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*Translated from*

*Lokkrazschuyya Materialy i Ikh Primeneniye*  
*[Paint and Varnish Materials and their Utilization], 1964, 3, 14-37*

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## CATHODIC POLARIZATION OF SPENT ZINC-CONTAINING PAINTS IN SEA WATER

A.G. Khanlarova, M.R. Khanmamedova and M.A. Ibrahimova

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For protecting steel against corrosion, zinc protective paints, containing not less than 90% of zinc, are widely used. The duration of the protective activity of these coatings in neutral aqueous media depends on the aeration of the water and its speed of movement; also on the water composition. Thus, for instance, according to laboratory tests in Caspian Sea water (water changed every 8-10 days) a protective zinc coating of thickness 100 microns keeps its protective powers for 21 months and more. Under natural conditions --- immersed at depth 1 m in the Caspian Sea --- the same coating continues to exhibit its protective action for 19-20 months.

It has been established that with the zinc coating used as anode there is a formation of corrosion products, consisting in the main of zinc hydroxide and oxycarbonate [basic zinc carbonates]. \* With the accumulation of these compounds on the zinc particles, the paint ceases to act as a protector. The composition of the zinc corrosion products in solutions containing chlorides may vary from  $Zn(OH)_2$  to  $4Zn(OH)_2 \cdot ZnCl_2$ , with the content of  $ZnCl_2$  steadily increasing [1].

To make clear how the protective action of zinc paints depends on the chemical composition of the electrolyte, we carried out tests with coatings of these paints in solutions of the salts  $NaCl$ ,  $KCl$ ,  $Na_2SO_4$ ,  $K_2SO_4$  and  $MgSO_4$ . These salts, in quantities corresponding to the amount of them contained in Caspian Sea water (calculated with respect to the anions), were dissolved in distilled water. In the solutions thus obtained we tested samples of steel coated with zinc paint (90% Zn + 10% polystyrene from still residues) for a period of two months. Observations of the change of potential of the paint film (Table 1) established that in the  $KCl$ ,  $NaCl$  and  $Na_2SO_4$  solutions there takes place a rapid shift of potential in the positive direction. The potential alters much more slowly with the test-pieces in a  $MgSO_4$  solution.

On the samples tested in the  $NaCl$ ,  $KCl$  and  $Na_2SO_4$  solutions, rust spots were discovered, and on the samples immersed in the  $K_2SO_4$  and  $MgSO_4$  solutions, a thick white precipitate.

Analysis of a film of zinc paint containing 10% of chlorinated rubber as binder, after exposure for 1.6 year to Caspian Sea water, showed that the precipitate on the surface of the paint contained 1.57%  $CaSO_4$ , 4.74%  $CaCO_3$ , 3.48%  $Mg(OH)_2$ , 3.15%  $ZnCO_3$ , and 4.68%  $Zn(OH)_2$ . The amount of soluble zinc compounds was 1.5%. The electrode potential of the test-pieces from which the sample was taken for analysis was -610 mV; thus the protective action of the zinc coating was about at its end.

\* Translator's note: See Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol.4, pp.645, 646. This reference was supplied by Mr. R. Buckett.

TABLE 1.

Alteration of the electrode potential (mv) of zinc paint coatings after exposure to salt solutions

Salts	Amount of the salt, in g per l of water	Initial potential mv	<u>Alterations of the electrode potential after exposure to salt solutions for</u>							
			10 days	15 days	24 days	29 days	42 days	51 days	60 days	
Na <sub>2</sub> SO <sub>4</sub>	4.338	-835	-750	-660	-390	-395	-400	-410	-420	
K <sub>2</sub> SO <sub>4</sub>	5.034	-800	-730	-575	-560	-510	-470	-500	-470	
MgSO <sub>4</sub>	3.666	-805	-790	-770	-770	-760	-760	-730	-680	
KCl	11.502	-800	-760	-650	-400	-350	-350	-340	-340	
NaCl	9.032	-800	-790	-650	-380	-350	-370	-350	-350	

Remark: Here and subsequently, potentials are corrected relatively to normal hydrogen electrode.

