# Disbonding of underwater-cured epoxy coating caused by cathodic

# protection current

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Cathodic disbonding of the underwater-applied, ultra-thick, solvent free epoxy coating subjected to various levels of cathodic protection was investigated during the period of the coating cure. The results indicate that the partially cured coating was of low resistivity, between  $10^3$  and  $10^5 \Omega$  cm<sup>2</sup> for the cathodic polarization of on-potentials between -0.98 and -1.4 V<sub>Ag/AgCl/sw</sub>. The coating was shown to be capable of withstanding normal levels of cathodic protection between off-potentials of -0.8 and -1.1 V<sub>Ag/AgCl/seawater</sub> while the IR drop, introduced by the coating in the same potential range, increased from 0.06 to 0.1 V and has to be taken into account at the design stage of the cathodic protection system. Beneficial influence of calcareous deposit formation on the cathodic protection current was confirmed, particularly for the failed coating. The initial period (1 week) of coating cure was shown as the most critical for disbonding processes caused by the excessive cathodic polarization.

Keywords: A. low alloy steel; B. organic coatings; B. polarization; C. cathodic protection;

## 1. Introduction

A severe corrosion damage of construction steel exposed to seawater is a well known phenomenon observed worldwide [1]. Combination of protective coating and cathodic protection is the most effective and the most economical method of protection. The selection of the type and specifications of coating should be carried out by considering the life cycle management of the construction. However, it should also be noted that protection effect will be obtained only if the cathodic protection system is compatible with the chosen coating [2-3].

When the thick coatings, mostly used under heavy-duty conditions, are applied, it is considered that corrosion does not occur at the intact coating/metal surface boundary but only at a small portion of the overall surface, i.e. at the bottom of the coating pores [4]. On such a coated structure subjected to cathodic protection, metal surface at the bottom of the pores is protected by the cathodic current. However, the coating itself is influenced by a strong electrical force which may change chemical and dynamic conditions and affect coating performance [2]. Influence of the electric stress may be particularly harmful when excessive cathodic potentials are applied. More importantly, the oxygen reduction reaction in coating pores and the transport of Na-ions through the conductive pathways in the coating result in NaOH accumulation [5]. Alkalization is the predominant reason for cathodic disbonding which proceeds either through hydrolysis of the interfacial bonds that attach the coating to the substrate resulting in direct disbonding, or through hydrolysis of the coating itself resulting in de-polymerization [6]. The resulting blisters contain alkaline solution (up to pH 13 - 14) which prevents corrosion and passivates steel. When a blister ruptures, the steel beneath it is under cathodic protection and calcareous sediment forms in the area of rupture. However, the exposure of larger portions of the metal surface as a consequence of blisters cracking, may result in the increase in current consumption in an attempt to maintain the requested cathodic protection level as well as in the early cathodic protection system failure [7].

In the work reported in this paper we investigated the cathodic disbonding of solvent free, epoxy-polyamine, ultra-thick coating intended for underwater application. Underwater paints are essential in a number of applications [8] some of which include agricultural and food processing facilities, drinking water systems, fertilizer plants, dairies, metal-packing operations and marine structures. Epoxy-polyamide type of underwater paint chosen as the subject of this study has been in use for decades [9] and is of particular importance in marine industry due to the savings associated with in-situ underwater repairs and coating projects. Additionally, these coatings have minimal occupational, health and safety issues and are considered environmentally friendly.

When the coating is applied to dry surface, cured and subsequently submerged, the cathodic disbonding consequences are usually visible after a few months or years [3]. However, in the case of coatings applied underwater, the period of the appearance of cathodic disbonding may be reduced to days, hours, or even have an immediate effect precluding the coating application i.e. the disbonding process occurs during the period of coating cure. For epoxy coatings, this phenomenon is easily understood knowing that the non reactive epoxide groups provide sites for electrophylic attack by cathodically formed OH<sup>-</sup> ions, and undergo ring opening to form diols [10]. Although it is reasonable to assume that the impressed current cathodic protection systems would be switched off in the period of coating application and cure, the sacrificial anode systems and/or the identified or unidentified sources of stray currents still pose a problem that is a site specific. Therefore, some paint manufacturers strongly recommend testing in the actual marine environment before committing to any underwater coating project.

Despite its great importance, the phenomenon of coating disbonding of underwater applied epoxy coatings during the stage of cure has not been investigated previously. In order to obtain results of practical value, the measurements in the present study were conducted as to simulate the situations in which cathodic protection is on during the coating application, or out of service for various times after the coating application. The results were interpreted within the theory of cathodic disbonding and the basic principles of cathodic protection in seawater.

