

Passivation of carbon steel in neutral chloride media by inhibited compositions based on normal alkanes

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Abstract

The cathodic and anodic polarization of steel electrodes covered by thin films of compositions containing a 10 wt.% mixture of amines of hydrogenated acids of tall oil or individual $C_{16}H_{33}NH_2$ amine in $n-C_{15}H_{32}$ or $n-C_{10}H_{22}$ has been studied in 0.5 M NaCl solution. At the polarization from the cathodic region to the anodic one, a potential range is observed where the process rate does not depend on the potential. This potential range spreads in both directions from the corrosion potential and is interpreted as the non-oxide passivity region.

Keywords: *passivity, adsorption, polarization, potential, amine, protection.*

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1. Introduction

In neutral chloride solutions (0.1–0.5 M NaCl) the polarization of St3 steel electrodes covered with a film of an oil based composition containing 10 wt.% TVK-1 inhibitor (reaction product of polyethylenepolyamine and synthetic fat acids C_{21} – C_{26}) [1] or a homologous mixture of aliphatic amines [2] shows a wide range of cathodic potentials (0.20–0.25 V) around the corrosion potential (E_{cor}) where the electrode reaction rate ($i = 10^{-3}$ – 10^{-2} A/m²) nearly does not depend on E . In our investigations we observed a range of independency of the process rate on potential (AB) spreading in both directions from E_{cor} (Fig. 1). This phenomenon is very important for practical purposes because the existence and width of this range characterizes the efficiency of protective formulations. The cathodic domain of the AB range (Fig. 1) corresponds to the potential range of cathodic protection, therefore its joint use with protective formulations can improve the protective efficiency. In the anodic domain, it is possible to apply similar compositions together with anodic protection of metals capable of passivation or even instead of it. It is doubtful that this effect in the anodic domain is caused by oxide passivity of carbon steel. Perhaps it results from the passivity of steel caused by adsorbed molecules of surface active substances (SAS) contained in a protective oil [1, 2]. The adsorption passivation of iron was first observed in sodium N-phenylanthranilate ($NaOOC_6H_4NH_2C_6H_5$) solutions [3]. Such non-oxide protection of iron is caused by adsorption of N-phenylanthranilate anions [4, 5]. This paper considers the nature of the above effect of independency of the partial

electrode reactions rates on potential in the presence of a film of protective formulation on the metal surface.

2. Experimental

Potentiostatic polarization curves were measured at room temperature in 0.5 M NaCl solution using a potential step of 20 mV. An electrode with a horizontal working surface was embedded in epoxy resin. Before recording a polarization curve, the specimen was polished, cleaned by rinsing with acetone and then covered with a film of a protective formulation. The electrode potentials were measured using a saturated silver/silver-chloride reference electrode, but all potentials are reported *versus* the standard hydrogen scale. The protective formulations were prepared on the basis of $n\text{-C}_{15}\text{H}_{32}$ alkane and amines of hydrogenated acids of tall oil (10 wt.%). In some cases, a formulation based on $n\text{-C}_{10}\text{H}_{22}$ and individual $\text{C}_{16}\text{H}_{33}\text{NH}_2$ (10 wt.%) was used. In the first cycle of polarization, a St3 steel electrode covered with a protective formulation film was kept at $E = -0.5$ V for 50 min, then potentiostatic polarization was carried out from the cathodic region to the anodic one with exposure for 30 s at each potential, up to a potential 0.15–0.20 V more positive than the potential corresponding to point A (E_A) (Fig. 1). Then, without removal of the electrode from the solution, it was polarized in reverse direction to $E = -0.5$ V. The electrode was then again kept at this potential for 5–60 min *in situ* and potential cycling was repeated three times.

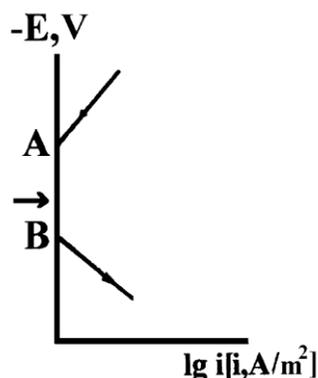


Fig. 1. Schematic representation of the polarization curves. The arrow indicates E_{cor} .

