

Current trends in the modification of zinc-filled polymer coatings

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Abstract

Zinc-filled polymer coatings and primer formulations are among the most common and well-proven methods for long-term anticorrosive protection of critical metal structures and equipment. These coatings are successfully used both for the protection of internal surfaces of equipment and pipelines and for external protection. The main ways to modify zinc-filled coatings (ZFC) include modification of the zinc filler, modification of the polymer base, and the use of diverse active additives. Various methods of modifying the zinc filler are considered, including modification of the zinc alloy composition, surface modification of zinc particles, and the use of particles with various shapes and sizes – from nanoparticles to flake-shaped pigments. An analysis of the incorporation of various electrochemically active additives into ZFC, including nanoscale carbon-containing additives (carbon nanotubes, graphene and graphene oxide), as well as nanoparticles based on montmorillonite and layered double hydroxides, is performed. The experience in the incorporation of activators of zinc particles and selective modifiers and corrosion inhibitors along with conductive polymers as additives is considered. Approaches to the modification of the polymer base of ZFC are considered, taking into account their use in multi-layer coatings, including the combinations with layers of inert insulating coatings and water-borne polymers.

Keywords: *corrosion protection, polymer composites, polymer coatings, Zn-rich coatings, modification, active additives, corrosion inhibitors.*

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Introduction

Zinc-filled primers (ZFP) are widely used to protect metal structures and large-sized equipment, for example, oil and gas tanks, bridge structures, drilling rigs, platforms, pipelines, as well as in chemical and metallurgical industries for repairing various communication structures and devices.

Improving the operational properties and increasing the useful life of ZFC may, in principle, provide a protective action for a period comparable to that of the sacrificial action of hot-dip galvanized coatings.

A solution to this problem can be found by a combined improvement of the main components, namely, modification of the polymer binder, modification of the active filler (Zn powder, *etc.*), as well as use of electrochemically active additives and optimization of

the coating layer structure. A modern development strategy for new efficient coatings also involves combining various materials in order to obtain complex structures and synergistic effects.

Both synthetic resins and thermoplastic polymers, which are usually characterized by low electrical conductivity, are used as binders in anticorrosive composite materials. Examples of thermosetting materials include epoxy, organosilicon, urethane, acrylic resins, *etc.* [1]. Polyethylene, polyvinyl chloride, polytetrafluoroethylene, *etc.* are used as thermoplastic binders [2]. All of the polymers listed above have a number of advantages and drawbacks and differ in a number of characteristics, such as chemical resistance, heat resistance, moisture resistance, and a set of mechanical characteristics (hardness, strength, ductility) [3].

ZFC belong to a broad class of potential electrically conductive materials due to the incorporation of metal powders in the polymer structure in combination with other additives, such as carbon black, graphite, *etc.* Generally speaking, a metal-filled polymer should be considered as a structured system of conductive particles dispersed in a low-conductivity matrix. The following classification of structures of filled polymeric materials is typically used: a) homogeneous structures, tightly packed structures; b) chain structures; c) islet structures.

As a rule, a homogeneous tightly packed electrically conductive system should contain more than 0.52 volume parts of the conductive component. Such systems are also characterized by a dependence of the specific volume resistivity on the ratio of the diameters of electrically conductive particles and the number of contacts between them.

If the relative volume of the conductive component is less than this value, a chain or islet system is formed.

If the volume fraction is in the range of 0.52–0.48, the formation of electrically conductive chains in the polymer matrix is characteristic of systems filled with dispersed particles.

The formation of an electrically conductive islet system occurs when the filler content is less than 0.48 volume parts and, in this case, dielectric polymer layers appear between the particles of the conductive component.

Depending on the structure of the polymer composite, various mechanisms of electrical conductivity can be expected. If direct close contacts exist between the powder particles, spreading resistance is predominantly present (system I); in case of a contact through thin interlayers or gaps, a tunneling conduction mechanism (system II) is implemented, while if conductive particles separated by dielectric interlayers with a thickness of more than 2 nm are present predominantly, then conductivity arises due to the internal capacitance of the composite conductor (system III).

The electrical properties of filled polymers are determined by the predominance of a particular conductive system or a combination of such systems. Systems differing in the conduction mechanisms operating in them are characterized by:

- tight contacts the resistance of which is the spreading resistance (system I);
- contacts through thin layers or gaps where the tunneling conduction mechanism operates (system II);
- conductive particles separated by dielectric layers with a thickness above 2 nm forming the internal capacitance of the composite conductor (system III).