## 2. Experimental

Electrochemical experiments were carried out in three-electrode cell shown in Figure 1. The working electrode was constructed of UNS 5L X52 steel plate (15 cm x 15 cm x 0, 6 cm) with a steel rod attached at the edge as a contact. Prior to all experiments, the plates were blast-cleaned with aluminium silicate to Sa 2 <sup>1</sup>/<sub>2</sub> according to EN ISO 8501-1 [11]. The counter electrode was a commercial titanium based/mixed metal oxide type electrode (Lida®). The reference electrode was an Ag/AgCl electrode in seawater (Ag/AgCl/sw). All the reported potentials refer to Ag/AgCl electrode in seawater. The electrolyte was natural seawater (58 mScm<sup>-1</sup>).

A commercial, 2-component, 100% solids, solvent free, epoxy-polyamide coating (Apsacoat 106, Carboline) was used in this study. After thorough mixing of the two pasty components, the coating was applied underwater by hand on the working electrode surface, in one layer of approximately 5 mm in thickness, according to the instructions of the manufacturer. Since the major goal of the investigation, was to determine the effect of the cathodic protection on the protective properties of epoxy type underwater cured coatings, applied in an identical manner as on a submerged structure, the main experimental parameter in this work was cathodic protection polarization potential. The precise coating formulation, its thickness and its physical properties, were not a variable. In fact, it may be assumed that the producer had already optimized such a type of product in order to obtain the maximum protection in the working conditions characteristic of seawater application. Moreover, the

results of this study should not be taken as a measure of the quality of the particular coating used, as they include cathodic protection polarization potentials exceeding the widely accepted limits for coated steel in seawater [12-15].

Comparative measurements were performed at the bare electrode and at the coated electrode. In some experiments the coating was damaged by drilling a hole of diameter 1, 6 or 14 mm in the centre of the sample, leaving the steel surface directly exposed to the environment. The experiments were carried out at room temperature, as the physical and corrosion resistance properties of this type of coating were found not to vary with application temperature within the temperature range from 5 to 25 °C [9].

Four types of measurements were performed:

(i) Linear polarization measurements were carried out on PAR 273 potentiostat. Luggin capillary tip of the reference electrode was placed close to the coating surface (Fig. 1) and away from the edge and the artificial defect (if present). Both, the coated and the uncoated samples were immersed for 24 hours before the beginning of the measurements. For each point of the polarization curve, the current was stabilized for 5 minutes at a certain cathodic potential and then the potential-time transient was measured after switching off the current in order to obtain the off-potential readings (off-potential method) [15]. The transient data acquisition was done by a separate electronic circuit that included A/D converter connected to a computer. The potential sampling frequency after the current switch-off was 100 Hz. In accordance to the common cathodic protection practice, the polarization potential before the current switch-off is denoted by  $E_{on}$  and after the current switch-off, by  $E_{off}$  [13, 14]. The off-potential is known as the polarised potential i.e. the potential across the structure/electrolyte interface that is the sum of the corrosion potential and the cathodic polarization, and is indicative of the level of cathodic protection achieved [15]. Comparative

measurements were performed at the bare electrode and at the coated electrode with and without a circular defect ( $\phi$  6mm)

(ii) Time evolution of the open circuit potential (OCP) was measured on bare and on coated samples for 32 days. Each measurement was carried out in triplicate showing excellent reproducibility (OCP readings for identically prepared samples were within the interval of 10 mV).

(iii) Cathodic polarization to low ( $E_{on} = -0.98 \text{ V}_{Ag/AgCl/sw}$ ), moderate ( $E_{on} = -1.10 \text{ V}_{Ag/AgCl/sw}$ ) and high ( $E_{on} = -1.40 \text{ V}_{Ag/AgCl/sw}$ ) levels [16], was applied to coated samples instantly after the coating application and prolonged for 30 days. The coating appearance was studied visually and by following the evolution of the protection current with time.

(iv) The polarization to  $E_{on} = -1.2 V_{Ag/AgCl/sw}$  ( $E_{off} = -1.1 V_{Ag/AgCl/sw}$ ) was applied after 7, 14, 24 and 32 days of immersion at the OCP. The current attained after 24 h of polarization was recorded.

