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Academic Research of the Protective Ability of Zinc-Filled and Epoxy Polyamide Paint Coatings against Atmospheric and Soil Corrosion

Abstract: Currently, zinc-filled coatings capable of providing protection against corrosion through a barrier and tread mechanism are becoming increasingly widespread. When exposed to an aggressive environment, the coating prevents steel corrosion by “healing” the damage. In this way, the corrosion process slows down, and the by-products formed during the activation of zinc are able to fill the space left by the defect. The article presents a description of the principle of “healing” with such coatings, as well as the results of laboratory and field tests carried out in order to study data on the effectiveness of protective characteristics in comparison with the traditionally used epoxy polyamide coating with parallel operation of electrochemical protection. It was noted that laboratory tests confirmed the “restorative ability” of the zinc-filled coating to prevent the formation of corrosion in places of applied defects.

Keywords: corrosion, paint and varnish coatings, corrosion protection, steel, zinc-filled coating.

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Introduction

In the process of pipeline transportation of oil and operation of oil trunk pipeline facilities, the issue of protecting metal structures from environmental influences and the occurrence of corrosion damage becomes vital. This factor can cause not only economic losses due to metal destruction, equipment downtime, and product loss, but also environmental damage due to oil release. Such critical production facilities as oil storage tanks, process pipelines and pipelines of the linear part of aboveground and underground construction operating under pressure are subject to corrosion destruction. To increase the maximum service life of these objects, both the active protection method is used - changing the electrochemical potential of the pipeline using cathodic protection means, and the passive protection method - applying anti-corrosion coatings to the metal surface.

Coatings insulate the metal and act as a protective barrier that prevents interaction with an aggressive environment. Such coatings must have resistance to chemical attack, abrasive wear, a high degree of adhesion and resistance to moisture. In addition, an important indicator is the durability of the coating, especially when operating equipment under conditions of electrochemical protection. Today, there are various types of protective coatings with different properties and composition. An important place is occupied by materials containing a metal component with a lower electrochemical potential compared to the protected metal, which are able to “work” simultaneously and according to the sacrificial protection mechanism (Pravin Deshpande, et al., 2021; Amrollahi et al., 2022; Chunping Qi et al., 2022; Kenzhaliyev, 2019).

Increasing the effectiveness of protection can be achieved by choosing the appropriate type of coating, taking into account the specific operating conditions of the equipment: type of metal being protected, weather and climatic conditions, corrosive components of an aggressive environment, probable mechanical impacts, etc. Considering the large length of oil trunk pipelines located in different climatic or soil conditions, safe oil pumping requires constant monitoring of the condition and increasing the degree of protection of equipment, pipelines and tank farms (Jinbao Huang et al., 2022; Kazakov & Grishina, 2022). In this regard, this article reflects work on comparing the protective properties of a two-component epoxy polyamide paint and varnish coating (hereinafter referred to as EPLP) and a zinc-rich paint and varnish coating (hereinafter referred to as TsLP) under operating conditions of electrochemical protection equipment for the purpose of possible use at production facilities.

Literature review (general information)

Nowadays, the protection of metal structures of main oil pipelines in open atmosphere conditions is provided by paint and varnish coatings. One example of an application is a two-component EPLP based on epoxy resins (Alibakhshi et al., 2022; Xiang Wang et al., 2021). Along with this, CLPs are becoming increasingly popular in the world, they provide protection against corrosion through the following mechanisms: tread, like traditional metal coatings, and barrier, like standard paint and varnish coatings. Sacrificial/cathodic protection is ensured due to the presence of zinc powder (particle diameter from 4 to 10 microns) with a low content of impurities and zinc oxides in the composition of the CLP. Thus, many iron-zinc micro galvanic couples are formed, capable of reacting upon contact with an aggressive environment, as a result of which zinc undergoes “sacrificial” dissolution with the formation of oxidation products (Figure 1). An important condition for tread protection is to ensure electrical contact of the zinc cluster with the steel surface, since when a defect is formed on the coating surface, zinc particles (cluster 2) begin to interact with the aggressive environment in the defect area, acting according to the cathodic mechanism (Wenting Xia et al., 2021). Anodic dissolution of zinc occurs, which proceeds until the defect and pores A are filled with the resulting poorly soluble zinc corrosion products, compacting them and stopping the access of the aggressive environment to the metal surface until the zinc particles dissolve. Thus, when a defect occurs, the steel is protected from corrosion by “healing” the damage.