With a decrease in the specific volume of conductive particles, the percentage of systems II and III increases, whereas that of system I decreases. An important condition for efficient sacrificial action is the presence of electrical contact of a zinc cluster with the metal surface being protected, as well as the electrical conductivity of the zinc-filled coating itself. This requirement is met if the binder does not form continuous shells around individual particles of the zinc powder. However, in this case, one may expect a sharp decrease in the physico-mechanical and adhesive properties of the coating layer.

Despite the obvious feasibility of increasing the content of a sacrificial additive that follows from the above considerations, this approach has limitations because the resulting composites have poor physical and mechanical properties, the resulting coatings are short-lived, and their application is low-tech.

2. Modification of the Zn filler

The main methods for modifying the Zn filler include:

1. Optimization of the particle shape and particle size distribution of zinc pigments;
2. Use of pigments made of a zinc alloy with other metals;
3. Treatment of the zinc pigment surface;
4. Incorporation of additional anti-corrosion pigments into zinc-filled materials.

If required, these approaches to the modification of ZFC properties can be combined [4–7].

2.1. The use of flake-shaped zinc pigments

For rather a long time, ZFP were produced using zinc powder with spherical particles. As shown by the experience of utilizing spherical Zn, coatings must be highly filled (80–90%), since a high conductivity and good protector ability are provided in this case only. A decrease in Zn content to 75% results in the deterioration of electrical conductivity and, as a consequence, a deterioration of the protector ability.

However, a high degree of filling causes a number of significant drawbacks: porosity, poor physico-mechanical and adhesive properties, *etc.*

According to ISO 3549, cold galvanizing formulations that provide the most efficient electrochemical protection must contain in a dry coating at least 94% pure Zn of the total mass with a particle size of 12–15 μm , and 88% pure Zn of the total mass of the working composition with a microparticle size of 3–5 μm [8].

In composite materials on inorganic base, the concentration of spherical Zn is 75% or higher, while in coatings based on organic binders it is from 85% to 90%. The electrical conductivity of organic-based ZFC is lower than that of inorganic-based ones, therefore, the effective Zn content in them is higher.

A significant improvement in the properties of ZFC was achieved using a Zn pigment with flake-shaped particles.

The method for producing Zn powder with flake-shaped particles (lamellas) involves spraying a melt in air. After that, the resulting Zn particles are ground to a lamellar state and the desired size in ball mills in the presence of a lubricant. The length of Zn lamellas can be from 10 to 50 μm . The thickness of Zn particles is approximately 100–200 nm.

Due to the lamellar shape of Zn flakes, their specific surface area is 4–5 times larger (1.0–1.25 m^2/g) than that of spherical Zn particles. An additional advantage of flake-shaped Zn is that it provides the possibility of multiple points of contact between the particles.

The use of flake-shaped particles allows a significant increase in the surface area/volume ratio, which makes it possible to reduce the concentration of the zinc filler in the composite material without a loss of technological properties. The resulting Zn layer has increased ductility and electrochemical protection owing to the developed pigment surface [9].

It has been shown that the use of flake-shaped Zn particles instead of spherical ones has a number of indisputable advantages, such as a reduction in the amount of Zn required for cathodic protection to 30 mass.%; a higher degree of cathodic protection by the coating; the absence of defects and pores on the surface; reduced Zn sedimentation during storage; the possibility of reducing the number of applied paint coatings, and reduced paint cost.

Kruba and Stuker [10] describe the advantages of using ZFCs containing Zn with various surface structures, *i.e.*, spherical and lamellar, in comparison with the compositions filled with a spherical-shaped Zn powder.

It is known that in the case of spherical Zn, the protector properties are limited by the small number of electrical contacts between two adjacent powder particles, which requires a high degree of Zn filling.

It has been found that if a mixture of spherical and flake-like Zn powders is used, the number of possible electrical contacts in the coating increases by a factor of 3. This effect allows one to significantly reduce the degree of filling with Zn to 35–40% and, at the same time, ensure high protective properties of the coating. The recommended filling of the polymer formulation is 15 mass.% flaky Zn powder and 25 mass.% spherical Zn powder.

Addition of Zn flakes to anticorrosive polymer coatings ensures the formation of a non-porous structure of the protective coating, *i.e.*, a barrier effect is observed due to which no “white corrosion” caused by exposure to the environment is formed on the coating surface during operation. The barrier effect allows one to use primers without applying an additional coating.

The advantages of the ZFC described above include the improvement of the physico-mechanical and adhesive properties of the coatings (spherical particles provide hardness to

coatings, whereas lamellar particles provide elasticity) and a several-fold reduction in the consumption of the material required for painting.

The improved adhesion of mixed powder-lamellar coatings is associated with an increase in the sites accessible to the binder on the substrate surface, since powders are spherical and their contact plane with the substrate is a point, whereas lamellas contact by planar areas and displace the binder from the substrate surface to a greater extent.

