Electrochemical properties of Zn-rich primers and composite coatings on various metal substrates

V.A. Golovin,* S.A. Dobriyan, V.A. Shchelkov and A.I. Shcherbakov

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation

**E-mail: golovin@rocor.ru*

Abstract

The peculiarities of formation of the potentials of metal substrates (Steel-3, Zn, and Pt) with Zn-rich primers deposited both individually and as a component of composite coatings with an upper insulating layer were studied. It was shown that upon long-term exposure to a 3% NaCl solution, the potentials of the composite coatings deposited to all the substrates were more positive than those established if primers alone were used. With an increase in exposure time, the potential of the substrate under a coating grew both in the case of solvent- and water-borne composite coatings. Temperature is an essential factor determining both the value and kinetics of the potential of substrates under composite coatings. At low temperatures, the corrosion protection properties of the composite coatings were poorly expressed, as distinct from that when only the primer was used. At low temperatures, the composite coatings are mostly exploited at positive potentials of the steel substrate. An increase in temperature radically activated the corrosion protection properties of the composite coatings, despite a growth in the impedance of the primers at temperatures close to +60°C. The potential of protective additives both for a primer itself and Zn-rich primer as a component of the composite coating system was estimated.

Keywords: *corrosion protection, polymer coatings, Zn-rich primers, EIS.*

Received: October 28, 2019. Published: January 23, 2020

doi: [10.17675/2305-6894-2020-9-1-4](https://doi.org/10.17675/2305-6894-2020-9-1-4)

Introduction

Protective Zn-rich primers are efficient protective polymer materials due to their inherent protective properties, ease of application, and long service life [1, 2]. The search for comprehensive ways to improve the operability of composite coatings with protective primers under severe operating conditions is relevant. This improvement can be achieved by implementing the most efficient electrochemical (protection) mechanism in combination with the effect of increased protection properties in the process of interaction with the corrosive environment [3].

When assessing the efficiency of protection, it is customary to use either the protective current density or the protective potential. In the case of polymer coatings that possess high ohmic resistance, it is almost impossible to determine the protective current density. Therefore, the protective effect is estimated in practice through the potential of a substrate

combined with the impedance of a coating film. The latter is determined both by the initial properties of the coating material and the value of sorption of the environment, taking into account the change in the chemical composition of the internal electrolyte solution compared to the external solution and the accumulation of corrosion products.

It is believed that a necessary condition for the protection mechanism of Zn-rich primers during operation involves the generation and stability of chains formed by particles of zinc powder that are in electrical contact with each other and with the metal substrate being protected [4, 5]. These contacts arise when the content of zinc is 50 vol.% (or 86 wt.%), provided that the filler is distributed homogeneously. However, heterogeneity in the distribution of the filler always exists in real highly filled systems, which results in the formation of Zn-chains when the zinc volume content is as low as about 48% [6]. Obviously, an increase in the content of zinc powder should increase the conductivity and electrochemical activity of protective coatings, but, on the other hand, it decreases the insulating and physicomachanical properties, which is undesirable.

In addition, the protective mechanism is significantly affected by the shapes [7, 8] and sizes of zinc particles, in particular, nanoparticles [9, 10].

The type of the polymer matrix is also of great importance since polymers with high adhesion, such as epoxy polymers, block a considerable fraction of the surface of the zinc filler. Another significant factor is the presence of reactive additives like water that facilitate or inhibit corrosion in the formulation.

And finally, the question of the effect of both electrochemical properties and the state of the metal substrate being protected on the sacrificial action of protective coatings is still open.

The aim of the work was to establish the specific features of the formation of the potentials of metal substrates of different nature being protected under Zn-rich primers and composite polymer coatings in NaCl solutions at various temperatures.

Experimental

Objects and methods of the study

Objects of the study

The following two types of Zn-rich polymer primers manufactured by NPO ROKOR (Russia) were the objects of the study: solvent-borne primer Metacor-01 (M-01) and water-borne primer Metacor-017 (M-017) with high (> 85 wt%) and low (< 85 wt%) content of Zn powder, respectively. Modified primer M-017 of brand B (M-017B) was also investigated [11]. These primers were chosen since the former contains water-binding components, while the latter contains free water. This fact significantly affects the kinetics and mechanism of their sacrificial action.

