# Protective conversion coatings based on rare-earth compounds for passivation of galvanized steel

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## Abstract

The publication deals with the development of a process for applying protective conversion coatings containing rare earth metals (REMs) on the surface of galvanized steel to replace environmentally hazardous chromating processes. The compositions of solutions for the deposition of individual protective/decorative or adhesive coatings have been optimized, and the physicochemical and mechanical properties of coatings that might be potential alternatives to toxic chromate coatings have been studied. The addition of rare-earth metal (REM) compounds and citric acid to the solutions increases the protective ability, abrasion resistance, frost and heat resistance of the coatings being formed, and improves the appearance and thickness uniformity.

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## Introduction

Zinc coatings deposited using galvanic or hot methods are widely used to protect steel items from corrosion. Zinc coatings feature a high protective ability for steel and provide electrochemical protection against corrosion in humid atmospheres. These features are due to the more negative potential of zinc $(E_{\mathrm{Zn^{2+}/Zn}} = -0.76\ \mathrm{V})$ compared to that of iron $(E_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V})$. However, due to the high negative potential, zinc coatings have low corrosion resistance and rapidly degrade in corrosive environments. Passivation in solutions based on hexavalent chromium compounds is currently the most common way to enhance the corrosion resistance of zinc coatings, despite a serious drawback of this process, namely, the high toxicity of the solutions used. In the case of uncontrolled spilling of chromate solutions into the environment (for example, due to accidents, leaks, or terrorist attacks), the chromate ions that they contain cause serious environmental damage [1, 2]. Passivating chromate coatings also contain toxic Cr(VI) compounds, *i.e.*, chromium and zinc hydroxochromates. For example, chromated parts of modern cars contain up to 200 mg/m$^2$

of hexavalent chromium, which is detrimental to people in contact with them and the environment [3–5].

By now, laws have been adopted in most developed countries that restrict or completely prohibit the use of Cr(VI) compounds in engineering and electronics products [6–11].

Another significant drawback of chromating processes is the low thermal stability of the coatings created: if they are heated to 160°C or higher, their protective ability decreases sharply, which is unacceptable for parts operating in “hot spots”, for example, in the engine compartment of a vehicle.

Passivation in solutions based on compounds of less toxic trivalent chromium has not found wide practical application, since the resulting passivating films fail to meet the requirements for mechanical strength, protective ability, and self-regeneration [12–14].

More promising in this respect are relatively new modern 4th generation chromitization processes followed by deposition of a finishing layer from solutions with silicon-containing nanoparticles, which is incorporated in a film to form a very thin top coating of nanoparticles, or sealing in the so-called sealers, *i.e*., film-forming organic compounds. Fourth-generation chromite coatings can, similarly to chromate films, self-regenerate and withstand up to 300 hours until white rust corrosion. However, these processes are not yet widely used in practice due to the relative complexity of implementation and control, and the high cost compared to chromating.

Given the tightening of environmental requirements for products of mechanical engineering and electronics, it is planned to limit the use of toxic compounds of such metals as nickel, cobalt, and chromium in the application of protective and decorative coatings on galvanized items. Therefore, the development of methods to obtain conversion coatings on zinc comprising no compounds of these metals is an urgent task [15, 16].

To replace the chromating process for application of protective and decorative coatings on galvanized steel, molybdate- [17–20], vanadate- [21–23], silicon- [24–27] or titanium-, zirconium-containing coatings [28] can be used [28–33]. However, molybdate and vanadate coatings are significantly inferior to chromate layers in protective ability, while silicon-titanium-, and zirconium-containing coatings have not yet become widespread in practice.

Inhibitors of galvanized steel corrosion that are alternative to chromates include salts of rare earth metals, in particular, cerium and lanthanum, which are environmentally safe and fairly efficient corrosion inhibitors of such metals as aluminum and zinc [5, 34–40]. Taking this into consideration, conversion coatings based on compounds of rare earth metals may be a replacement for conversion chromate coatings.

It should be noted that in some cases, the list of requirements for passivating layers on zinc includes the lack of color (similarly to colorless chromate coatings), while they should not be inferior to iridescent chromate layers in terms of protective ability.

In this work we studied whether it is possible to obtain coatings with such a set of properties from solutions containing rare-earth metal ions to replace the environmentally hazardous chromating processes.