It has also been found that if the ratio of the spherical and flake-like zinc filler is chosen correctly, mixed coatings may have better protective and adhesive properties than coatings filled with flake-like zinc only.

2.2. Surface modification of Zn pigment particles

An efficient method for reducing the degree of Zn filling in anticorrosive coatings without reducing the galvanic protection ability involves surface modification, namely, partial lyophilization of the surface of Zn particles. This treatment helps arrange the particles of Zn powder as disordered chains in the coating bulk.

Stepin *et al.* [11] describe the positive results of testing Zn-filled coatings based on an epoxy oligomer. The lyophilization of Zn particles incorporated in the ZFC was carried out using a lyophilizing agent, Silane 6040, containing an epoxy group. The lyophilizing agent is incorporated in a ZFC in the amount of 0.1–1.5% of the Zn filler mass.

It was found that the use of a lyophilizing agent promotes an increase in impact strength and coating elasticity and a decrease in Zn filling to 60–70% without declining the cathodic protection.

In order to improve the technological characteristics of Zn-organic formulations, the pigment component is modified. To do so, various structuring agents are added to a Zn powder, for example, Zn oxide, aluminum powder, bentonite [12–14], *etc.*

2.3. Combining a Zn pigment with hollow glass spheres and activators of Zn particles

It is known that only a fraction of metallic Zn finely dispersed in the anticorrosive layer is involved in the galvanic protection of the metal surface, that is, electrochemical protection is provided by Zn particles located in the adhesive layer with a thickness of 20...30 μm .

The thickness of the polymer ZFC layer is about 60...80 μm , thus, it turns out that the major fraction of the Zn filler is located too far from the surface of the metal being protected to allow their electrochemical oxidation. Accordingly, they are unable to provide efficient steel protection.

An increase in the galvanic effect without increasing the Zn content in the ZFC can be achieved by activating a larger number of Zn particles, owing to which the total electric current to the metal surface required for corrosion protection will increase.

It is possible to involve the entire Zn filler in the anti-corrosion process without increasing the Zn content in the epoxy system by modifying the filler composition with additional components, such as activators and hollow glass spheres. Conductive polymers (*e.g.*, polyaniline) added to a ZFC in amounts up to 1% are used as Zn activators [15].

When a coating is operated, Zn powder particles and Zn activators react with water and atmospheric oxygen contained in the environment, with activation of a greater amount of Zn in the coating, which significantly increases the efficiency of electrochemical protection.

Due to the close electrical contact between Zn particles and the substrate that is achieved by using a modifying additive, the efficiency of the protector action, the completeness of Zn consumption, and the overall efficiency and duration of corrosion protection by ZFPs increase considerably. At the same time, the mechanical strength and durability of the protective polymer coating also increase.

The added activator forms bridging bonds between Zn particles and glass microspheres. As a result, the ZFC acquires the ability to trap chloride ions by forming chloride salts around the glass spheres. As a result, the corrosion process slows down significantly since chloride ions are intercepted by the coating and cannot reach the steel surface.

The ZFC in question are also resistant to cracking under mechanical stress and abrupt temperature changes, which is explained by the ability of hollow glass spheres to hinder the growth of cracks.

In addition, products formed during the interaction of Zn powder particles and the Zn activator fill the space formed by a microcrack and prevent the transformation of a microcrack into a macrodefect. In other words, a self-healing effect is observed in the coating.

2.4. The use of nanoscale fillers in zinc-filled polymer materials

Fillers with particle sizes from a few nanometers to tens of nanometers are increasingly used in the preparation of nanocomposites.

Nanocomposites are unique materials. Their main differences from macro- and microcomposites are a huge specific area of the filler-matrix interface, a large volume fraction of the interface, and small average distances between the filler particles.

Table 1 shows the total number of atoms, the number of surface atoms, as well as their ratio in cubic crystalline particles with various sizes (for a simple cubic lattice and a lattice constant of 0.5 nm).

The filler distribution in the polymer matrix is largely determined by the interaction at the interface between an individual filler particle and the polymer medium [16]. It was assumed in the simulation that the filler is not distributed uniformly in a polymer melt, but both agglomerates and individual filler particles are surrounded by polymer layers. As particles move, the polymer layers are destroyed and electrical contacts are formed between particles or agglomerates. As a result, a three-dimensional conductive frame is formed from chain structures. It has been shown that the minimum filler amount required for that is determined by the expression:

$$v_f = \frac{0.61(1-c)\Phi_0}{\Phi_c} \cdot \left[\frac{x}{\left(\sqrt{\gamma_f} + \sqrt{\gamma_m}\right)^2} + y \right]$$

where $(1-c)$ is the volume fraction of the amorphous part in the polymer matrix at room temperature;

x is a value that depends on the molecular weight of the polymer;

y is a constant;

Φ , Φ_0 are coefficients taking into account the presence of adsorbed polymer layers on the surface of particles [17].

