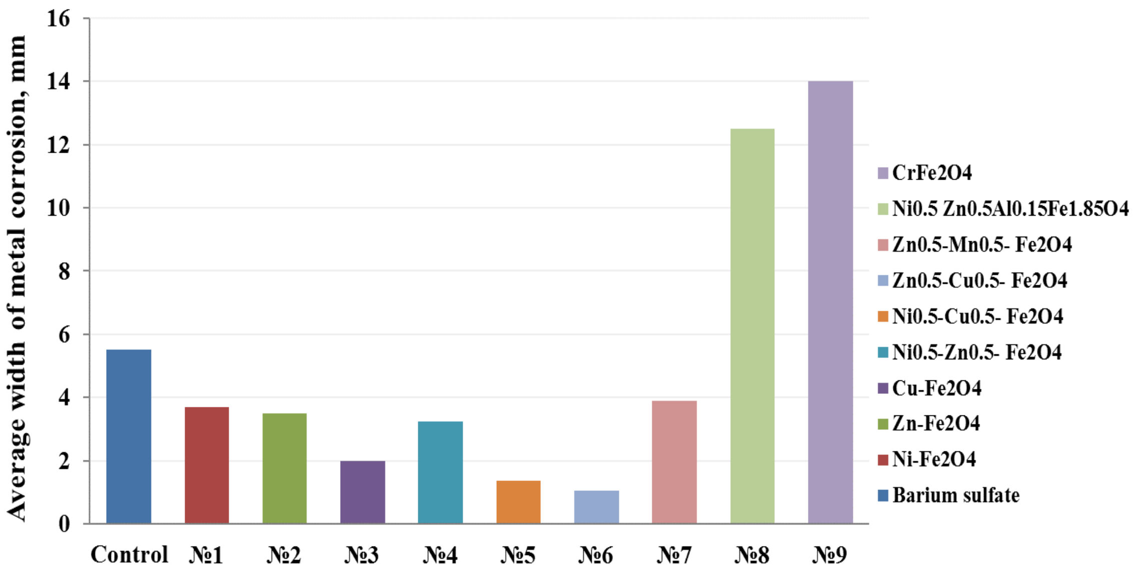

Fig. 2. Average width of metal corrosion

Introduction of the obtained waste $NiFe_2O_4$ (sample No. 1) also contributes to the increase in the corrosion resistance of the powder coating. Thus, the average width of coating delamination is reduced by 12 % and reaches 6.6 mm, with the average width of metal corrosion of 3.7 mm, which is 33% less if compared to the reference composition. The corrosion category corresponds to class C4 (high), with the medium class of durability (M) ensured from 7 to 15 years.

A similar result is demonstrated when using such waste as $Ni_{0.5}\ Zn_{0.5}Fe_2O_4$ (sample No.4) in the powder paint, which contributes both to the reduction of the average width of coating delamination up to 6.5 mm and the width of metal corrosion expansion up to 3.25 mm as compared to the reference composition. The category of corrosion durability corresponds to class C4 (high), with the medium class of durability (M) ensured from 7 to 15 years.

In its turn, introduction of such wastes as $Ni_{0.5}Zn_{0.5}Al_{0.15}Fe_{1.85}O_4$ (sample No. 8) and $CrFe_2O_4$ (composition No. 9) is not effective, as evidenced by the essential reduction in the corrosion resistance of the coating due to 100%-delamination of the tested coatings from the substrate surface, and by the increased metal corrosion up to 12…14.5 mm as compared to the reference composition. The category of corrosion durability of the coating corresponds to class C1 (very low). As a result, the examples of typical environments where it is allowed to apply powder coatings with the use of such wastes as $Ni_{0.5}Zn_{0.5}Al_{0.15}Fe_{1.85}O_4$ (sample No. 8) and $CrFe_2O_4$ (sample No. 9) according to the regulatory document are the inside of a building, where they are not exposed to the outside environment.

Such waste as $CuFe_2O_4$ (sample No.3) introduced to the powder paint is effective. Thus, its use contributes to the reduction of the average width of coating delamination from 7.5 mm (reference composition) to 3.75 mm, as well as the average width of metal corrosion expansion from 5.5 mm (reference composition) to 2 mm. The category of corrosion resistance corresponds to class C4 (high), with the high class of durability (H) ensured from 15 to 25 years.

Such wastes as $Ni_{0.5}Cu_{0.5}Fe_2O_4$ (sample No. 5) and $Zn_{0.5}Cu_{0.5}Fe_2O_4$ (sample No. 6) are the most effective in order to increase corrosion resistance of the power coating. In case of introduction of $Ni_{0.5}Cu_{0.5}Fe_2O_4$, the average width of coating delamination reduced by 71 % as compared to the reference composition from 7.5 to 2.2 mm, and the average width of metal corrosion expansion reduced by 75 % – from 5.5 to 1.35 mm. When $Zn_{0.5}Cu_{0.5}Fe_2O_4$ was used as a filler, the average width of the coating delamination reduced by 79 % to 1.55 mm, and the average width of metal corrosion expansion reduced by 80 % to 1.05 mm. The category of corrosion resistance of coatings corresponds to class C4 (high), with the high class of durability (H) ensured from 15 to 25 years.