The composite (multi-layered) coatings were formed by depositing an upper isolating coating without active additives to a layer of a Zn-rich primer. Water-borne enamel Rocor-5095 (R-5095) was used to form the upper isolating coating.

The coatings were applied to corrosion-prone substrates (carbon steel (St3), zinc (Zn)) and an inert substrate made of platinized titanium (Pt).

From the electrochemical point of view, the Steel/Zn-rich primer system is a system with two anodes, while the Pt-substrate/Zn-rich primer and Zn-substrate/Zn-rich primer systems can be considered as systems with one Zn-anode. A study of the Zn-substrate/Zn-rich primer system is of particular interest since it allows one to estimate the potentials of Zn particles in the primer without the additional effect of a substrate made of another metal, if the substrate is considered, in first approximation, as an additional zinc cluster.

The coatings were applied under laboratory conditions according to the manufacturer's instructions.

Research methods

In this work, a series of electrochemical methods were used. Potentiometry combined with electrochemical impedance spectroscopy (EIS) [12, 13] was employed as the main research method. The area of a working electrode (a coated sample) amounted to 6.2 cm².

The potentials of coated substrates relative to a silver chloride electrode were measured directly in a cell designed for impedance measurements using the following circuit: investigated sample / working solution / saturated KCl solution / AgCl / Ag with a platinum auxiliary electrode. All the potentials are given with respect to the standard hydrogen electrode (SHE).

Local measurements of the potentials of metals in contact pairs were carried out according to a standard procedure using a movable capillary of the reference electrode, which was connected to one or another electrode of the contact pair. The ratio between the areas of the protector and protected electrodes was 4:1.

The impedance was measured using an FRA-1 analyzer produced in the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences according to the ISO technique recommended for polymer coatings [14] in a frequency range from 100 kHz to 0.1 Hz. The area of the platinum auxiliary electrode was 16.9 cm². This value was found to be sufficient, as confirmed by the fact that its decrease did not affect the results of the measurements. The parameters of the equivalent electric circuit were calculated from the spectra obtained using DCS software.

1. Kinetics of changes in the potential of a substrate under Zn-rich primers

Primers that differed in the content of active components were chosen for comparative tests. Primer M-01 contains water-binding components, and as a result, there is no water on the surface and in the bulk before the exposure. At the same time, the deposition and hardening of water-borne primer M-017 occurred in the presence of water both in the bulk of the primer material and on the metal substrate/primer surface.

Below are the results of the kinetic study of the potentials of various (corrosive and inert) metal substrates coated with commercial primers.

Figure 1. Kinetics of changes in the potential of the substrate with commercial solvent-borne primer Metacor-01 (85 wt.%) with a thickness of 40 μm : 1 – steel substrate; 2 – platinum substrate; 3 – zinc substrate. 3% NaCl solution, +25°C.

Figure 2. Kinetics of changes in the potential of the substrate with commercial water-borne low-porous primer Metacor-017 (79 wt.% Zn) with a thickness of 100 μm : 1 – steel substrate; 2 – platinum substrate; 3 – zinc substrate. 3% NaCl solution, +25°C.

As one can see, the kinetics of changes in the potential for the investigated primers on various substrates is characterized both by common patterns and specific features:

- A sharp drop in the potential of the working electrode is observed on the corrosive Zn substrate for both primers regardless of the Zn content and the presence of water. In this

case, the recorded potentials of the Zn substrate under the primer after 7 days of exposure (-1000 mV) is lower than the potential of pure Zn in 3% NaCl solution (-830 mV) [15, p. 178]. The lower values of potentials can be attributed to the changes in the effective areas of anodic metal dissolution and cathodic depolarization, and the concentration polarization, where:

- The composition or pH of the internal solution penetrated into the pores on the adhesive interface is substantially different from that of the external electrolyte (3% NaCl), which results in a mixed oxygen-hydrogen mechanism of corrosion. Hydrogen bubbles that appeared sporadically on the surface of primers can be considered as indirect evidence.
 - The fact that the potential of the Zn substrate under Zn-rich primers remained more negative during the entire period of the study (for 100 days) allows us to state that the contribution of concentration is more significant than the ohmic contribution of the layer of corrosion products formed.
 - The potential of the steel (St3) substrate, which is also corrosion-prone, under Zn-rich primers changed significantly, but there was a qualitative difference in the behavior of the studied primers in the initial stage of exposure. The potential dropped to -780 mV when the substrate was impregnated with thin and porous solvent-borne primer M-01, *i.e.*, to values that were close to, but still were more positive than the potential of pure Zn (-830 mV). At this stage, it is clear that zinc particles, which possess electron linking with the substrate and contacts with the environment, display their protective properties. Later on (3–20 days), a potential increase followed by its stabilization was observed. At this stage, the protective properties of zinc particles weakened, apparently due to a loss of either electron linking with the substrate or the contact with the environment. In the case of the thicker water-borne primer M-017, no initial shift of the potential of the St3 substrate to the region of negative potentials was observed; only its smooth decrease and stabilization were recorded. It is evident that, in this case, zinc particles did not manifest protective properties for the same reasons as listed previously. It is essential to note that at long times of exposure, the potentials of both primers deposited to the St3 steel substrate were more positive than those of the uncoated St3 substrate.
- Analysis of the kinetics of potential variation on the corrosion-inert Pt substrate revealed that its potential was closer to the potential of St3 than to that of Zn. For both primers, the potential of the Pt substrate was lower than that of similar systems made of steel for most of the study period. Lower potential values were found for solvent-borne M-01 compared to water-borne M-017. With increasing exposure time, a slow potential growth was observed. For long times (100 days), the potentials of the Pt substrate under the water-borne low-porous primer occurred to be higher than those under the solvent-borne coating.

Thus, it can be concluded from the results of the comparative kinetic studies performed for different substrates:

1. The behavior of primer-coated zinc plates differs radically from that of steel and platinum plates coated by the same materials. However, it is noteworthy that the potentials of the Zn substrate under Zn-rich primers occurred to be more negative by 50 to 200 mV than that of the uncoated Zn substrate. A possible explanation, besides the changes in the effective area of cathodic and anodic reactions, is the fact that the composition or pH of the internal electrolyte in the primer can differ from the external 3% NaCl solution, and a combined oxygen-hydrogen depolarization mechanism operates.
2. The behavior of commercial Zn-rich protective primers on the corroding steel (St3) and on inert platinum (Pt) substrates is qualitatively similar, and at long times of exposure, the potentials of primer coated Pt and St3 substrates approach each other and become almost equal. This result allows one to conclude that even for long times of exposure, the steel surface under a Zn-rich coating does not show any corrosion activity and remains inert to some extent.

Below are the results of the study on the impact of temperature on the potentials of the St3 substrate under the primers exposed in 3% NaCl.

Figure 3. Kinetics of changes in the potential of the steel substrate coated with a 100 µm thick solvent-borne primer Metacor-01 (85 wt.% Zn) at different temperatures of exposure: 1 – 20°C; 2 – 40°C; 3 – 60°C; 4 – 80°C; 5 – 20°C (the thickness was 40 µm). The potentials were measured after cooling and exposure for 2 hours at 20°C.

Figure 4. Kinetics of changes in the potential of the steel substrate coated with a 100 µm thick solvent-borne primer Metacor-017B (85 wt.% Zn) at different temperatures of exposure: 1 – 20°C; 2 – 40°C; 3 – 60°C; 4 – 80°C. The potentials were measured after cooling and exposure for 2 hours at 20°C.

The temperature variation is a complex factor that can alter the basic processes in the protective Zn-rich primer. First of all, these processes include sorption and diffusion of the components of the corrosive media, as well as changes in the adhesion and elastic properties of the polymer base and in the potentials and corrosion rates of the zinc filler and steel substrate.