Table 1. Dependence of the number of atoms in cube-shaped crystalline particles on the particle size.

Cube edge length, nm	N (the number of atoms in a particle)	Ns (the number of surface atoms)	Ns/N
5	10^3	490	0.49
50	10^6	$5.9 \cdot 10^4$	0.059
500	10^9	$6 \cdot 10^6$	$6 \cdot 10^{-3}$
5000	10^{12}	$6 \cdot 10^8$	$6 \cdot 10^{-4}$

As one can see from Table 2, the fraction of surface atoms and the specific surface of particles increase sharply with a decrease in the particle size:

Table 2. Dependence of the number of surface atoms and specific surface of particles on the particle size

Cube edge length, microns	Number of particles per 1 cm^3	Specific surface, cm^2/cm^3
10^4	1	6
10^3	10^3	$6 \cdot 10$
1	10^{12}	$6 \cdot 10^4$
10^{-3}	10^{21}	$6 \cdot 10^7$

Several methods for the synthesis of polymer nanocomposites exist. Methods such as wet chemical reduction, sonochemical, microemulsion, laser-mediated, hydrothermal, microwave, and biogenic methods are used for synthesizing polymer nanocomposites in the practice of corrosion protection [18–21].

These methods may be classified into two groups: *ex situ* and *in situ* methods.

The *ex situ* methods include all approaches where nanoparticles are formed outside the polymer matrix, that is, the prepared nanoparticles are incorporated directly into the polymer base. The advantage of the group of *ex situ* methods is that it is possible to control the particle size, shape and density [22] and that they can be used in large-scale industrial production. The drawback is that it is difficult to distribute the nanoparticles uniformly in the polymer matrix and maintain long-term resistance to aggregation [23].

In situ methods involve the creation of nanoparticles directly inside the polymer matrix. The advantage of these methods include the simplicity of the technology, the absence of particle agglomeration and their good spatial distribution [24–26]. A disadvantage of *in situ* methods is that that unreacted educts may have undesired effects on the properties of the nanocomposite.

Incorporation of nanoparticles of an inorganic material into polymer matrices markedly enhances the corrosion inhibition [27, 28].

Combining nanostructured materials with environmentally friendly hybrid and/or organic polymers allows one to create a new class of coatings with enhanced efficiency and new functionality, for example, the self-repair capability [29].

The typical and most commonly used types of nanoscale fillers include:

- montmorillonite-based organoclays
- carbon nanofibres
- carbon nanotubes (single-walled, multi-walled)
- silicon nanooxide
- aluminum nanooxide
- titanium nanooxide
- nanometallic particles

2.5. Incorporation of montmorillonite as a modifying additive into ZFCs

Layered aluminosilicates are widely used in barrier nanocomposites that have a low permeability coefficient for gases and low molecular weight liquids. The filler particles are lamellar in shape, so gas molecules need to go through a long winding path in order to penetrate a film of a barrier nanomaterial.

Montmorillonite clays are most widely used for the preparation of clay-polymer nanocomposites. The efficiency of modifying zinc-filled polymer materials by means of montmorillonite is described in [30, 31].

Montmorillonite is a clay mineral belonging to the subclass of layered silicates. The chemical composition is unstable $[(OH)_4Si_8Al_4O_{20} \cdot nH_2O]$ and strongly depends on the varying water content. The crystal structure of montmorillonite is distinguished by a symmetrical configuration of layer stacks. Interlayer water molecules and atoms of Ca, Na and other exchange cations are arranged between the “pyrophyllite” packets. Montmorillonites are characterized by a large distance between the layer stacks. If wetted, this mineral swells strongly due to penetration of water into the gaps between the structure layers.

If Na^+ ions prevail in MMT, the clay exhibits hydrophilic properties, absorbs water and swells, while in the case of Ca^{+2} ions the clay has hydrophobic properties.

It was found that montmorillonite incorporated into a polymer coating can improve the mechanical and barrier properties of anticorrosion coatings and increase adhesion and hydrophobicity. In addition, studies have shown that montmorillonites are not inert

pigments. They perform two important functions: active inhibition of corrosion and control of H^+ penetration.

Studies performed by a team of Iranian scientists [32] have shown that addition of 1 wt.% of montmorillonite clay nanoparticles to epoxy-Zn coatings significantly increase the efficiency of steel cathodic protection.