3. Results and Discussion

Figure 2 (curve 1) shows the polarization curves of a steel electrode covered with a film of the formulation containing 10 wt.% of a $\text{C}_{10-16}\text{H}_{21-33}\text{NH}_2$ homologous mixture in $n\text{-C}_{15}\text{H}_{32}$ obtained by polarization from the cathodic region to the anodic one. Curve 2 in this Figure shows the iron ionization rate obtained from the data of chemical analysis of the solution for iron content after electrode exposure at the applied potentials. Both curves suggest that a potential range exists where the process rate does not depend on the potential. The observed difference between curves 1 and 2 is explained by differences in the surface condition when different investigation methods are used.

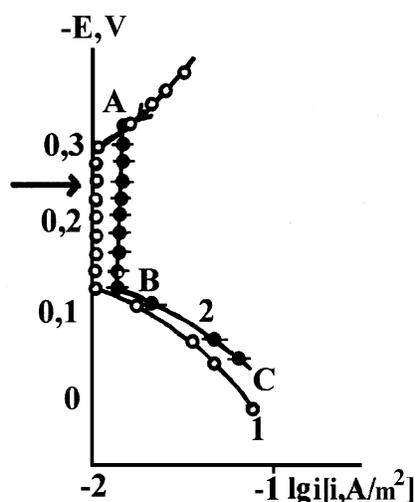


Fig. 2. The cathodic and anodic branches of the polarization curve (1) of St3 steel covered with a film of the formulation containing 10 wt.% of the $C_{10-16}H_{21-33}NH_2$ homologous mixture in $n-C_{15}H_{32}$ and the process rate (2) based on data of chemical analysis for iron content in a 0.5 M NaCl solution. The arrow indicates E_{cor} .

The peculiarities of the observed phenomenon in this case are:

- independence of i on E is observed for carbon steel both in the anodic and cathodic range of potentials;
- carbon steel covered with a hydrocarbon film is evidently passivated due to adsorption of RNH_2 particles;
- the passivator is adsorbed from the hydrocarbon phase covering the metal surface, rather than from the solution bulk.

The adsorbed SAS molecules suppress almost completely both the cathodic reduction of dissolved oxygen in the neutral medium



and the steel ionization reaction at anodic potentials. At a certain anodic potential, the region with $i_j \neq f(E)$ turns into a region characteristic of the $lg i, E$ dependence matching the requirements of electrochemical kinetics.

The results of cyclic polarization of steel electrodes covered by a protective film based on $n-C_{15}H_{32}$ alkane and amines of hydrogenated acids of tall oil from the cathodic region to the anodic one and back repeated three times are shown in Fig. 3. In the case of forward polarization direction, a region with $i_j \neq f(E)$ is observed in which E_{cor} is located. Hence, amine molecules retard both the cathodic and anodic reaction. A change in the polarization direction causes essential narrowing of this region (Fig. 3a).