When considering the data presented, one should pay attention to the following:

1. A higher temperature leads to lower values of the potential in the minimum zone and faster achievement of the minimum. It cannot be due to changes in the corrosion potential of the Zn filler since the changes in the potential observed under the coatings are significantly larger (~250 mV) than the temperature-induced changes of the potential of zinc in water (~30 mV) and in salt solutions (~20 mV in 0.3% NaCl and ~100 mV in 3% NaCl) (see Table 1).
2. At elevated temperatures, the potentials of the substrates noticeably shift to the cathodic region for both primers, and extremums on the kinetic curves are observed.
3. It should be noted that the potentials of the substrates under Zn-rich protective primers are highly dependent on the structure and composition of the material. It follows from the data mentioned above (see Figure 3) that the porous primer M-01 applied not in one but in three layers 100 µm thick demonstrates a behavior typical of insulating coating at low temperatures [16].

Table 1. Temperature dependences of the corrosion potential of zinc in water and in NaCl solutions.

Medium	Corrosion potential of Zn, mV (SHE), at temperature, °C					
	20	40	50	60	70	80
Water	–620	–655	–660	–675	–655	–650
0.3% NaCl	–735	–740	–720	–720	–720	–730
3% NaCl	–860	–880	–835	–830	–780	–755

When analyzing the above, one could have assumed that the reason for the enhancement of the protective action (a potential drop) with rising temperatures lies in a growth in the corrosion rate of the Zn filler. However, as one can see from the data presented (see Figure 5), the corrosion rate of Zn does not change monotonously, but has an extremum both in water and in NaCl solutions. It was shown in [16] that upon corrosion in water at temperatures up to 60°C, zinc hydroxide is mainly formed on Zn surface, while at higher temperatures, a denser layer of zinc oxide (ZnO) is observed.

Figure 5. Temperature dependences of the corrosion rate of zinc in various corrosive media: 1 – in distilled water; 2 – in 0.3% NaCl solution; 3 – in 3% NaCl solution.

In contrast to metallic zinc, no extremal temperature dependences of both the minimum and steady, conditionally stationary potentials were found in the case of Zn-rich primers deposited to steel substrate exposed to 3% NaCl (Table).

In this context, there must be an additional reason for the enhancement of the protective action of Zn-rich primers at temperatures exceeding 60°C. This could be a change in the insulating properties of the polymer base and an increase in the accessibility of Zn particles to corrosion.

Table 2. The minimum potentials of steel substrate under Zn-rich primers (Figures 3 and 4) exposed to 3% NaCl at various temperatures.

Material / Characteristics of primers	Potential, mV (SHE), at temperature, °C			
	20	40	60	80
Solvent-borne zinc-rich primer M-01 / 100 μm thick	–380	–430	–620	–780
Water-borne zinc-rich primer M-017B / 100 μm thick	–360	–600	–700	–770

Below, the results of the study on the changes in the insulating properties of water-borne and solvent-borne Zn-rich primer compositions at different temperatures are presented (see Figures 6 and 7).

Figure 6. Kinetics of changes in total impedance $|Z|$ at a frequency of 6700 Hz for solvent-borne zinc-rich primer M-01 on steel substrate at different temperatures: 1 – 20°C; 2 – 40°C; 3 – 60°C; 4 – 80°C.

Analysis of the data shows that the increase in the impedance after the impregnation stage is observed at temperatures within 40–60°C. With a further increase in the temperature to 80°C, this effect disappears regardless of the type of the polymer material. This effect apparently manifests itself in a further enhancement of the protective properties of the primers.

Figure 7. Kinetics of changes in total impedance $|Z|$ at a frequency of 6700 Hz for water-borne zinc-rich primer M-017B on steel substrate at different temperatures: 1 – 20°C; 2 – 40°C; 3 – 60°C; 4 – 80°C.

It is known that Zn-rich primers are almost not used as the only component of a coating, but serve as an element of multi-layered composite coatings with upper insulating layers [3].

The insulating coatings can affect the electrochemical properties of a substrate mainly due to changes in the amount and composition of the medium penetrating the substrate. Detailed studies of an individual insulating coating applied directly to a substrate were carried out to assess this effect (Table 1).