## 3. Results and discussion

#### 3.1. Linear polarization of samples in seawater

In order to exclude the influence of the IR drop on the polarization potentials, resulting from the coating resistance, each point of the polarization curves in Figure 2 was measured by the off-potential method. As expected, the lowest currents were obtained at the coated electrode (for  $E_{off} = -0.9 \text{ V}_{Ag/AgCl/sw}$ ,  $j = 90.4 \text{ mA m}^{-2}$ ). At the coated electrode with a circular defect ( $\phi$  6 mm) the currents were somewhat higher compared to the undamaged electrode (for  $E_{off} = -0.9 \text{ V}_{Ag/AgCl/sw}$ ,  $j = 154.6 \text{ mA m}^{-2}$ ), while the highest currents were obtained at the uncoated electrode (for  $E_{off} = -0.9 \text{ V}_{Ag/AgCl/sw}$ ,  $j = 568.72 \text{ mA m}^{-2}$ ). The shape of the curves and the current densities are comparable to those found in literature for thick epoxypolyamine coatings with artificial defects [17]. The increase in the current caused by the defect existence was significantly higher than that calculated for the increase in the bare metal area (i.e. the area of the defect multiplied by the current density obtained on a bare electrode). Margarit et al. [17] have shown that for a coating with artificial defect, instead of what would be expected, the electric field may not be completely concentrated in the area of metal exposure. Higher currents were found to flow in the system with failure causing higher polarization at weak areas of the coating, changes of the electrolyte at the coating/metal interface and the appearance of blisters. Hence, the disproportional increase in the current may partly be attributed to the increased passage of the current through the coating itself. Generally, whenever the polarization of steel is changed, the polarization level at various spots of the sample also changes, but not homogenously. The local properties of the coating, that define the level of the current passing through those points, determine the polarization level.

Off-potential measurements may be understood through the analysis of the equivalent circuit of the electrolyte/coating/metal interface. The impedance of coated metals has been extensively studied and the interpretation of the impedance data exhibits various degrees of complexity [4, 7, 18 - 24 ]. However, the impedance of the continuous coating without an artificial defect may be approximated by a simple equivalent circuit shown in Figure 3.  $C_{\rm e}$  represents the capacitance of the intact coating. Typically, its value has been shown to be much lower than that of a double layer capacitance  $C_{\rm dl}$  and its units are pF or nF, not  $\mu$ F [9, 22].  $R_{\rm po}$  (pore resistance) is the resistance of the ion conducting paths that develop in the coating. It should be noted that these paths may not be physical pores filled with electrolyte.  $R_{\rm s}$  is the uncompensated solution resistance between the reference electrode tip and the coating. In the present study, the Luggin capillary tip of the reference electrode was positioned in the immediate vicinity of the coating, away from the artificial defect and the plate edges. Taking into account the high conductivity of the electrolyte, it is reasonable to

assume that the measured IR drop includes only the ohmic resistance of the coating. The component of the potential shift, due to the cathodic polarization of the metal/electrolyte interface as a result of the applied cathodic current, can be excluded from the IR drop reading because the capacitor  $C_{dl}$  across the metal/electrolyte boundary discharges in the exponential manner over a long period of time, as seen from Figure 4. Hence, the ohmic resistance of the coating, as a function of  $E_{on}$  polarization potential, was calculated from the IR data and shown in Figure 5. The ohmic resistance decreases sharply with polarization potential probably due to the opening of the new conductive pathways in the coating as the higher polarization and consequently more intensive hydrogen evolution put more stress on the coating. This assumption was confirmed by a visual observation of the hydrogen bubble formation at the macroscopic pore openings, present at a progressively larger portion of the coating surface, when more negative cathodic potentials were applied. It appears that the excessive cathodic polarization increased porosity to the extent that hydrogen release through pores became possible in large scale. When the low cathodic polarizations were applied, the resistance was of the order of  $10^5 \ \Omega \ cm^2$ , while for the high cathodic polarizations, the resistance attained a steady value of the order of  $10^3 \Omega$  cm<sup>2</sup>. The observed, relatively low resistances [22, 25] are concordant with the fact that the coating was not completely cured and was cured underwater.

# **3.2. Time evolution of OCP**

Porosity of the coating is one of the basic characteristics that affect coating performance under the cathodic protection. Hereby, the term porosity does not necessarily imply existence of electrolyte columns penetrating the organic coating but rather any type of ionic conductive pathway. For epoxy coatings, there is a possibility of ion transport through the polymer matrix via the areas of low cross-link density [10]. Generally, the OCP values of coated surfaces are more positive than those of the uncoated surfaces and only for porous coatings, the OCP values approach those of the uncoated metal [7, 8, 21, 26, 27]. Hence, the OCP may be taken as indicative of the degree of the coating porosity.