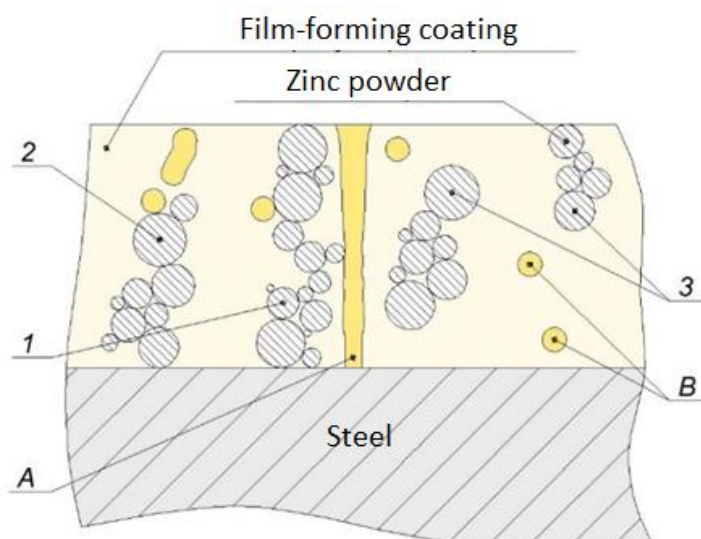


Figure 1. Main structural elements of the CLP: Pores: A – open (through); B – micropores;

At the same time, zinc is not an easy material to use and apply, which is characterized by clumping and settling in a short time. Poor coating preparation and surface contamination prevent the formation of contacting clusters of types 1 and 2 necessary for protection and their contact with the metal surface (Figure 1). Therefore, the main condition for the use of such coatings is abrasive blasting of the surface (up to Sa 2.5) and application of prepared and thoroughly mixed material. Protective protection is provided when the mass fraction of zinc particles is more than 65%.

Clusters are collections (chains) of zinc particles in contact with each other:

- 1 – infinite clusters, determined through conductivity, participate in the implementation of the tread protection mechanism immediately upon contact with an aggressive environment;
- 2 – clusters in contact with the base metal, but not coming to the surface, begin to actively influence the protective properties as the aggressive environment penetrates deep into the film;
- 3 – “hanging” clusters that are not in contact with the metal, and therefore do not participate in the operation of galvanic couples (Moradi et al., 2023; Lu Shen et al., 2022).

Experimental part

The protective ability of the coatings was determined using field and laboratory corrosion tests, which made it possible to identify the likely occurrence of defects and evaluate their behavior in specific corrosive environments.

The laboratory corrosion tests carried out are accelerated. During such tests, samples were exposed to artificial highly aggressive corrosive environments at high humidity and temperature. This causes accelerated destruction of the tested samples, which makes it possible to judge the presence of defects in the coating and predict, with varying degrees of reliability, its corrosion resistance under various operating conditions. However, due to the complexity of the ongoing corrosion processes, which depend on many factors and are not always amenable to accurate assessment, direct transfer of the results of laboratory or bench corrosion tests to the actual operating conditions of coatings in specific aggressive environments may not always be justified. Therefore, the results of accelerated corrosion tests of coated samples were compared with operating conditions in full-scale tests.

After receiving samples. Anti-corrosion coatings were applied to metal samples made of 17G1S steel. Before application, the samples were cleaned by abrasive blasting to Sa 2½ with an average roughness of 50-70 µm. Next, we coated the EPLP and TsLP.

Before application, the CLP was mixed to a homogeneous mass (with a drill with an attachment) and applied in three layers: the first - 20-30 µm dry film thickness (DFT), the second - 125 µm wet film thickness (WFT) or 60 µm DFT; the third – 125-150 µm TMP or 60 µm TSP, resulting in an average thickness of 140 µm TSP without taking into account roughness.

EPLP, having previously mixed the first component in the form of epoxy resin to a homogeneous consistency (with a drill with an attachment) and diluted the material with the hardener (second component) to no more than 10% of the volume, was applied in one layer of 180 µm TMS or 150 µm TSP.