Montmorillonite introduced into conductive polymers (polyaniline, poly(*o*-methoxyaniline), poly(*o*-ethoxyaniline), polycarbazole and polypyrrole), thermoplastic polymers (polymethylmethacrylate, polystyrene), thermosetting polymers (polyimide), as well as into epoxy resins, increased the protective properties of polymer coatings deposited onto various metal substrates in a number of corrosive environments [33–35].

2.6. Modification of the composition of ZFC by means of nanotubes

The possibility of using carbon nanotubes in multilayer coatings was considered in studies by Z. Iqbal *et al.* [36–38]. In those works, various types of passive and smart insulating anticorrosive coatings created by nanotechnologies were studied.

It was found that polymeric materials containing carbon nanotubes could form smart protective coatings with *p-n* conductivity between the layers, owing to which the corrosion process could be stopped at electrical level [39]. However, due to the high cost of nanotubes, they are currently not widely used in anticorrosive polymer coatings.

Nanotubes can be up to hundreds of microns long and 5–50 nm in diameter, though the shape of real nanotubes is often far from an ideal structure. CNTs can be represented by single-walled, double-walled, and multi-walled structures. Due to the high shape factor, carbon nanotubes are efficient as electrically conductive fillers [40].

Halloysite clay nanotubes filled with corrosion inhibitors (benzotriazole, 2-mercaptobenzimidazole and 2-mercaptobenzothiazole) are used in polymer coatings for the protection of copper alloys from corrosion caused by chlorides [41].

Incorporation of halloysite into a polymer coating gives it the self-repair capability in the case of crack initiation [42].

2.7. Incorporation of graphene and graphene oxide into zinc-filled materials

Modification of zinc-filled polymer coatings (ZFPC) with graphene is a promising method for providing a high degree of corrosion protection of metals. Graphene is an allotropic modification of carbon whose atoms form a two-dimensional hexagonal crystal lattice with a thickness of one atom. Graphene has a number of unique properties: high mobility of current carriers (which causes high electrical and thermal conductivity), flexibility, strength, hydrophobicity, and low density [43, 44]. Graphene nanoparticles have some similarity to carbon nanotubes in terms of characteristics, but the production of graphene nanoparticles is significantly less expensive.

Graphene/polymer nanocomposite coatings can be obtained by various methods (polymerization, solution mixing, micromechanical separation, melt compounding) [45–47].

It has been found that incorporation of graphene, even in small amounts, into a ZFC provides improved adhesion and electrical conductivity. The protective effect in such ZFCs is provided by the Zn filler even at late dissolution stages. In addition, the presence of graphene in paint coatings can increase their wear resistance. Studies on the efficiency of graphene incorporated into primers are described in the project “The Sixth Element”, (Changzhou) Materials Technology Co., Ltd. (Jiangsu, China).

A promising option for increasing the corrosion resistance of ZFC involves their modification with graphene oxide. Graphene oxide (GO) consists of graphene particles with oxygen-containing functional groups and/or molecules attached at the edges or inside the carbon network. Graphene oxides are significantly superior to polymer-based ion-exchange resins and other traditional sorbents in terms of the sorption capacity [48].

GO nanostructures in polymer coatings greatly enhance corrosion protection. GO particles are impermeable to water. The major fraction of the surface provides good barrier properties against oxygen diffusion [49].

A new strategy for improving the mechanisms of cathodic and barrier protection of ZFC, which involves the use of graphene oxide modified with polyaniline nanofibers, was reported [50].

Accelerated tests showed that incorporation of modified nanoplasts (GO-PANI) into a ZFC in an amount of 0.1 wt.% significantly improved its anticorrosion characteristics. The results obtained by SEM, FT-IR and XRD analysis showed a decrease in the degree of oxidation of Zn particles and corrosion rate of a steel substrate upon modifying a ZFC by graphene oxide with polyaniline nanofibers (GO-PANI) in comparison with other samples.

It was shown that incorporation of the GO-PANI modifying additive into the ZFC provides improved the electrical contact between the Zn particles and the steel substrate and decreased the electrolyte diffusion rate, which in turn resulted in a decrease in the rate of Zn oxidation, an increase in the cathodic protection of the ZFC, and an increase in the coating life time. An increase in adhesive strength was also noted.

The oxidation of spherical Zn particles gives corrosion products (Zn oxide). As a result, the porosity of a coating decreases. It has been shown that ZFC that contain no modifying additives are characterized by a considerable oxidation rate of Zn particles, higher density and, as a result, lower cathodic protection characteristics. In contrast, incorporation of GO-PANI modifying additives into ZFC results in a significant decrease in the oxidation rate of Zn particles.

2.8. Modification of ZFC with graphite

The use of carbon and graphite is caused by the combination of their electrical properties, chemical inertness and resistance to heating.