## Experimental

Galvanized plates of cold-rolled steel of 08ps grade from which car bodies and other car parts are made were used as the samples. Zinc plating was carried out in a weakly acid electrolyte with the following additives: $ZnCl_2$ 60–120 g/L; $NH_4Cl$ 200–220 g/L; $H_3BO_3$ 20 g/L; and TsKN-3 (brightening agent) 30 ml/L; pH 4.5–6.0; $t$=18–30°C; $i_c$=1.0–2.0 A/dm$^2$. The electrolyte was prepared from "pure" and "analytically pure" grade reagents and distilled water.

The following solution was used to deposit colorless chromate coatings selected for comparison: TsKN-25 18–22 g/l; $HNO_3$ 5–15 ml/L; $t$=18–30°C; pH 1.1–1.8; $\tau$=20–40 s; $t_{drying}$=50–60°C.

The following solution was used to deposit iridescent chromate coatings selected for comparison: TsKN-23 40–60 g/L; $H_2SO_4$ 1–5 ml/L; $t$=15–30°C; pH 1.5–2.0; $\tau$=20–90 s; $t_{drying}$=50°C.

The conversion solutions based on REM compounds were prepared from nitrate salts of cerium, lanthanum, yttrium, and neodymium with addition of hydrogen peroxide and an organic acid.

The protective ability of the coatings was determined by the drop method according to GOST 9.302-88 using a 5% solution of lead acetate. In this method, the protective ability of the coating is evaluated as the time (in seconds) until the appearance of zinc corrosion products, which is observed as a change in the color of the surface area under the drop from gray to black.

Color characteristics were measured using a portable X-Rite series Ci6x spectrophotometer by the CIELAB method, which presents color in three-dimensional coordinates: $L^*$, $a^*$ and $b^*$, where $L^*$ is the brightness. The value $L^*=0$ implies that no light is reflected from the sample (completely black), while $L^*=100$ corresponds to complete reflection of incident light (completely white). Coordinate $a^*$ is a measure of the intensity of the green (negative) or red (positive) component of the spectrum in the range from –120 to +120, and $b^*$ is a measure of the intensity of the blue (negative) or yellow (positive) component in the range from –120 to +120. The sample color was recorded by plotting a point in three-dimensional Lab space (Figure 1). The color difference was automatically calculated in comparison with the reference color (chromatic coating) in Lab coordinates and in percent.

To determine the coating thickness using a Sentech SEN research 4.0 SER 800 ellipsometer with a fast monochromator, the values of ellipsometric parameters $\Psi$ and $\Delta$ were plotted as functions of the wavelength in the spectral range from 240 to 1000 nm at a goniometer angle of 70°. The three-layer model used for the calculations comprised two Drude–Lorentz layers and one Cauchy layer. The model parameters (thickness $d$ and refractive index $n_2$) were determined using the measured values of $\Psi$ and $\Delta$ (the so-called inverse ellipsometry problem) by the software of the instrument in accordance with the selected mathematical model. The calculated result was considered valid if the parameters of the physical model matched those of the mathematical model and were not beyond the limits of specified errors [41].

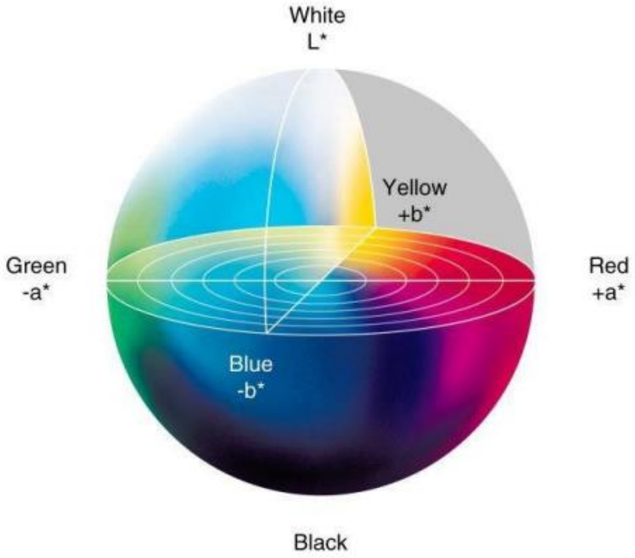


**Figure 1.** 3D ($L^*$, $a^*$, $b^*$) coordinate system.

Polarization measurements were performed using an Autolab PGT302N potentiostat operating in potentiodynamic mode in 3% NaCl solution at a scan rate of 0.5 mV/s. Samples of galvanized steel with coatings being developed were used as the working electrodes. The electrode potentials were measured with respect to the silver chloride electrode, and the values were recalculated to the standard hydrogen scale. A graphite electrode was employed as the auxiliary electrode. The Tafel extrapolation method was used to determine the corrosion potential $E_{\text{corr}}$ and corrosion current density $i_{\text{corr}}$ [42, 43]. The $E_{\text{corr}}$ and $i_{\text{corr}}$ values are defined as the coordinates of the intersection points of the extrapolated anodic and cathodic Tafel segments of the polarization curves.