As follows from the data presented above, some specific features are observed in the system with the insulating coating without active additives (Table 3, No. 4). The insulating coating can affect significantly the potential of the substrate. Unlike protector primers, no period of the substrate potential growth was observed. The potential of the steel substrate under the insulating coating only decreases with time, and after 30 days, it passes to the negative region. In this case, the potentials of the steel substrate under the insulating coating (No. 4) are higher than those of unprotected steel (No. 1) and higher than for the systems with Zn-rich primers of different nature (No. 2 and 3). The potential of the substrate under an insulating coating at long exposures (100 days) remained more noble by 250 mV than under the primers.

Thus, the upper insulating layer can contribute significantly to the protection properties of composite coatings.

Table 1. Comparison of the kinetics of changes in the potential of the steel substrate under protective Zn-rich primers and insulating coating R-5095 after exposure to 3% NaCl at 20°C.

No.	System	Characteristics of the system	Potential of a substrate (mV(SHE)) after exposure in the medium for the following periods (days):				
			1	7	30	65	100
1	St3 without a primer and coating	High accessibility of the surface for the corrosive medium	–430	–	–	–	–
2	St3 with deposited primer M-01	The thickness of a primer layer is 40 µm, high porosity, Zn content = 85 wt. %	–736	–476	–381	–392	–376
3	St3 with deposited water-borne primer M-017B	The thickness of a primer layer is 100 µm, low porosity, Zn content = 85 wt. %	108	–304	–331	–332	–343
4	St3 with deposited water-borne coating R-5095 (without a primer)	The thickness of a primer layer is 100 µm, low porosity, no electrochemically active fillers	144	91	–35	–93	–100

The present data show that the most important factors affecting the potentials of the substrates with coatings are: the substrate material, temperature and time of exposure in a chloride-containing medium, as well as the composition and thickness of the polymer coating.

The substrate material under the same Zn-rich primer has a significant impact on both the kinetics of the substrate potential and the level of the conditionally steady potentials. However, after prolonged exposures (for 100 days), it was found that the potential of the corrosion-active steel substrate is almost the same as that of the platinum substrate, while the kinetic behavior of the potentials of these substrates is different. The potential of the most corrosion active Zn substrate remained more negative compared to the corrosion potential of zinc throughout the entire period of the study.

The temperature is the second most important factor, which stimulates both the electrochemical activity and the corrosion rate of the Zn filler in the primer, as well as the changes in the electric resistance of the coating material caused by the accumulation of the products of Zn corrosion in it. Moreover, the observed significant temperature and kinetic changes in the potential of the steel (St3) substrate (Figures 3 and 4) cannot be attributed solely to the temperature-induced changes in the Zn corrosion potential (see Table 1).

The composition of the coating is also a significant factor. First, one has to note the filler type, *i.e.*, electrochemically active (Zn) or inert (TiO₂). Second, the presence of water

in the composition of the primer as a component that stimulates corrosion is of importance. Third, the thickness and number of the primer layers are also essential.

2. Potentials of Zn-rich primer/insulating coating composite systems

Let us consider the results of the study of composite coatings according to the previously used scheme.

In the case of a composite coating comprising a Zn-rich primer layer and an upper insulating layer, the kinetic of potentials and their temperature dependences are expected to differ from the above-mentioned behavior of individual coatings (primers and insulating layers).

The following are the kinetic dependences of the potentials of various metal substrates with deposited solvent- and water-borne composite coatings (Figures 8 and 9).

Figure 8. Kinetics of changes in the potential of the solvent-borne primer M-01 / insulating water-borne coating R-5095 at 20°C on substrates made of: 1 – steel*; 2 – platinum; 3 – zinc.

* Data averaged over 5 samples are given for the steel substrate.

Like in the case of individual primers, the coating material has a decisive effect on the kinetics of changes in the potential under the composite coatings.

The changes observed on Zn substrate upon exposure to the corrosive medium are similar for the two composite coatings under study: at the beginning (3–7 days), a sharp decrease to a potential minimum (within –820 to –780 mV) followed by a growth to –200 mV.

Figure 9. Kinetics of changes in the potential of the solvent-borne primer M-017B / insulating water-borne coating R-5095 at 20°C on substrates made of: 1 – steel*; 2 – platinum; 3 – zinc; 4 – steel* at 60°C.