Testing. In order to study the effectiveness of anti-corrosion protection of coatings, a visual assessment of the surface was carried out, adhesion was determined using the lattice notch method and changes in the thickness of coatings were determined based on the results of the following tests:

1) Resistance to static effects of liquids to determine the decorative and protective properties of coatings after exposure to liquids for a specified time. The test consisted of keeping the samples in the following liquids (Figure 2, a): 1) 12.5% sulfuric acid solution; 2) 12.5% potassium hydroxide. The desiccator with these liquids was placed in a drying cabinet heated to a temperature of (60±2) °C, and after 8 hours the desiccator was removed from the oven and kept at a temperature of (20±2) °C for 16 hours; 3) a 3% solution of “sea salt” (consisting of sodium chloride 75%, potassium chloride 4%, magnesium chloride 10%, calcium sulfate 5%, magnesium sulfate 6%) was kept at a temperature of (20±2) °C in within 24 hours.

2) Testing on the “Laboratory installation for modeling pipeline transport technologies” to determine the protective properties of coatings in a corrosive soil environment with the following parameters of the cathodic protection station (CPS): mode U = 0.1 V, I = 0.001 A; with a protective potential of -1.18 V; with natural potential without coating = -0.52 V. The electrical conductivity of the soil was 4998 µS/cm; Physico-chemical soil parameters: humidity in the range of 7-19%; chloride ions 15.5 mmol/100 g; sulfate ions 1260 mmol/100 g; pH = 6.098; Test time = 2515 hours.

The corrosion rate in a model soil environment for 17G1S steel without any coatings, determined practically, was: 0.08 mm/year without electrochemical protection (ECP) and 0.01 mm/year with ECP.

Steel samples (coated, uncoated, as well as with defects applied to the coatings in the form of a notch) were installed in a container with model soil at the ground-air interface, with some samples connected to the ECP system (Figure 2, c). The acid-base balance of soils was regulated by irrigating the soil with salt solutions and controlled by determining moisture content and chemical analysis of the soil. After testing for 2515 hours, the samples were removed from the ground to determine the decorative and protective properties of the coatings.

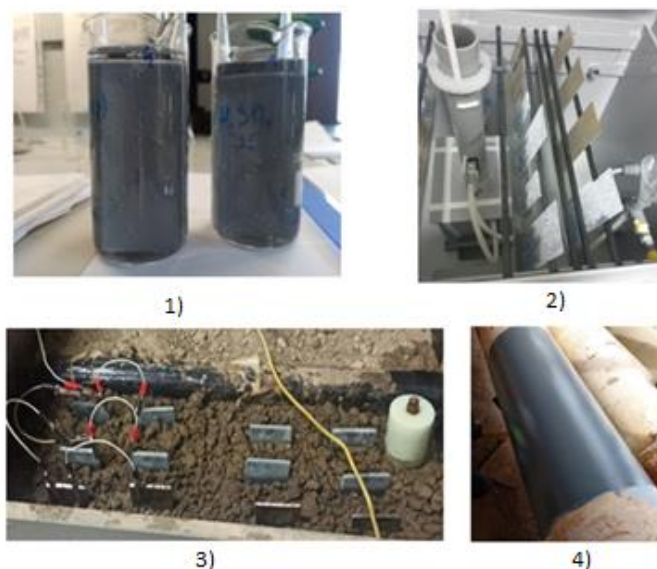


Figure 2. View of samples when tested for: 1) resistance to static effects of liquids; 2) for corrosion in an artificial atmosphere (salt fog); 3) laboratory installation for modeling pipeline transport technologies; 4) full-scale (real) conditions at production facilities

3) Testing under full-scale (real) conditions at production facilities. EPLP and TsLP were applied to above-ground process pipelines of the oil loading berth in Aktau (in marine atmosphere conditions) and under opposite conditions in the pump room at the oil pumping station in Ekibastuz at the initial section of the process pipeline with increased vibration (Figure 2, d). After 3689 hours (≈ 5 months), a visual assessment of the condition of the coating was carried out, and the thickness and adhesion of the coating were determined.

4) Corrosion test in artificial atmosphere (salt fog). The test samples were installed in a Biuged BGD 880 salt fog chamber with a spray of 5% sodium chloride solution in the pH range from 6.5 to 7.2 at a temperature of (35 ± 2) °C for 24 hours (Figure 2, b). After the tests, the resistance of the coatings to salt fog is determined by the spread of corrosion from the cut.