To assess the thermal stability of the coatings, they were subjected to thermal shock, *i.e.*, heating in an ShS-80-01 SPU oven for 1 h at a temperature of 160°C followed by cooling in air. After the treatment, their protective ability was determined. Coatings were considered heat-resistant if the reduction in protective ability as a result of thermal shock was insignificant (less than 5%).

The frost resistance of the coatings was determined using the Arctico laboratory horizontal freezer, in which the samples were kept for 1 hour at temperatures of –30 to –60°C. After that, their protective ability was determined.

The wear resistance of passivating coatings was studied using a modified rotary Taber Elcometer 5135 abraser. Flat samples with the coatings under study were attached to the arms of the device and pressed against a felt disk with an equal pressure of 3.5 N/cm$^2$. The samples were abraded by a felt disk rotating at a speed of 60 rpm. The abrasion resistance of the samples was evaluated by the number of revolutions of the disk until the coating thickness determined by the ellipsometric method decreased to zero.

The strength of coating adhesion to the substrate was determined by the normal pull-off method using a PosiTest AT digital adhesion meter. The method is based on measuring the minimum breaking stress required to separate or break the coating in the direction perpendicular to the base surface [44].

Corrosion resistance was tested in an Ascott S450iP salt spray chamber in accordance with the international standard ASTM B117. The depth of corrosion propagation from a notch was evaluated immediately after the end of a test. The samples were washed with water and dried with filter paper. The paint-and-lacquer coating (PLC) was then carefully separated from the sample surface using a knife blade held at an angle to the separation surface between the coating and the painted surface. The PLC was softened with a special Elcon S® paint remover in accordance with the usage instructions and then removed from the sample by carefully peeling off the exfoliated coating with a knife blade or spatula, without damaging the area adjacent to the notch.

The corrosion propagation depth was measured at no less than six points evenly distributed along the notch. The depth of corrosion propagation from the notch was determined as the mean value calculated taking into account the maximum damage every 10 mm of the notch line (ISO 9227). In addition, according to the ASTM D 1654-08 standard, the width of underfilm corrosion propagation was evaluated, and a score from 0 to 10 was assigned (the higher the score, the higher the protective ability) [45, 46].

## Results and Discussion

Previously, a solution based on lanthanum and neodymium nitrates and gallic acid was developed at the Department of Innovative Materials and Corrosion Protection of the Mendeleev Russian Chemical Technical University [47], which makes it possible to deposit coatings whose protective characteristics are comparable to those of chromate passivating coatings (Table 1).

**Table 1.** Working solution composition and process parameters.

| Component | Concentration |
|---|---|
| $La^{3+}$, g/L, as $La(NO_3)_3 \cdot 6H_2O$ | 2.5 |
| $Nd^{3+}$, g/L, as $Nd(NO_3)_3 \cdot 6H_2O$ | 0.5 |
| Gallic acid, g/L | 8.5 |
| $H_2O_2$, mL/L | 10 |
| **Process parameters** | |
| pH=3, $t$=25°C; $\tau_{\text{formation}}$=90 s; $t_{\text{drying}}$=80°C | |

However, the resulting coatings were not colorless: the deviation from colorlessness measured using an X-Rite series Ci6x handheld spectrophotometer was 19%. We have experimentally established that the color of the coatings depends on the acid present in the solution. After testing a number of acids, we have found that the smallest deviation from colorlessness (6%) compared with a colorless chromate coating is shown by the coatings formed in the presence of citric acid at a concentration of 2.0 g/L. It should be noted that such a deviation from colorlessness compared to the reference colorless chromate coating is virtually indistinguishable visually.

The possibility of enhancing the protective ability of coatings by introducing ions of a third rare-earth metal into the conversion solution was studied. Table 2 shows the compositions of the tricationic solutions studied and the process parameters. The total concentration of REM ions did not exceed 3 g/L of the metals, like in the dicationic solution. It should be noted that in the absence of citric acid in the solution, uneven and inhomogeneous coatings were deposited.