**Data averaged over 5 samples are given for the steel substrate.*

Thus, the behavior of the composite coatings on Zn substrate are qualitatively different from those of the above considered Zn-substrate/Zn-rich protective primers systems without an upper insulating layer. In the case of the latter, the potential remained more negative than the Zn corrosion potential within the range of exposure times studied (Figures 1 and 2).

The values of the potential of the Zn substrate with all composite coatings and are more positive than the potential of Zn corrosion for all times of exposure.

The kinetic behaviors of changes in the potential of all studied systems on the steel (St3) substrate are qualitatively similar: a stabilization stage (14–50 days) followed by subsequent decrease was observed after the initial impregnation. The decrease of the potential occurs to be more pronounced in the system with water-borne primer M-017B (to –300 mV), while the systems with the composite coating including solvent-borne primer M-01 showed only a mild trend after 50 days of exposure. Also, the increase in temperature to 60°C led to the decrease in the potential of the substrate with water-borne primer M-017B to –780 mV, which was indicative of a startup of the sacrificial protection mechanism on steel, probably due to easier access of the electrolyte to the surface of Zn particles. It is noteworthy that the maximum values of the potential (at the stabilization stage) in the composite coatings (from +180 to +220 mV) were significantly more positive than those in the systems with similar primers (from –400 to –300 mV) (see Table 4).

Table 4. Kinetics of changes in the potential of the steel substrate with various coatings after exposure to 3% NaCl at 20°C.

System	Potential of the substrate (SHE), mV after exposure for a period, days				
	1	7	30	65	100
M-01 (h=40 μm)	–736	–476	–381	–392	–376
M-01 (100 μm)	–314	–325	–327	–380	–400
M-017 (100 μm)	108	–304	–331	–332	–343
M-017B (100 μm)	–331	–282	–395	–337	–317
R-5095 (100 μm)	144	91	–35	–93	–100
M-01+R-5095 (40+100 μm)	211	–6	227	145	235
M-017+R-5095 (100+100 μm)	–100	–231	–245	–212	–234
M-017B+R-5095 (100+100 μm)	180	197	176	–313	–531

Significant changes in the potential were found for the composite systems on the Pt substrate. In this case, the potentials of the systems with composite coatings occurred to be essentially higher than those of substrates coated with a primer layer only. For example, the potentials of the M-01/R-5095 system were within the range from –500 to +50 mV, while those of the system coated with primer M-01 only varied from –600 to –450 mV.

The kinetics of changes in the potentials of the composite coatings based on different primers varied significantly. In the case of the system based on the solvent-borne primer, a long growth of the potential from –500 to +50 mV was observed after the impregnation stage (7 days). As one can see in Figure 8, the kinetics of potential variation on the Pt substrate coated by the solvent-borne primer was almost the same as that on the Zn substrate.

The fast growth of the potential up to +400 mV with a subsequent prolonged stage of stabilization (to 50 days) and a decrease was observed in the system with the water-borne primer.

It is noteworthy that for both types of composite coatings, the potentials on Pt at long times of exposure are close to those found on steel.

Thus, the potentials of the substrates under the composite coatings are significantly more positive compared both to the potentials of the metal being protected in this electrolyte and the potential of the same metal substrates with the primers without an upper insulating layer.

As shown above, for all considered types of Zn-rich primers, the kinetic behaviors of changes in the potentials of the substrate were largely determined by a temperature of exposure to an aggressive medium. Below, Figures 10 and 11 demonstrate the results of the study obtained for the composite coatings primer/enamel on the steel substrates within a temperature range of 20–80°C.

Figure 10. Kinetics of changes in the potential of the steel substrates with the composite coating (primer M-01 / enamel R-5095) exposed at temperatures: 1 – 20°C; 2 – 40°C; 3 – 60°C; 4 – 80°C. The measurements were carried out after cooling at 20°C.

Figure 11. Kinetics of changes in the potential of the steel substrates with the composite coating (primer M-017B / enamel R-5095) exposed at temperatures: 1 – 20°C; 2 – 40°C; 3 – 60°C; 4 – 80°C. The measurements were carried out after cooling at 20°C.