It is known that graphite particles cannot form chain structures. In addition, as the filler concentration increases, the physical and mechanical properties of the composite material deteriorate. Therefore, though natural graphite is inexpensive, it was not considered before as a promising electrically conductive filler. However, recent data on new filling methods may change this attitude.

It was found [51] that incorporation of strong electron acceptors (SbF_5 , AsF_5) into graphite, which results in intercalated (layered) graphite compounds, increases its electrical conductivity to values exceeding that of copper. The use of such compounds as electrically conductive fillers is extremely interesting in some applications.

2.9. Modification of the composition of ZFC by means of Zn nanoparticles

A metallic zinc pigment is the most expensive component in ZFCs; therefore, a scientific search for ways to reduce its content in anticorrosive coatings continues is continuing.

As described above, the content of Zn in ZFC can be reduced to 25 mass.% by using it in the form of scales, flakes, and their combinations with Zn dust. The simultaneous use of Zn particles with various shapes in a coating provides high cathodic protection and forms a barrier against penetration of a corrosive medium into the substrate, and also prevents the movement of corrosion products to the coating surface.

This fact allows us to conclude that the use of metallic Zn in the form of nanoparticles is a promising approach to the development of protector primers characterized by high physicochemical properties and low Zn consumption [52].

Studies on the protective properties of polymer coatings filled with a Zn nanoparticles have shown that primers filled with 1.2 and 5 vol.% of zinc nanoparticles, in comparison to a primer filled with zinc dust of standard size with a volume concentration of 67%, demonstrate resistance to salt fog for 42 days and their corrosion resistance is not inferior to the control sample [53, 54]. They are also more resistant to direct and reverse impact, have the best adhesion characteristics, as well as elasticity, chemical resistance and abrasion resistance.

However, a primer containing Zn nanoparticles that has good anticorrosive properties under salt spray conditions shows worse indicators concerning destruction along a cut and formation of blisters and does not provide the required cathodic protection on immersing the sample in an aqueous salt solution (NaCl , concentration 0.5 M). This fact indicates that the protection mechanism differs from the cathodic protection mechanism.

In [55], the beneficial effect from incorporation of nano-Zn and nano-clay particles into ZFC particles is described.

Currently, zinc nanoparticles are not widely used because of their high reactivity and high cost.

3. The use of selective modifiers and inhibitors in ZFCs

The efficiency of inhibitors is largely determined by their solubility in water. Limited solubility is the best variant, since if the inhibitor solubility is high, its anticorrosive activity

is exhausted in the first few months of the paint life. The dissolved part of the inhibitory additive reacts with the metal surface to form protective films that inhibit the corrosion processes.

Promising alternatives to the traditional anti-corrosion pigments include ion-exchange pigments whose action is based on the release of an inhibitory ion from the pigment in exchange for a corrosive ion, for example, sulfate.

In order to protect metals from corrosion, capsules were used that contained nanoscale reservoirs with a corrosion inhibitor incorporated into the polymer coating.

The shell of these capsules is created by layer-by-layer deposition of polymers (*e.g.*, gelatin, cellulose) or polyelectrolytes (*e.g.*, polyallylamine/polystyrene sulfonate) with opposite charges, *i.e.*, positively charged and negatively charged polyelectrolytes are alternated.

The resulting capsule shell is sensitive to a specific trigger, such as a change in pH, humidity, temperature, mechanical stress, magnetic or electromagnetic field. A change in pH is the preferred trigger, since it is known that corrosion processes result in local pH changes in the cathodic and anodic spaces. This, in turn, provides a controlled release of the corrosion inhibitor from the shell, *i.e.*, the inhibitor is released on demand.

Capsules of this kind can also be obtained using skeleton-forming nanoparticles of metal oxides, for example, SiO₂, ZrO₂, TiO₂, CeO₂, natural alumina, and nanotubes (carbon, silicon). Nanoparticles can be hollow or porous. Depending on this, the inhibitor is loaded into the cavity or into the pores of the solid substrate.

A positive experience of using layer-by-layer deposited nanocapsules in a protective coating for the protection of aluminum alloy AA2024 was reported in [56]. It is recommended to use benzotriazole, mercaptobenzotriazole, quinaldic acid or quinolinol as the corrosion inhibitor.

The use of nanocapsules created by layer-by-layer deposition in a protective polymer coatings makes it possible to create smart systems for metal corrosion protection that have the self-healing effect and increase the service life of paint coatings.

Self-healing occurs either due to the formation of protective layers of corrosion products that block the access of corrosive media and/or oxygen to active sites, or due to the formation of protective media by organic or inorganic corrosion inhibitors that are often incorporated into “smart” particles.