**Table 2.** Working solution compositions and process parameters.

| **Component** | **Concentration** | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| $La^{3+}$, g/L, as $La(NO_3)_3 \cdot 6H_2O$ | 2.5 | 2.5 | 2.5 | 2.5 |
| $Ce^{3+}$, g/L, as $Ce(NO_3)_3 \cdot 6H_2O$ | – | 0.4 | – | 0.4 |
| $Nd^{3+}$, g/L, as $Nd(NO_3)_3 \cdot 6H_2O$ | 0.1 | 0.1 | 0.1 | – |
| $Y^{3+}$, g/L, as $Y(NO_3)_3 \cdot 6H_2O$ | 0.4 | – | 0.4 | 0.1 |
| Citric acid, g/L | – | 2 | | |
| $H_2O_2$, mL/L | 10 | | | |
| **Process parameters** | | | | |
| pH=2.5–3; $t$=30°C; $\tau$=90 s; $t_{drying}$=80°C | | | | |

Figure 2 shows that the coatings with the appearance closest to that of a colorless chromate include the La–Y–Nd, La–Ce, and La–Ce–Y containing coatings, with the color deviation from the reference being 1.19, 1.95, and 2.54%, respectively. The La–Y–Nd containing coating was found to be the best one in terms of protective ability (110 s).

Ellipsometric measurements have shown that, regardless of the nature of the organic acid (citric/gallic), the thickness of the coatings formed in the conversion solutions studied is 180–230 nm, which is about 5 times less than that of chromate coatings, while they are not inferior to the latter in terms of protective ability.

Studies of the wear resistance of the coatings have shown (Figure 3) that the La–Ce–Nd and La–Ce–Y containing coatings feature the best wear resistance (3600 cycles until complete abrasion of the coating).

Corrosion diagrams and corrosion current values measured using a high-precision Autolab PGT302N potentiostat are shown in Figure 4 and Table 3. Since the corrosion diagrams are processed and the tangents to the Tafel sections of polarization curves are plotted by the potentiostat software, the error in corrosion current determination is minimized.