In sulfate solutions denser precipitates are formed on the surface of the zinc than in chloride solutions. This explains the smaller speed of zinc corrosion in the first of these two media, a fact of importance for the practical employment of paints under Caspian Sea conditions, where the waters are rich in sulfates.

The formation of corrosion products even in the initial period of the existence of a zinc paint coating is a factor markedly affecting the protective effect. When the potential of the coating approaches the potential of the steel, the protective action of the paint is terminated.

Over the period of service of paint coatings in sea water, the zinc hydroxide and basic zinc carbonates that are formed progressively consolidate, and continuous films of zinc corrosion products develop, which hinder the passage of current. On this account the protective action of the coating ceases at a stage when there still remains in it a quite adequate amount of unexpended metallic zinc (as much as 74.5%). The restoration of the negative potential of a spent zinc paint [2] is therefore a matter of great [economic] interest, since it thereby becomes possible to prolong the activity and avoid repaintings.

Study of the cathodic polarization of spent zinc-paint coatings in sea water (Fig. ...) has shown that their polarizability depends both on the chemical composition of the binder and on the degree to which the zinc is spent.

In measuring the potentials of polarized painted metals one must allow for the fact that the measured anode or cathode potential includes a voltage-drop due to the ohmic resistance of the paint film. But in contrast to ordinary paint films, the electron polarizability of coatings of zinc paints, which possess an electron conductivity, does not depend on the resistance of the film [but on the electrolytic contact potential].

As we see from Figure 1, the maximum cathodic polarizability is exhibited by coating of paints having chlorinated rubber and polystyrene bases. The specific resistance of all the spent coatings was  $0.96 \text{ ohm}\cdot\text{m}^2$ , with the exception of the polystyrene-base paint, the specific resistance of which was  $0.84 \text{ ohm}\cdot\text{m}^2$ . Since the paint coatings with maximum and minimum polarizability have identical specific resistances, the cathode polarizability of spent zinc paints is mainly influenced, not by the value of the resistance, but by the structure of the zinc corrosion products, a structure which probably depends on the spatial grouping of the molecules and the chemical composition of the binder. Restoration of the negative potential of spent paints occurs at a low cathode current density.

The difference in the spatial arrangement of the zinc particles in paints prepared with different binders affects, it seems, the cathodic polarization even of fresh, non-spent paints (Fig. 2).

Figure 3 shows the speed of restoration of the protective activity of a paint coating of one and the same composition (zinc + polystyrene from still residues) but of different degrees of exhaustion. From the figure it is seen that restoration takes place the faster, the smaller the degree of exhaustion; that is, the more negative the electrode potential of the paint before polarization begins. The degree of exhaustion of the paint coating also shows an

effect on the persistence of the negative potential after the switching-off of the external current. With paint-coating pre-polarization potentials in the range from -620 to -510 mV the protective negative potential may persist for some days after switching-off of the cathodic polarizing current, while with potentials more positive than -400 mV the protective potential is preserved, after the switching-off of the current, for just a few hours.

The restoration of the protective potential of spent paint coatings may probably be explained by a change in the porosity of the film of zinc corrosion products under the influence of the cathodic polarizing current and the liberated hydrogen. The electrical conductivity of the zinc particles is thereby restored and the paint coating again acts for some time as a protector.

The restoration of the negative potential of a spent paint coating by cathodic polarization could also be due to the formation, on the surface of the protected steel, of a metallic zinc layer resulting from the electrochemical reduction of the water-soluble zinc corrosion products.

To test these hypotheses, experiments were carried out on two samples of paint coatings. In the first sample the pigment consisted of 75% zinc dust and 25% zinc hydroxide. The electrode potential of this coating in sea water (-530 mV) did not provide cathodic protection for steel. The pigment of the second paint consisted of 75% zinc dust, 23.5% zinc hydroxide and 1.5% zinc sulfate. The initial electrode potential of this sample in sea water was also equal to -530 mV (the zinc hydroxide and zinc sulfate must have constituted a good "model" of the zinc corrosion products).