Results and analysis

Analysis of the surface condition of the samples after testing for resistance to static effects of liquids showed the following results (Figure 3):

CLP after exposure:

- in a solution of sulfuric acid has undergone a significant change, with almost complete peeling of the coating and the presence of general corrosion of the metal under the coating;
- in an alkaline solution there was a significant appearance of bubbles (swelling) on the surface, with the appearance of a large number of minor cracks (weak cracking) with no signs of corrosion;
- in a solution of “sea salt” showed a slight change in color and chalking of the coating.

EPLP after exposure:

- in a solution of sulfuric acid slightly changed color with the formation of general corrosion of the metal under the coating at the site of the defect;
- in an alkaline solution changed color without signs of corrosion;
- in a “sea salt” solution showed a slight change in color, but with the appearance of general corrosion of the metal under the coating at the defect site.

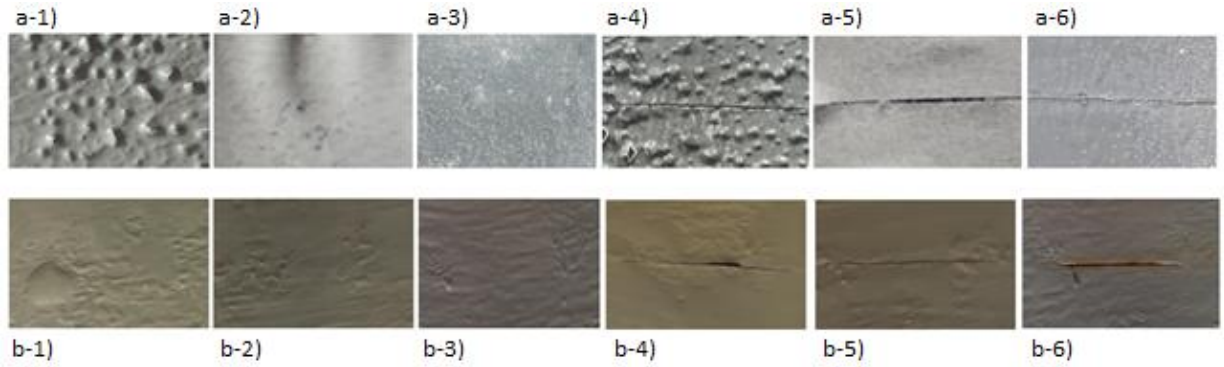


Figure 3. View of samples after testing for resistance to static effects of liquids

Samples with CLP without an applied defect: a-1) in an alkaline solution; a-2) in a solution of sulfuric acid; a-3) in a solution of “Sea salt”; with a defect applied: a-4) in an alkaline solution; a-5) in a solution of sulfuric acid; a-6) in a solution of “Sea salt”.

Samples with two-component EPLP without an applied defect:

b-1) in an alkaline solution; b-2) in a solution of sulfuric acid; b-3) in a solution of “Sea salt”; with a defect applied: b-4) in an alkaline solution; b-5) in a solution of sulfuric acid; b-6) in a solution of “Sea salt”.

The condition of the surfaces of the samples according to the results of testing in soil at the “Laboratory installation for modeling pipeline transport technologies” changed as follows (Figure 4):

- in samples with CLP with connected ECP, a change in color, absence of corrosion, slight cracking, and salt deposits were observed; without a connected ECP, a change in color was also noticed, but with the appearance of general corrosion and a moderate number of cracks.

- for samples with a two-component EPLP with a connected ECP, a slight change in color and no corrosion were observed; on samples with an applied defect without connecting an ECP, in addition to a slight change in color, the appearance of corrosion can be observed.