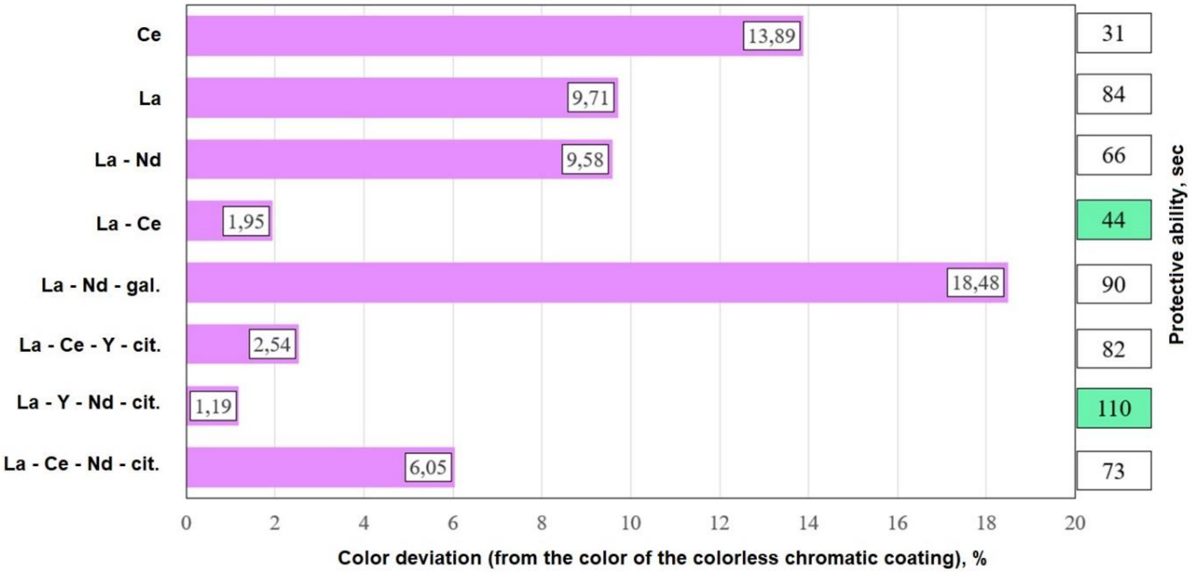


**Figure 2.** Color characteristics and protective ability of the coatings.

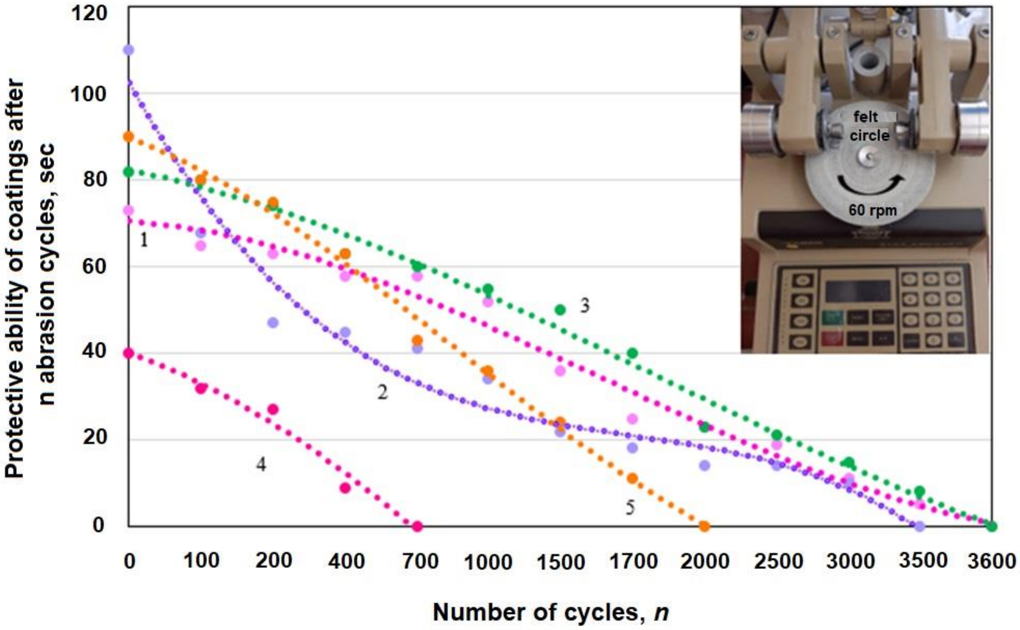
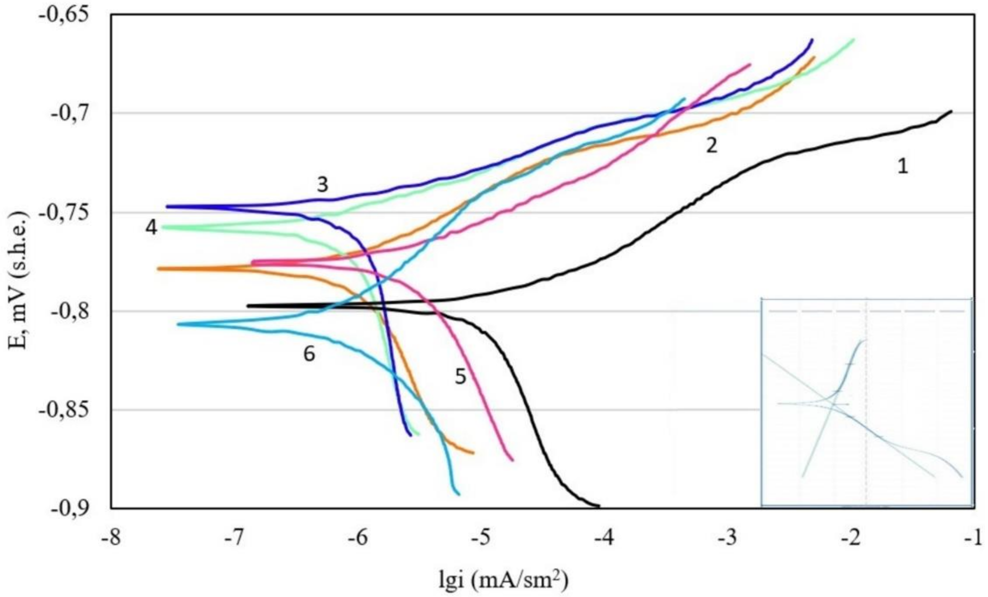


**Figure 3.** Protective ability of the coatings after *n* abrasion cycles. 1. La–Ce–Nd–cit.; 2. La–Y–Nd–cit.; 3. La–Ce–Y–cit.; 4. Cr(VI); 5. La–Nd–gal.