As one can see, the temperature-kinetic dependences for the composite coatings with the studied Zn-rich primers possessed a number of specific features:

1. The system of solvent-borne primer M-01 with coating R-5095 at low temperatures (20–40°C) is characterized by a presence of a region of initial impregnation with a

decrease in the potential down to -200 mV followed by a long stationary period (up to 70 days) at a level of $+200$ mV.

2. As the temperature increased to 60°C , the potential of the steel substrate grew after the stage of impregnation, at which a significantly lower potential (-400 mV) was formed, but it remained negative (-200 mV), which is greater than that of steel corrosion (-430 mV). With further increase in temperature up to 80°C , an oscillation of the potential within a wide range (growth from -300 to $+70$ mV followed by a drop) was observed at the initial stage. At long times of exposure, the protective mechanism manifested at the potentials (-720 mV), which are close to the values observed for zinc corrosion.
3. More negative potentials were recorded for the system with water-borne primer M-017B compared to those for the system with solvent-borne primer M-01; the passage to the cathodic region was observed even at $+20^{\circ}\text{C}$, and the protective mechanism started to show at the temperature of $+60^{\circ}\text{C}$.

3. Conclusions

As the discussion above revealed, there are specific features of the formation of the potentials of metal substrates with Zn-rich primers deposited both individually and as a component of composite coatings. The main features are:

Behaviors of one and the same composite coating applied to metal substrates of different natures vary significantly.

Kinetics of changes in the potential of composite coatings on the zinc substrate qualitatively differed from that observed for the systems without an upper insulating layer.

At that, growth in the potential of the substrate under the system of primer (of different nature) / coating was observed both for solvent- and water-borne primers. In the same conditions and at comparable times of exposure, the potential of the zinc substrate coated only by the primer remained constant, and no growth of the potential was observed.

No passage of the potential to the region of more negative values compared to the potential of Zn corrosion (-830 mV) was found when the composite coatings were applied. This allows us to state that the process with oxygen depolarization is superior in the systems with these coatings. The results obtained allowed us to conclude that the more positive results are generated in the system with the upper insulating layer, which is able to put an additional diffusional control of the medium penetration through diffusion that can be interpreted as deactivation of sacrificial metal.

The role of the inert Pt substrate is reduced to a function of a charge accumulating electrode. Indeed, as seen from Figure 8, the kinetic behaviors of changes in the potential of the composite coating with solvent-borne primer M-01 are close to those of the coating on zinc, while the absolute potentials are somewhat more positive (by 50 – 200 mV).

The behaviors of the potential of the most practical systems on the steel substrate differ both from the Zn- and Pt-substrates. Temperature is the essential factor, which determines the potential of the steel substrate under a composite coating.

At low temperatures, unlike the systems coated only by primers, the protective properties of composite coatings are poorly expressed. In the case of the systems with both solvent- and water-borne Zn-rich primers, the protective stage takes only a small part of the operating time. The operational activity of the composite coatings at low temperatures is carried out mostly at positive potentials of the steel substrate.

The increase in temperature radically activates the protective properties of the composite coatings despite the growth of the total impedance of the primers at temperatures near +60°C.

In conclusion, one should note a methodological aspect of the testing on the Zn-substrate. It seems that this substrate can be considered as a macroscopic Zn-particle in the lowest layer of primer since, with a high probability, the electrochemical properties of the Zn-substrate are similar to that of the Zn-particle.

With this assumption, the measurements of the potential of the Zn-substrate allowed us for the first time to evaluate the potential of metal sacrificial additives both for the individual Zn-rich primer and when it is a component of the composite coating system.