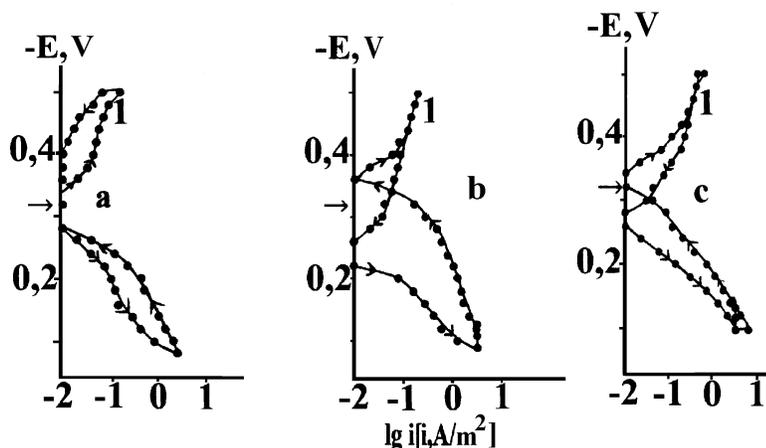


Fig. 3. Polarization of steel sample covered by a protective film based on $n\text{-C}_{15}\text{H}_{32}$ alkane and amines of hydrogenated acids of tall oil from the cathodic to the anodic region and back in 0.5 M NaCl solution. Cycles: *a* – first, *b* – second, *c* – third. The exposure time at $E = -0.5$ V at the beginning of each cycle is 5 min. The arrow parallel to the horizontal axis shows E_{cor} . The arrows on the curves show the polarization direction.

It is assumed that SAS molecules are adsorbed on steel surface at cathodic potentials and suppress the anodic and cathodic reaction in the AB region (Fig. 2). At anodic potentials more positive than E_B , desorption of SAS molecules occurs and a wide hysteresis loop is observed during the reverse polarization (Fig. 3) because desorbed particles do not have time for repeated adsorption and retardation of the corresponding partial electrode reactions. Hence, by creating conditions that promote adsorption of SAS molecules, reversible stable appearance of the range with $i_j \neq f(E)$ can be made possible. On increase in the exposure time of the electrode at $E = -0.5$ V during repeated cycling, the potential range with $i_j \neq f(E)$ increases (Fig. 4). The averaged picture is shown in Fig. 5.

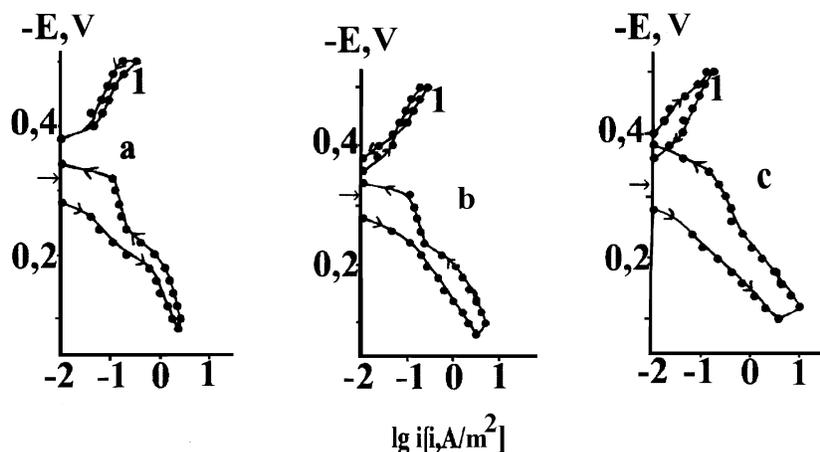


Fig. 4. The exposure time of the electrode at $E = -0.5$ V under repeated cycling conditions is 15 min. The rest of the designations are the same as in Fig. 3.

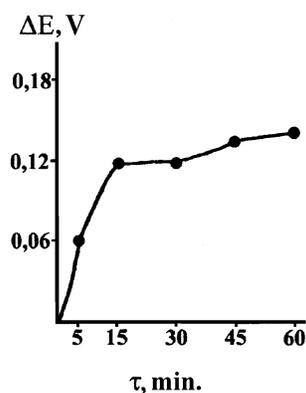


Fig. 5. Effect of exposure time of a steel electrode covered by the protective film based on $n\text{-C}_{15}\text{H}_{32}$ alkane and amines of hydrogenated acids of tall oil at $E = -0.5$ V in 0.5 M NaCl solution upon repeated cycling on the width (ΔE) of the potential range with $i_j \neq f(E)$.

The potential range in question is observed if the SAS or the solvent in the protective formulation are varied. For instance, the same picture is observed when a steel electrode is covered with protective formulations based on $n\text{-C}_{15}\text{H}_{32}$ and hexadecylamine ($\text{C}_{16}\text{H}_{33}\text{NH}_2$) (Fig. 6) or based on n -decane and $\text{C}_{16}\text{H}_{33}\text{NH}_2$ (Fig. 7).