Conclusion. As a result of the research, the use of galvanic ferritization waste in general contributes to increasing the corrosion resistance of the coating. The efficiency of their use depends on the chemical composition of ferritization waste. Among the studied samples, the most effective is the introduction of waste in the form of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ and $Zn_{0.5}Cu_{0.5}Fe_2O_4$ into the composition of powder systems, which helps to reduce the width of coating peeling by 65...79 %, as well as the width of metal corrosion by 75...80 % compared to the control composition. Powder coating systems were obtained using ferritization waste, the category of corrosion resistance of which corresponds to class C4 (high) with a high durability class (H) from 15 to 25 years. The least effective among the studied samples is the use of waste in the form of $Ni_{0.5}Zn_{0.5}Al_{0.15}Fe_{1.85}O_4$ and $CrFe_2O_4$ due to a significant decrease in the corrosion resistance of the powder coating.

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КОРОЗІЙНА СТІЙКІСТЬ ПОРОШКОВИХ ЛАКОФАРБОВИХ МАТЕРІАЛІВ З ВИКОРИСТАННЯ ФЕРИТИЗОВАНИХ ПРОМИСЛОВИХ ВІДХОДІВ

[1]**Гоц В.І.,** д.т.н., професор,
Gots.volodymyr@gmail.com, ORCID: 0000-0001-7103-1234
[1]**Кочетов Г.М.,** д.т.н., професор,
gkochetov@gmail.com, ORCID: 0000-0003-0041-7335
[1]**Ластівка О.В.**, к.т.н. доцент,
oles.lastivka@gmail.com, ORCID: 0000-0002-7499-4744
[1]**Самченко Д.М.,** к.т.н., с.н.с,
sama30071988@gmail.com, ORCID: 0000-0003-3305-8180
[1]**Мегеть В.С.**, аспірант,
ss9164669@gmail.com, ORCID: 0000-0002-2830-9419
[1]*Київський національний університет будівництва і архітектури*
пр. Повітрофлотський, 31, м. Київ, 03037, Україна

Анотація. Розглянуто перспективи підвищення корозійної стійкості порошкових лакофарбових матеріалів в результаті залучення до їх складу продуктів феритизаційної переробки відходів гальванічного виробництва. Показано результати впливу цих відходів на формування корозійної стійкості покриттів на основі порошкових фарб.

Виявлено, що введення отриманих відходів феритизаційної очистки до складу порошкових лакофарбових систем по різному впливають на формування корозійної стійкості покриття. Порошкове покриття з використанням наповнювача у вигляді сульфату барію протягом 480 годин витримки в камері сольового туману характеризується відшаруванням покриття на рівні 7,5 мм. Середня ширина корозії металу становить 5,5 мм. Категорія корозійної стійкості покриття відповідає класу С3 (середній) при забезпечені середнього класу довговічності (М) від 7-ми до 15-ти років. Прикладами типового середовища (згідно ДСТУ ISO 12944-2:2019) де можуть експлуатуватись отримані покриття є міська та промислова атмосфера, помірне забруднення діоксидом сірки, прибережні райони з низькою солоністю.

Використання гальванічних відходів у цілому сприяє підвищенню корозійної стійкості порошкового покриття. Ефективність їх використання залежить від хімічного складу відходів феритизації. Серед досліджуваних зразків найбільш ефективним є введення відходів у вигляді $Ni_{0.5}Cu_{0.5}Fe_2O_4$, та $Zn_{0.5}Cu_{0.5}Fe_2O_4$ до складу порошкових систем, що сприяє зниженню ширини відшарування покриття на 65…79 %, а також ширини корозії металу на 75…80 % порівняно з контрольним складом

Найменш ефективним серед досліджуваних зразків є застосування відходів у вигляді $Ni_{0.5}Zn_{0.5}Al_{0.15}Fe_{1.85}O_4$ та $CrFe_2O_4$ з огляду на зниженням корозійної стійкості порошкового покриття.

Отримано порошкові лакофарбові системи з використанням відходів феритизаційної очистки стічних вод, категорія корозійної стійкості яких відповідає класу С4 (високий) при забезпечені високому класу довговічності (Н) від 15-ти до 25-ти років. В загальному, використання відходів феритизаційної очистки, забезпечує кращу корозійну стійкість покриттів порівняно з традиційними системами на основі сульфату барію, що в свою чергу дає підставу розглядати такі системи як альтернативу для захисту від корозії будівельних металевих виробів та конструкцій.

Ключові слова: порошкова фарба, покриття, корозія металу, гальванічні відходи, феритизація.

Стаття надійшла до редакції 17.04.2023