A technology for producing “core-shell” nanocontainers filled with benzotriazole (BTA) as the corrosion inhibitor by electrostatic self-assembly was reported [57].

Kaolinite and hematite particles were used as the core of nanocapsules. The resulting capsules are incorporated into protective ZFC. Tests of the protective coatings in 5% NaCl showed that nanocapsules created using kaolinite were advantageous.

A successful experience in modifying a water-borne zinc-filled primer coating based on an epoxy resin by incorporating microcapsules with corrosion inhibitors into it was reported [58–60].

The microcapsules consisted of an inert sorbent with an impregnated corrosion inhibitor (nitrilotrimethylphosphonic acid, NTP) and were coated with a polymer shell. Al_2O_3 was used as the inert sorbent. The size of the resulting capsules ranged from 10 to 50 microns. Microcapsules were incorporated into the composition of the ZFP. Epoxy resins are the optimal material for building a polymer coating matrix and the shell of microcapsules since they can be cured with different types of hardeners. This allows one to obtain coatings with different diffusion characteristics and provide a controlled release of a corrosion inhibitor [61] from the microcapsule to the zone being protected, thereby providing the necessary electrolyte composition inside the polymer coating during operation in a liquid medium.

The mechanism of action of a microencapsulated corrosion inhibitor is that during operation, the electrolyte penetrates into the polymer coating. Under certain conditions, it also begins to penetrate into the polymer shell of the microcapsules, thereby causing the diffusion of the corrosion inhibitor from the sorbent particles. In this case, an extremely important part in the ZFC modification is to provide the required rate of inhibitor diffusion through the polymer shell and create an efficiently functioning electrolyte composition between the metal substrate and the ZFC. One of the main tasks here is to slow down the steel corrosion rate and reduce the need for zinc dissolution. A diagram of operation of a microencapsulated inhibitor (Figure 1) and a photograph of the microcapsules obtained (Figure 2) are shown below.

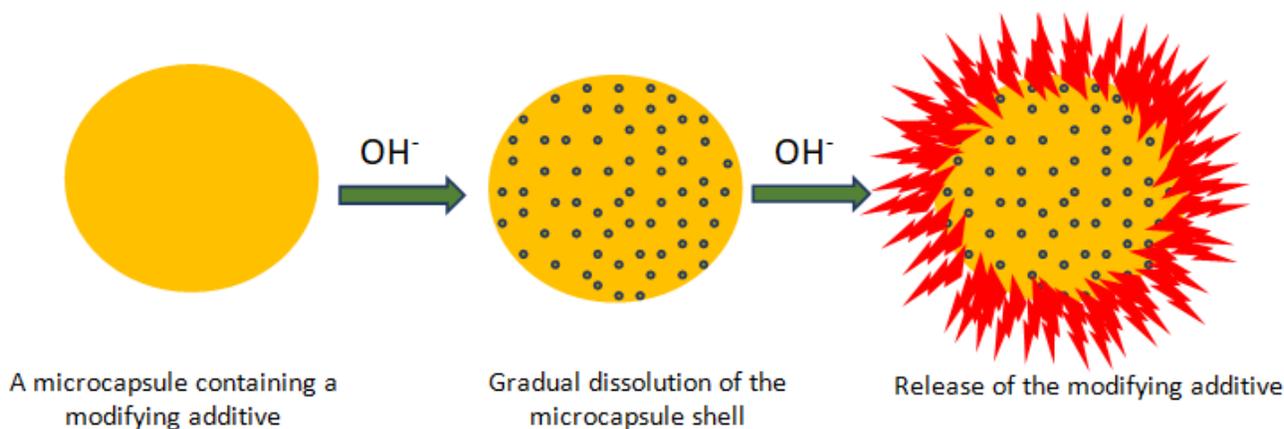


Figure 1. Scheme of operation of a microencapsulated inhibitor.

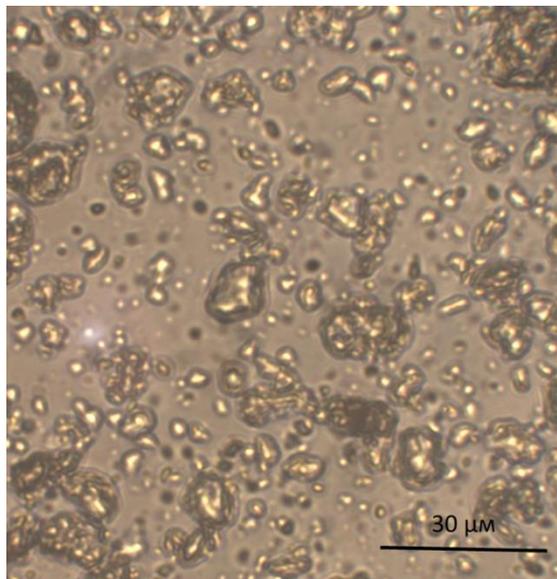


Figure 2. Photo image of microcapsules obtained using Al_2O_3 as the inert sorbent and NTP as the corrosion inhibitor.