The results obtained in the cathodic polarization of these paint coverings are shown in Table 2. From this table it is seen that when no water-soluble

TABLE 2

Duration of polarization, hrs.	Effect of pigment composition on cathodic polarization of zinc paint coatings			
	Potential (mV) of a coating of paint with pigment containing 75% Zn + 1.5% ZnSO <sub>4</sub> + 23.5% Zn(OH) <sub>2</sub>		Potential (mV) of a coating of paint with pigment containing 75% Zn + 25% Zn(OH) <sub>2</sub>	
	At current density 0.03 mA/dm <sup>2</sup>	After switching off the current	At current density 0.12 mA/dm <sup>2</sup>	After switching off the current
0	-530	-	-520	-
1/60	-550	-730	-535	-560
1/30	-630	-730	-	-540
1/20	-650	-730	-	-530
1/15	-670	-730	-	-520
1/12	-700	-730	-	-500
1/10	-750	-730	-	-490
1/2	-770	-730	-550	-490
1	-800	-730	-	-490
24	-800	-700	-600	-
48	-800	-700	-590	-
72	-	-670	-	-
120	-	-660	-	-
262	-	-600	-	-

zinc compounds were included in the composition of the paint, cathodic polarization for a period of 2-3 days with a current of density 0.12 mA/dm<sup>2</sup> did not lead to the development of any protective properties in the coating, since the reaction potential for the reduction of zinc hydroxide



which is -0.83 V, was never attained. With 1.5% of zinc sulfate present, polarization of the paint at a current of density 0.03 mA/dm<sup>2</sup> did offer the

possibility of attaining the requisite negative protective potential in the course of a few minutes, since at this current density the reaction potential (-0.762 V) for the discharging of zinc ions on the metal is indeed established:



After the current is switched off, a sufficiently negative value of the potential persists for a period of ten days. Thus one cause of the persistence of the paint coating's negative potential after the switching-off of the cathodic current is the electrolytic reduction of water-soluble zinc salts to metallic zinc.

The degree of restoration of the protective properties of paint coatings depends on the ratio of soluble to insoluble zinc corrosion products formed on the coating.

We made up "model" paint coatings with a pigment composition corresponding to that of spent zinc paints, and we determined their cathodic polarizability after exhaustion by exposure to sea water. All those that contained significant amounts of ZnO, ZnCO<sub>3</sub>, Zn(OH)<sub>2</sub> and metallic zinc possessed an adequately negative initial potential. When they were kept in sea water the potentials gradually dropped to -550 mV and even to -350 mV. The spent coatings were then subjected to cathodic polarization (Fig. 4).

As we see from Figure 4, paint composed of a 9:1 mixture of zinc dust and zinc hydroxide has the greatest cathodic polarizability, and retains its protective potential, after the switching-off of the current, longer than paints of all other compositions.

The polarization of coatings 1 and 2 is similar in character to the polarization of spent zinc paints. With the replacement of Zn(OH)<sub>2</sub> by zinc oxide, the cathodic polarizability decreases. Consequently the current density required for the reduction of zinc oxide admixed with powdered zinc is considerably greater than the current density required for the reduction of zinc hydroxide. When the amount of Zn(OH)<sub>2</sub> in the pigment mixture is increased to 20%, the polarization is markedly impeded.

Comparison of the cathodic polarization curves for a paint coating with a 3% content of Zn but not subjected to aging in sea water (Fig. 4a, curve 3) with the polarization curves for a paint coating with 80% Zn plus 20% Zn(OH)<sub>2</sub> (Fig. 4a, curve 4) which had been for some time in sea water shows that with the formation, on the paint, of zinc corrosion products insoluble in water, the zinc hydroxide reduction is markedly impeded.

It should be noted that if zinc paint coatings, after their protective action in sea water has come to an end, are dried in the air for a period of 2-3 days, the coating recovers, for a lengthy period (over 30 days), a negative potential adequate for protective effect.

From the adduced facts it follows that by means of a brief cathodic polarization with currents of small density it is possible to restore the protective action of spent zinc paint coatings. This is confirmed by data on the cathodic polarization of spent paint coatings tested for 600 days in sea water under natural conditions. The polarization was carried out at a current density of 0.03 ma/dm<sup>2</sup> for a period of a few days (Fig. 5).