Comparison of the corrosion currents of a zinc coating with a passivating conversion coating shows that, in what regards the protective ability, the La–Y–Nd-containing coating is comparable to the iridescent one and is superior to the colorless chromate coatings, the corrosion currents being $9.11 \cdot 10^{-7}$, $7.68 \cdot 10^{-7}$, and $1.01 \cdot 10^{-5}$ A/cm$^2$, respectively (Table 3).



**Figire 4.** Corrosion diagrams of galvanized specimens with conversion coating: 1. Zn without coating; 2. La–Ce–Nd–cit.; 3. La–Ce–Y–cit.; 4. La–Y–Nd–cit.; 5. colorless chromating (TsKN-25); 6. iridescent chromating (TsKN-23).

**Table 3.** Corrosion rate of galvanized steel with conversion coating.

| Coating | $I_{corr}$, A/cm² |
|---|---|
| Without a coating | $1.61 \cdot 10^{-4}$ |
| La–Ce–Nd | $1.25 \cdot 10^{-6}$ |
| La–Y–Nd | $9.11 \cdot 10^{-7}$ |
| La–Ce–Y | $1.54 \cdot 10^{-6}$ |
| Iridescent chromate coating | $7.68 \cdot 10^{-7}$ |
| Colorless chromate coating | $1.01 \cdot 10^{-5}$ |

The results of corrosion tests in a salt spray chamber (GOST ISO 4042-2015) correlate with the electrochemical studies (Figure 5). The La-, Y-, and Nd-containing coatings have the highest protective ability: 86 hours until “white” corrosion (corrosion of galvanized steel) and 260 hours until “red” corrosion (corrosion of steel).

To determine the possibility of using the coatings at high and low temperatures, the samples were subjected to thermal treatment. The experiments were carried out at the same time at an absolute air humidity of 60% in the laboratory room.

It was found that heating galvanized specimens with a deposited conversion coating to 160°C led to a slight decrease in the protective ability of REM-containing coatings, while chromate coatings virtually lost their protective function (protective ability 5 s).

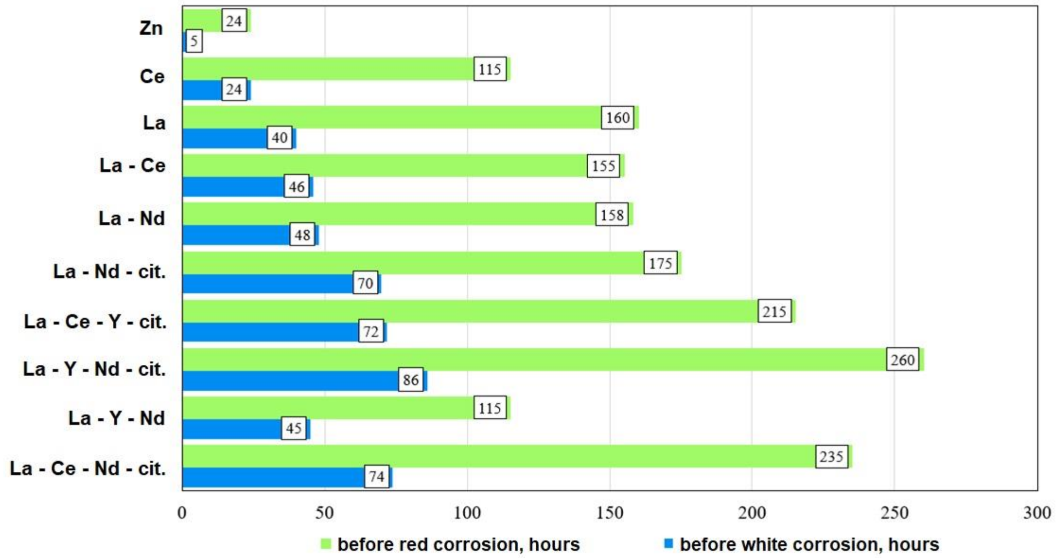


**Figure 5.** Results of corrosion tests in a salt spray chamber (ISO 9227; GOST ISO 4042-2015).

Electrochemical methods were used to determine the corrosion rate of galvanized steel samples after exposure to negative temperatures (minus 40°C) in comparison with that of non-cooled samples. Table 4 shows that the corrosion rate of galvanized steel with the conversion coatings containing La–Ce–Nd and La–Ce–Y decreases by an order of magnitude after exposure to negative temperatures, while in the case of La–Y–Nd-coating it decreases about 3-fold, due to which they are attractive for application at negative temperatures.