The measurement of the OCP was performed at the uncoated steel plates (representative curve shown in Figure 6) and the four coated samples that were used for further polarization experiments. Stationary state was attained at least 4 days after the immersion. The OCPs of the coated samples were, on average, 0.110 V more positive than the OCP of the uncoated sample, indicating relatively high porosity. Typically, a positive shift of few hundred milivolts between the uncoated and the coated samples could be observed for nonporous, highly-resistive (> M $\Omega$  cm<sup>2</sup>) coatings [7, 26, 27]. Furthermore, a clearly visible discharging of the structure-to-electrolyte boundary on a coated sample in Figure 4, supports the assumption of high porosity, as resistive and nonporous coatings almost exclusively show a sharp increase in potential corresponding to the IR drop due to their high resistance and low capacitance. In such systems, discharging of  $C_{dl}$  is not observed on transient off-potential measurements as the coating resistance is much higher compared to the electrochemical parameters  $R_{ct}$  and  $C_{dl}$ . Consequently, it is impossible to determine a time constant related to the faradaic process at the metal/highly resistive coating interface by fitting the impedance data [24].

## 3.3. Cathodic disbonding test during the initial stage of coating cure

Instantly after the underwater coating application, pairs of samples were subjected to the  $E_{on} = -0.98$ , -1.10,  $-1.40 V_{Ag/AgCl/sw}$  and inspected after 2 hours of polarization. At the plates polarized to potentials  $E_{on} = -1.1$  and  $-1.4 V_{Ag/AgCl/sw}$ , defects in the form of cracks in the coating developed at the edges and intensive hydrogen evolution was observed. Although small cracks in the coating developed at the edges of the electrode polarized to  $E_{on} = -0.9$   $V_{Ag/AgCl/sw}$ , cathodic disbonding and/or blistering did not appear. The experiment was further prolonged for 30 days.

The protection current was recorded after 2 h, 24 h, 1, 2, 3 and 4 weeks, and the results are presented in Figure 7. Samples polarized to  $E_{on} = -0.98$  and  $-1.1 V_{Ag/AgCl/sw}$  with time showed a continuous drop in the protection current from the initial values of 95.2 and 238.0 mA m<sup>-2</sup>, respectively. Within the first two weeks, the sample polarized to  $E_{\rm on}$  = -1.4 VAg/AgCl/sw showed an increase of the protection current compared to the initial value of 3641.4 mA m<sup>-2</sup> followed by a continuous decrease until the final value was attained. For the sample polarized to  $E_{on} = -1.4 V_{Ag/AgCl/sw}$ , it may be observed that the weak zones within the coating constitute a source of blister initiation [17, 23]. It has been shown by Le Thua et al. [18], by measurements made on the modified wire beam electrode, that the local protection current reflects well the weak zones within the coating. On the other hand, due to the enhanced alkalinity of the steel environment during the cathodic polarization, calcareous layers deposit on the exposed steel surface [28 - 30]. The presence of the calcareous layer reduces the oxygen diffusion rate thereby lowering the cathodic protection current. It may be concluded that the variation of the cell current resulted from the competition of the two opposite processes - the increase of the bare metal area due to the cathodic disbonding and the decrease of the bare metal area due to the formation of a visible calcareous layer having limited protective properties. Hence, the ratio of the cathodic current measured after a certain period of time and the cathodic current at the beginning of the experiment may be considered as indicative of the prevalence of either of the two processes. The ratio >1 indicates a predominant influence of the cathodic disbonding while the ratio <1, indicates a predominant influence of the calcareous deposit formation on the protection current.

The final appearance of the samples polarized to  $E_{on} = -0.98$  or  $-1.1 V_{Ag/AgCl/sw}$ potential is shown in Figure 8a) and of the sample polarized to  $E_{on} = -1.4 V_{Ag/AgCl/sw}$  is shown in Figure 8b). Laboratory and field tests [28, 29] have shown that a rapid polarization of a steel cathode upon immersion to potentials of -0.9 to -1.05  $V_{Ag/AgCI/sw}$  generates a more protective calcareous deposit compared to the deposit generated by a slower polarization to potentials of -0.8 to -0.9  $V_{Ag/AgCI/sw}$ . This is consistent with the observation in this study; the highest decrease of the protection current was observed for the sample polarized to  $E_{on} = -1.1$   $V_{Ag/AgCI/sw}$  ( $E_{off} = -1.02 V_{Ag/AgCI/sw}$ ). After 30 days, at the sample polarized to  $E_{on} = -1.4 V_{Ag/AgCI/sw}$ , the coating was detached from the metal base at approximately 60 % of the sample surface, forming cracks and blisters. Calcareous layers were observed in the form of thick, white deposits in the areas of cracks or near the rim of a blister, at the site of its puncture (Figure 8b) [30]. At the sample polarized to  $E_{on} = -1.1 V_{Ag/AgCI/sw}$ , coating was only marginally cracked at the edges (probably due to the insufficient coating thickness) while at the sample polarized to  $E_{on} = -0.98 V_{Ag/AgCI/sw}$  none of the above phenomena were observed.