From Figure 5 it is seen that after the switching-off of the polarizing current the potential of the paint coating stays at a sufficiently negative value for two days.

On the above basis the authors see quite good prospects in the simultaneous use of zinc protective paints and cathodic polarization (cathodic protection) for the defense of steel structures, ships and hydromechanical installations against corrosion. In this procedure the cathodic protection device need only be switched on periodically, for whatever time is necessary to restore the protective action of the paint film.

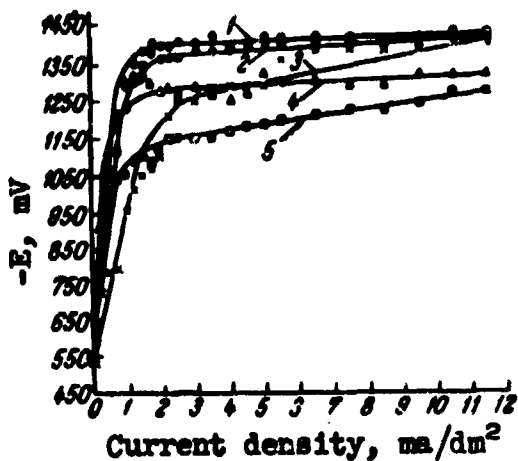
#### CONCLUSIONS

1. It is shown that cathodic polarization of a spent zinc paint coating effects a restoration of its protective potential. The displacement of the potentials of the spent zinc coating in the negative direction depends on the chemical composition and the amount of insoluble zinc corrosion products, and also on the amount of zinc formed by the electrolysis of the water-soluble corrosion products of zinc ( $ZnCl_2$ ,  $ZnSO_4$ ).

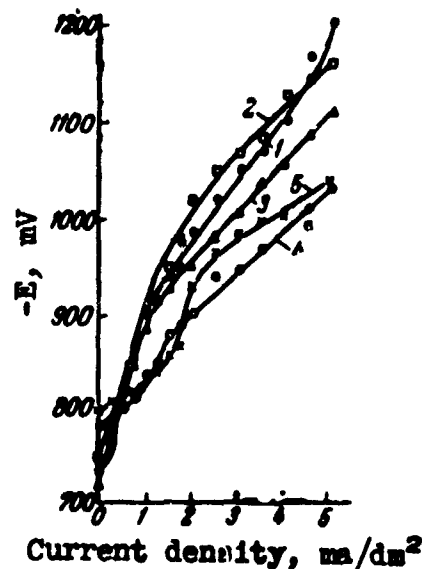
2. The use of cathodic protection simultaneously with protective coatings of zinc paint for the preservation of steel structures, marine petroleum equipment and ships makes possible a reduced expenditure of electric current and an increase in the period of effectiveness of the paint coatings.

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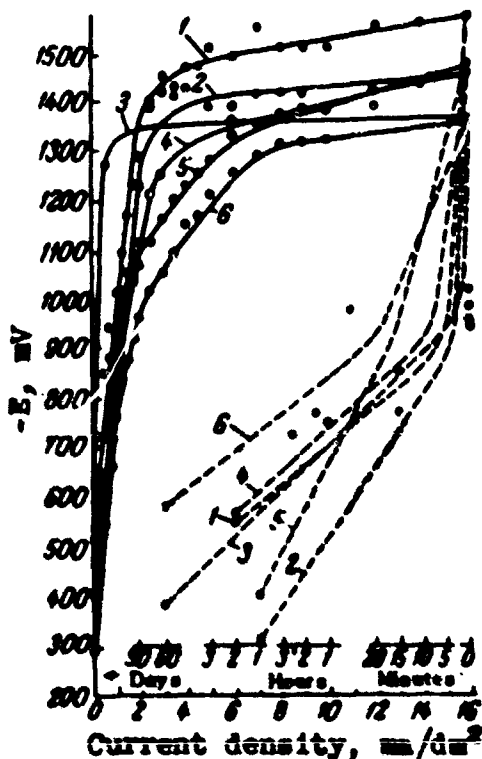
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**Fig. 1.** Cathodic polarization of sea-water-spent zinc paint coatings containing 90% of zinc and 10% of various binders:  
 1 - chlorinated rubber;  
 2 - polystyrene from still residue; 3 - ED-6 epoxy resin; 4 - bakelite varnish;  
 5 - BF-2 glue.