4. Modification of ZFC with nanostructured layered double hydroxides (LDH)

A promising technology for modifying ZFC is described in [62]. The method involves the incorporation of nanocontainers into zinc-filled epoxy coatings (ZFEC). The nanocontainers consist of intercalated layered double hydroxides (LDH) with a corrosion inhibitor loaded into them.

Layered double hydroxides (LDH) are a class of natural and synthetic materials with general formula:



where M(II) and M(III) are cations of divalent and trivalent metals, such as Mg(II), Zn(II), Ni(II), Al(III), Fe(III), and Cr(III); A^{n-} is the interlayer anion, for example, nitrate, sulfate, or chloride anion; x is the fraction of trivalent metal ions in the LDH layer; and y is the number of water molecules in the interlayer space of the compound [63].

LDH layers can be arranged in different ways relative to each other [64].

An important property of LDH lies in their ability for intercalation (reversible incorporation of a molecule or group between other molecules or groups), which allows one to obtain materials with predetermined properties for specific practical purposes [65].

It has been found that addition of nanocontainers (LDH) to a ZFC results in strong inhibition of the corrosion of the carbon steel substrate due to smart capture of penetrating chloride ions and on-demand release of organic or inorganic corrosion inhibitors from the intermediate particle layers of LDH due to the presence of corrosive anions, namely, chloride ions [66].

Moreover, particles of layered double hydroxides have two-dimensional morphology and can partially block small pores in the coating, thereby providing efficient barrier

protection against the penetration of corrosive agents that stimulate the development of corrosion processes. Coatings of this kind are recommended for ensuring long-term corrosion protection of metal surfaces operated in industrial and marine environments.

5. Modification of the polymer base

Various methods of structural and chemical modification are used in the practical production of anticorrosive coatings to give them a required set of properties. For example, these include copolymerization [67, 68], incorporation of functional additives or synergistic combinations of compounds [69, 70], creation of composite materials [71], and layered application of functional coatings.

Copolymerization can be used to affect the solubility, porosity, and adhesive strength of a polymer [72, 73].

Numerous studies have shown that by mixing conductive polymers with polymers that are not electric conductors, it is possible to obtain coatings with excellent physicochemical, physico-mechanical and anticorrosive properties [74–76]. Modification of epoxy and alkyd coatings with a small amount of conductive polymers makes it possible to obtain coatings with improved characteristics, such as enhanced chemical resistance, high adhesion and corrosion resistance [77].

It should be noted that ZFP are typically used as part of multilayer coatings. It is important to note that a multilayer structure does not ensure complete isolation of the metal substrate from penetration of corrosive ions that cause the development of corrosion processes.

When multilayer heterogeneous coating systems are used, the lower layer typically performs anodic protection, while the upper layer has a barrier effect. The experience of using two-layer polypyrrole systems with polyphenol, organosilanes and poly(5-amino-1-naphthol), polyrodanine/isobutyltriethoxysylene, polyaniline/polybithiophene and polyaniline/poly(N-methylaniline) was reported [78–80]. They were shown to have better adhesive and anti-corrosion properties compared to the corresponding monolayer coatings.

Ultrasonic irradiation of two-layer coatings was suggested as a method for maintaining the substrate passivity [81].

A physical impact on a polymer coating during its formation, in particular, by ultrasonic irradiation, shortens the curing time and improves the physical and mechanical properties of coatings. Studies describing the positive experience of exposing polymer coatings to magnetic fields, IR and UV radiation during the curing are also available.

Recently, the number of studies on the possibility of replacing solvent-borne anticorrosive compounds with water-borne ones has been increasing. This trend is explained by the high toxicity, fire and explosion hazard of organic diluents, as well as a higher cost of solvent-borne materials. The results of comparative tests of water-borne and solvent-borne primer coatings modified with a microencapsulated corrosion inhibitor based on phosphonic acids MK-1 [82] are described in [83].

It has been found that the protective properties of water-borne primer coatings are higher than those of solvent-borne formulations.

The difference in the protective properties of the ZFC studied is explained by the significant effect of the differences in porosity of the coatings studied and the degree of interaction of the surface of Zn particles with the molecules of the film-forming compound [84].

6. Conclusion

To summarize the above material, it can be stated that the methods currently available to researchers for modifying polymer zinc-filled materials have all the prerequisites for creating a wide range of efficient coatings with a desired set of properties.

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