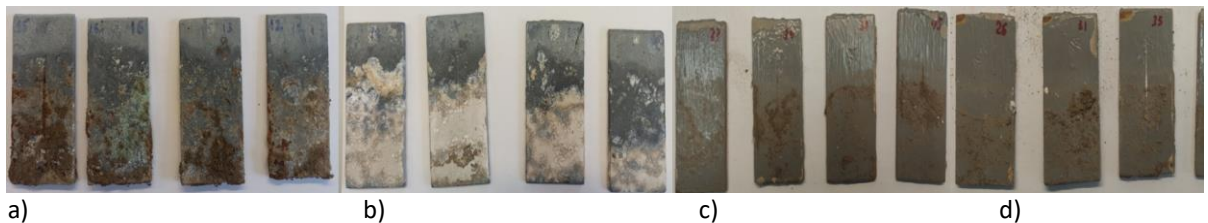


Figure 4. View of samples after testing on the “Laboratory installation for modeling pipeline transport technologies”: Samples with CLP: a) without ECP; b) with ECP. Samples with two-component EPLP: c) without ECP; d) with ECP

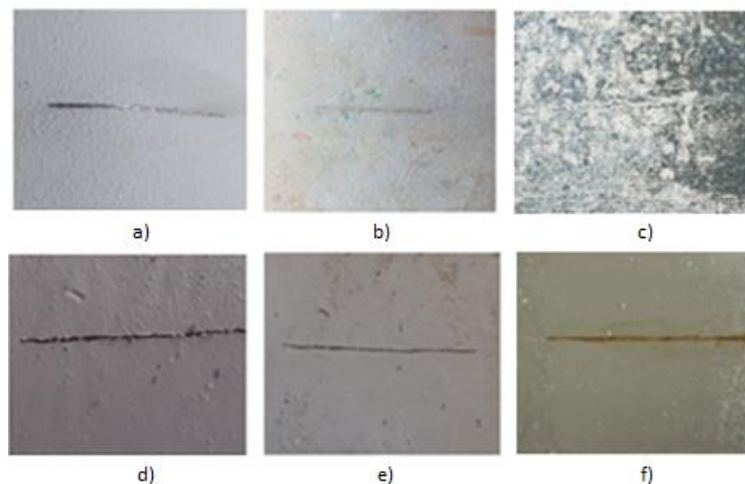


Figure 5. Type of samples: Samples with CLP: a) before testing under full-scale conditions; b) after testing under natural conditions; c) after testing in a salt fog chamber.

Samples with two-component EPLP: d) before testing under full-scale conditions; e) after testing under natural conditions; f) after testing in a salt fog chamber.

After testing the coatings in question under natural conditions at production facilities, the following result was obtained. The surface has a clearly visible color change, there are no signs of corrosion, including in places of applied defects (Figure 5, a, b, d, e). There is no change in coating thickness.

Based on the results of the corrosion test in an artificial atmosphere, it was noticed that corrosion products were present on the EPLP at the site of the applied defect (Figure 5, e). On the CLP at the site of the defect, a “self-healing” effect (overgrowing of the defect cavity) is observed without the occurrence of a corrosion process with a change in the color of the sample due to the formation of salt deposits (Figure 5, c).

Determination of the adhesion of coatings by the method of lattice cuts on samples after the tests showed the following results. EPLP after exposure to solutions of sulfuric acid and alkali has a slight partial peeling of the coating in the form of small flakes at the intersection of grating lines, exceeding 35% of the surface, and in the area of the applied defect there is complete peeling. CLP in solutions of sulfuric acid and alkali showed complete peeling of the coating. Based on the result obtained - a violation of the apparent continuity of the coatings - adhesion determination was not carried out on these samples (Figure 6, a-1, a-2). After exposure to the “sea salt” solution on both coatings, no signs of peeling were observed in any square of the gratings (Figure 6, a-3, b-3).

After testing the coatings in soil at the “Laboratory installation for modeling pipeline transport technologies”, the CLP showed only slight peeling of the coating in the form of small flakes at the intersections of the grid lines (Figure 6, a-4, a-5). Samples with EPLP that were under ECP showed both partial, exceeding 35%, and complete peeling at the site of the applied defect (Figure 6, b-4). EPLP samples placed without ECP show in some places complete peeling, in others partial peeling along the grid cut lines and at their intersections (Figure 6, b-5).

The adhesion of the two coatings after full-scale testing under production conditions showed satisfactory results, since the edges of the cuts remained completely smooth, without signs of peeling in any square of the lattice (Figure 6, a-6, b-6).

The adhesion of the two tested coatings after testing in an artificial atmosphere (salt fog) showed a good result without signs of peeling in any square of the lattice (Figure 6, a-7, b-7).