**Fig. 2.** Cathodic polarization of non-spent coatings of zinc paint containing 90% of zinc and 10% of various binders:  
 1 - polystyrene from still residues; 2 - BF-2 glue;  
 3 - ED-6 epoxy resin; 4 - chlorinated rubber;  
 5 - 100% metallic zinc.



**Fig. 3.** Cathodic polarization of coatings of polystyrene-base zinc paints, with initial negative potentials as follows:  
 Curves 1, 2, 3, 4, 5, 6 - respectively 540, 290, 620, 560, 400 and 510 mV (the broken lines show the cathodic polarization after switching off the polarization current).



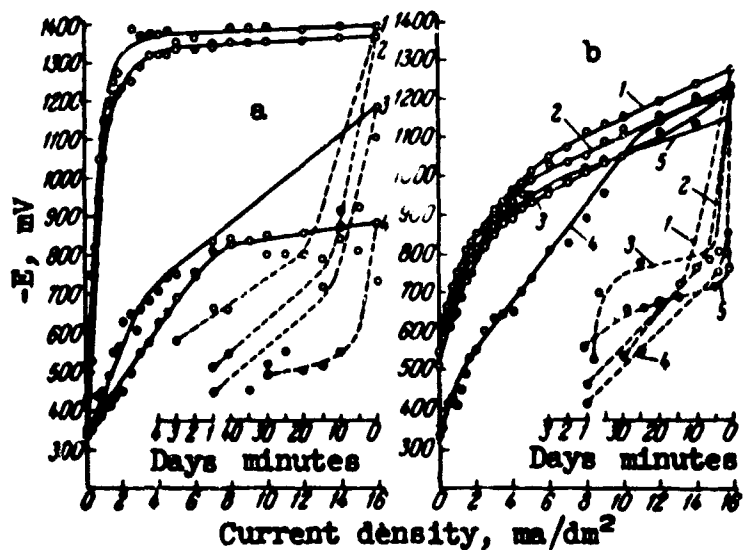


Fig. 4. Effect of zinc corrosion products on cathodic polarization of films of protective zinc paint (the broken lines show the cathodic polarization after switching off the polarizing current).

In Fig. 4a:-

- 1 - pigment containing 90% Zn + Zn(OH)<sub>2</sub>;
- 2 - the same, with 95% Zn + Zn(OH)<sub>2</sub>;
- 3 - the same, with 3% Zn + Zn(OH)<sub>2</sub>;
- 4 - the same, with 80% Zn + Zn(OH)<sub>2</sub>.

In Fig. 4b:-

- 1 - with pigment containing 70% Zn + ZnO;
- 2 - the same, with 90% Zn + ZnCO<sub>3</sub>;
- 3 - the same, with 90% Zn + ZnO;
- 4 - the same, with 3% Zn + ZnO;
- 5 - the same, with 80% Zn + ZnCO<sub>3</sub>.

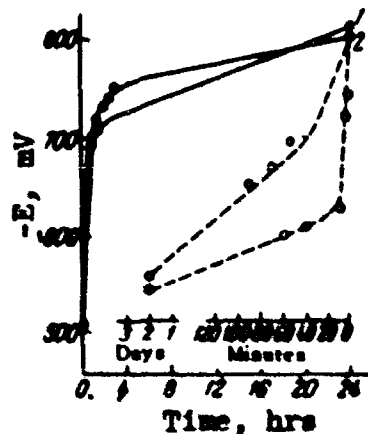


Fig. 5. Cathodic polarization of spent zinc paint coatings of different composition (the broken lines show the cathodic polarization after switching off the polarizing current):

- 1 - pigment consisting of 100% Zn, polarizing current density 0.03 ma/dm<sup>2</sup>, electrode potential of sea-water-spent film, -0.51 V;
- 2 - the same, with electrode potential of spent film 0.48 V.