# **3.4.** Influence of the time of the coating cure at the OCP before the application of cathodic potentials

Influence of the time of the coating cure at the OCP, on the appearance of the cathodic disbonding, was tested.  $E_{on} = -1.2 V_{Ag/AgCV/sw}$  ( $E_{off} = -1.1 V_{Ag/AgCV/sw}$ ) was chosen as a marginal potential of cathodic protection [12 - 15] and 24 h polarization was performed after 7, 14, 24 and 32 days of coating cure at the OCP (Figure 6). The initial currents, after various times of sample immersion at the OCP (Figure 9), decreased with the time of immersion, showing that either the gradual solidification of the coating and/or the accumulation of the corrosion products in the coating pores [7, 25, 26] affected the protection current. Relatively stable values were attained after approximately 15 days of immersion.

Since the appearance of disbonding and blistering also depends on the defect area, the samples with artificial defects were tested. After the coating cure at the OCP, the artificial

defects of various diameters (0, 1, 14 mm) were formed in the coating. Subsequently, the samples were polarized to  $E_{on}$  potentials down to -1.4 V<sub>Ag/AgCI/sw</sub> for 3 days (results not shown). A visible cathodic disbonding and/or blistering did not appear at any of the samples tested showing that the initial period of the coating cure (1 week) is the most critical for disbonding processes caused by excessive cathodic polarization.

## 4. Conclusions

From the presented results it may be concluded, that although exhibiting high porosity and low resistance (between  $10^3$  and  $10^5 \Omega$  cm<sup>2</sup>), the uncured 100% solids, solvent free, epoxy-polyamide coating is capable of withstanding normal levels of cathodic protection that are widely accepted and prescribed by the international standards (off-potentials between -0.8 and -1.1 V<sub>Ag/AgCU/sw</sub>). The IR drop introduced by the coating in the same potential range increases from 0.06 to 0.1 V and has to be taken into account at the design stage of the cathodic protection system. The cathodic protection current decreases with the time of the immersion at the OCP, and attains stable value after approximately 15 days, probably due to the solidification of the coating and/or the accumulation of the corrosion products in the coating pores. Measuring time evolution of the protection current on a partially cured coating represents a sensitive tool for the follow up of the coating disbonding and calcareous deposit formation processes, as may be concluded from consistency of the results obtained in the present study and from the excellent correlation with visual observations.

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# **Figure captions**

Figure 1. Cell setup for polarization experiments.

Figure 2. IR corrected cathodic polarization curves measured on coated samples with and

without a circular defect (6 mm in diameter) and on an uncoated sample.

Figure 3. Equivalent circuit of a coating without or far from the artificial defect.

Figure 4. Off-potential measurements on a coated sample and an uncoated sample polarized to

the  $E_{\rm on} = -1.1 V_{\rm Ag/AgCl/sw}$ .

Figure 5. IR drop ( $\bullet$ ) and coating resistivity ( $\circ$ ) as a function of potential on coated samples without a circular defect.

Figure 6. Representative time dependence of the OCP of the uncoated samples and of the four coated samples used for subsequent polarization measurements.

Figure 7. Ratio of the measured and the initial protection current as a function of time for the

 $E_{\rm on} = -0.98$ , -1.1 and -1.4 V<sub>Ag/AgCl/sw</sub>.

Figure 8. Final appearance of the samples after 30 days of polarization to: a)  $E_{on} = -0.98$  or -

1.1  $V_{Ag/AgCl/sw}$  and b)  $E_{on} = -1.4 V_{Ag/AgCl/sw}$ .

Figure 9. Cathodic protection currents after various times of sample immersion at the OCP and subsequent 24 h polarization to  $E_{on} = \text{ of } -1.2 \text{ V}_{Ag/AgCl/sw}$ .

