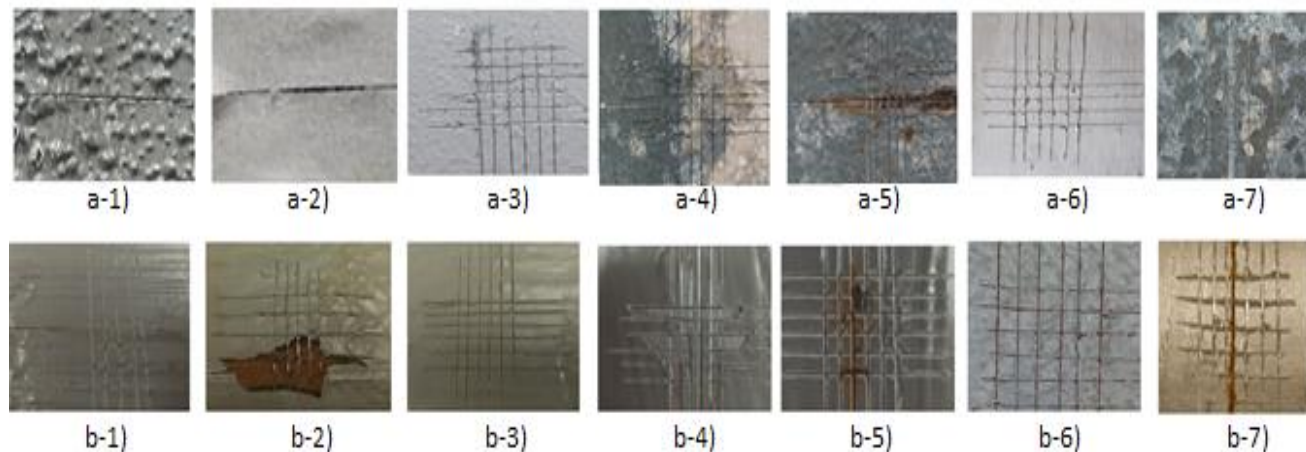


Figure 6. Determination of adhesion of paint and varnish coatings using the lattice cuts method. On samples with CLP: a-1) after a solution of sulfuric acid; a-2) after an alkaline solution; a-3) after the “Sea salt” solution; a-4) after tests in soil on a “Laboratory installation” with ECP; a-5) after tests in soil on a “Laboratory installation” without ECP; a-6) after testing under natural conditions at the production facility in Aktau; a-7) after testing in corrosion tests in an artificial atmosphere.

On samples with two-component EPLP: b-1) after a solution of sulfuric acid; b-2) after an alkaline solution; b-3) after the “Sea salt” solution; b-4) after tests in soil on a “Laboratory installation” with ECP; b-5) after tests in soil on a “Laboratory installation” without ECP; b-6) after testing under natural conditions at the production facility in Ekibastuz; b-7) corrosion tests in an artificial atmosphere.

After all tests, the thickness of the coatings did not show any significant changes in the direction of thinning. At some measurement points, thickening of the coating was observed due to salt deposition on the surface of the samples.

Results and conclusions

1. In the presence of a defect in an acidic solution and soil environment, samples with coated EPLP turned out to be the most susceptible to corrosion processes. Electrochemical protection significantly slows down the formation of corrosion products under these conditions. CLP in acidic and alkaline solutions is subject to complete or significant destruction with swelling, the appearance of cracks, ruptures, etc. From here, as a result of destruction, corrosion processes begin to occur. On the CLP placed under the ECP in the soil environment, a “self-healing” effect is observed without the appearance of signs of corrosion.

2. The coatings under consideration showed a good protection result after testing in air under natural conditions at production facilities.

3. When tested for corrosion in an artificial atmosphere, the protective properties of CLP prevail over the protective properties of EPLP due to the possibility of “self-healing” of defects (overgrowing of the defect cavity) without the corrosion process occurring.

4. Determination of coating adhesion after testing in corrosive environments confirmed the conclusions in points 1, 2, 3 and also showed corresponding results for all tests.

5. After testing the samples under field and laboratory conditions, no change in the thickness of the CLP and EPLP is observed.

6. It should be noted that the “restorative ability” of the CLP, confirmed during tests (tested on a “Laboratory installation for modeling pipeline transport technologies” and for corrosion in an artificial atmosphere or salt fog), is able to prevent the formation of corrosion in places of applied defects (provided that the aggressive environment influences gradually, or indirectly, as in the full-scale tests).

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