References

1. I.V. Frishberg, L.P. Yurkina, O.Yu. Subbotina and Yu.P. Posokhnin, *Sovremennye otechestvennye tsink- napolnennye kraski. Opyt ikh primeneniya* (Modern domestic zinc-rich paints. The experience of their application), *Lakokrasochnye Materialy i ikh Primenenie* (Paint-and-lacquer materials and their applications), 1997, **1**, 8–13 (in Russian).
2. V.A. Golovin, A.B. Il'in, V.A. Shchelkov, S.A. Dobriyan, S.A. Tyurina and I.I. Reformatskaya, *Kontseptsiya kompozitsionnykh polimernykh pokrytii dlya neftegazovykh sred* (Concept of composite polymer coatings for oil and gas environments), *Korrozi.: mater., zashch.* (Corrosion: materials, protection), 2015, no. 1, 14–22 (in Russian).
3. V.A. Golovin, S.A. Dobriyan and V.B. Lukin, *Rost izoliruyushchei sposobnosti polimernykh pokrytii s aktivnymi tverdogaznymi i ingibiruyushchimi dobavkami pri ekspozitsii v agressivnoi srede* (The increase of the insulating ability of polymer coatings with active solid-phase and inhibitory additives upon exposure in an aggressive environment), *Korrozi.: mater., zashch.* (Corrosion: materials, protection), 2018, no. 6, 23–31 (in Russian).
4. S. Feliu, J. Barajas and J.M. Bastidas, Mechanism of cathodic protection of zinc-rich paint by electrochemical impedance spectroscopy, *J. Coat. Technol.*, 1989, **61**, no. 775, 63–69.
5. C.M. Abreu, M. Izquierdo, P. Merino, X.R. Novoa and C. Perez, New Approach to the Determination of the Cathodic Protection Period in Zinc-Rich Paints, *Corrosion*, 1999, **55**, no. 12, 1173–1181. doi: [10.5006/1.3283955](https://doi.org/10.5006/1.3283955)

6. V.G. Shevchenko, *Osnovy fiziki polimernykh kompozitsionnykh materialov (The fundamentals of physics of polymer composite materials)*, MSU, Moscow, 2010, p. 99 (in Russian).
7. L.Y. Zhang, A. Ma, J. Jiang, D. Song, J. Chen and D. Yang, Anti-corrosion performance of waterborne Zn-rich coating with modified silicon-based vehicle and lamellar Zn (Al) pigments, *Prog. Nat. Sci.: Mater. Int.*, 2012, **22**, no. 4, 326–333. doi: [10.1016/j.pnsc.2012.07.001](https://doi.org/10.1016/j.pnsc.2012.07.001)
8. F. Vizek, Tsinkovye khlop'ya – effektivnoe sredstvo antikorrozionnoi zashchity (Zink-Flakes – efficient corrosion protection, *Lakokrasochnye Materialy i ikh Primenenie (Paint-and-lacquer materials and their applications)*, 2006, no. 2–3, 50–51 (in Russian).
9. B.B. Kudryavtsev, N.B. Gurova, S.S. Moiseev, A.V. Timonin and L.M. Vasil'eva, *Patent 2246513 Russian Federation, MPK C09D5/10, C09D5/08, C09D163/02*, Sacrificial primer (Patentee AOZT Lakma-Imeks, 2003127013/04; appl. 05.09.2003, published 20.02.2005, Bull. No. 5).
10. P. Vertuest, Anti-Corrosion Properties of Zinc Powder Paints Using Nano Zinc Metal Powder, *China Coat. J.*, 2009, July, 24–36.
11. V.A. Golovin, A.B. Il'in, V.T. Kuznets and A.R. Vartapetyan, Patent Russian Federation No. 2358036, The method of corrosion protection of metal surfaces by inhibited polymer compositions and microcapsules with a corrosion inhibitor, 2009 (in Russian).
12. C. Gabrielli, *Use and application of electrochemical impedance techniques*, Farnborough, 1990, p. 78.
13. N.A. Poklonsky and N.I. Gorbachuk, *Fundamentals of impedance spectroscopy of composites*, Minsk, BSU, 2005, p. 130 (in Russian).
14. ISO 16773-1, 2, 3, 4, *Electrochemical impedance spectroscopy (EIS) on high – impedance coated specimens*.
15. N.P. Zhuk, *Course in the theory of corrosion and protection of metals*, Metallurgiya, Leningrad, 1976, p. 472.
16. V.A. Golovin, S.A. Dobriyan, V.B. Lukin and K.V. Kolenko, On the Choice of an Equivalent Circuit for the Description of Electrochemical Impedance Spectra of Zn-Filled Polymer Primers and Coatings, *Prot. Met. Phys. Chem. Surf.*, **53**, no. 7, 1221–1229. doi: [10.1134/S2070205117070061](https://doi.org/10.1134/S2070205117070061)