**Table 4.** Corrosion rate of galvanized steel with conversion coating before and after exposure to negative temperatures.

| **Coating** | **No exposure to negative temperatures** | | **After exposure to negative temperatures (–40°C)** | |
|---|---|---|---|---|
| | **$I_{corr}$, A/cm$^2$** | **Conversion coating, mm/year** | **$I_{corr}$, A/cm$^2$** | **Conversion coating, mm/year** |
| La–Ce–Nd | $1.25\cdot10^{-6}$ | 0.039 | $2.22\cdot10^{-7}$ | 0.006 |
| La–Ce–Y | $1.54\cdot10^{-6}$ | 0.046 | $1.79\cdot10^{-7}$ | 0.005 |
| La–Y–Nd | $9.11\cdot10^{-7}$ | 0.037 | $3.85\cdot10^{-7}$ | 0.011 |
| Colorless chromating | $1.01\cdot10^{-5}$ | 0.291 | $9.91\cdot10^{-7}$ | 0.029 |
| Iridescent chromating | $7.68\cdot10^{-7}$ | 0.022 | $2.46\cdot10^{-7}$ | 0.007 |
| Zn without coating | $3.81\cdot10^{-5}$ | 1 | $6\cdot10^{-6}$ | 0.182 |

The possibility of using the developed coatings as an adhesive sublayer under paints was examined. To this end, a digital adhesion meter (pull-off method) was used to determine the adhesion of the PLC to the zinc base with an adhesive sublayer. The adhesion strength of PLC to a zinc base with the developed REM-containing adhesive coatings was found to be higher than to a chromated zinc substrate. Adhesion reduction (%) after 240 hours of corrosion testing in a salt spray chamber was 8% and 16%, respectively.

Corrosion testing of zinc samples painted with polyester powder paint and conversion coatings applied showed that the developed coatings meet the requirements for adhesive layers in terms of protective ability, since the depth of corrosion penetration under the PLC from the notch point does not exceed 2.0 mm after 240 hours of testing. In the absence of an adhesive layer, corrosion penetrates by 6.2 mm, while in the case of a chromated zinc coating, by 0.13–0.2 mm (Table 5).

**Table 5.** Results of corrosion testing of painted samples with an adhesion sublayer.

| No. | Coating | Width of corrosion propagation from the notch, h (ISO 9227) | Evaluated corrosion propagation from the notch (ASTM D 1654-08) | |
|---|---|---|---|---|
| | | | Width of corrosion propagation from the notch, mm | Classification (from 0 to 10) |
| 1 | La–Ce–Nd–PLC | 0.8 | 1.1 | 7 |
| 2 | La–Y–Nd–PLC | 0.08 | 0.05 | 10 |
| 3 | La–Ce–Y–PLC | 0.15 | 0.2 | 9 |
| 4 | Colorless chromating | 0.2 | 0.18 | 9 |
| 5 | Iridescent chromating | 0.13 | 0.1 | 9 |
| 6 | Zn | 6.2 | 6.8 | 4 |

The smallest depth of corrosion propagation under the PLC film from a notch is observed in samples with adhesive chromate and La–Y–Nd-containing coatings, which corresponds to class 10 on a ten-point scale set by the US standard.

## Conclusions

Solutions for colorless passivation of galvanized surfaces have been developed. They contain:

- $La^{3+}$ 2.5 g/L, $Y^{3+}$ 0.4 g/L, $Nd^{3+}$ 0.1 g/L, $H_2O_2$ 10 mL/L, $H_3Cit$ 2 g/L;
- $La^{3+}$ 2.5 g/L, $Ce^{3+}$ 0.4 g/L, $Y^{3+}$ 0.1 g/L, $H_2O_2$ 10 mL/L, $H_3Cit$ 2 g/L,
- pH 2.5–3, $t=30°C$, $\tau=90$ s, $t_{drying}=70–80°C$, $\tau_{drying}=10–15$ min

The color of the conversion coatings formed is similar to that of colorless chromate coatings, and, in terms of protective ability, they are comparable to iridescent ones.

The developed coatings withstand exposure to high and low temperatures without degrading of their performance.

The coatings developed can be used as an alternative to toxic chromate coatings on zinc.

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