If the exposure time of the electrode at $E = -0.5$ V is 60 min, the potential range with $i_j \neq f(E)$ remains constant at direct and reverse directions of polarization and no hysteresis loop is observed (Fig. 8), but in this case polarization in reverse direction was started at an anodic potential smaller than E_A by 0.02 V.

The influence of an increase in electrode exposure time at $E = -0.5$ V on the potential range with $i_j \neq f(E)$ testifies that SAS (amines of hydrogenated acids of tall oil and $\text{C}_{16}\text{H}_{33}\text{NH}_2$) are adsorbed on the surface from the protective coating at high negative potentials.

Under conditions of steel surface energy non-homogeneity, amines are evidently adsorbed on the most active centers. This results in a small rate of the cathodic process (1) and metal ionization at anodic potentials. However, desorption of amines takes place at a certain anodic potential, therefore a hysteresis loop is observed during polarization in reverse direction. On the other hand, the inhibiting action of amines is observed at $E \geq E_A$ but not at $E < E_A$. This fact requires additional investigation.

4. Conclusions

The cathodic and anodic polarization of the steel electrode covered by thin films of formulations containing a 10 wt.% mixture of amines of hydrogenated acids of tall oil or individual $\text{C}_{16}\text{H}_{33}\text{NH}_2$ amine in $n\text{-C}_{15}\text{H}_{32}$ or $n\text{-C}_{10}\text{H}_{22}$ has been studied in 0.5 M NaCl solution. During polarization from the cathodic region to the anodic one, a potential range is observed where the process rate does not depend on potential. This potential range spreads in both directions from the corrosion potential. Its existence is due to adsorption of

amines on steel surface from the protective coating. It causes the non-oxide passivity of steel and suppression of the electrode processes.

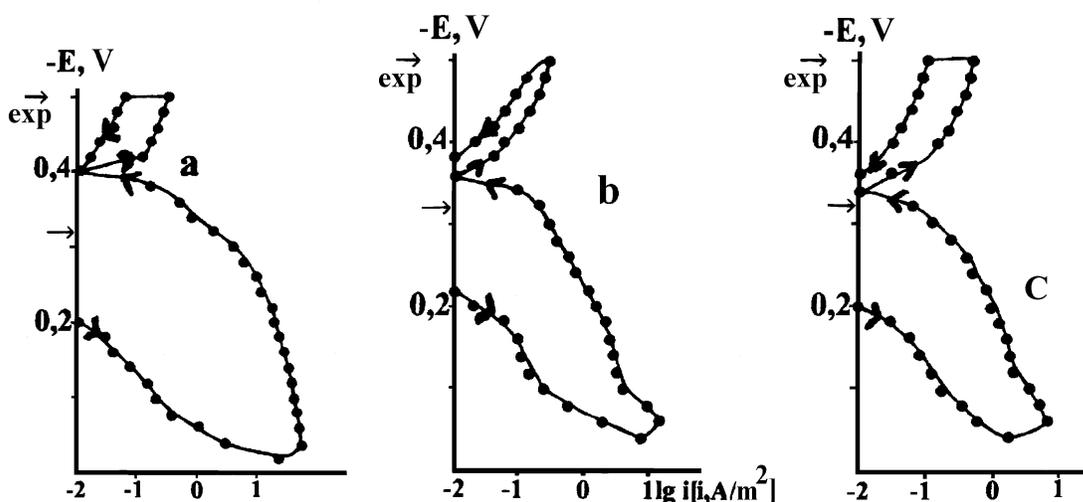


Fig. 6. Polarization of steel electrode covered by a protective film based on $n\text{-C}_{15}\text{H}_{32}$ alkane and $\text{C}_{16}\text{H}_{33}\text{NH}_2$ amine from the cathodic region to the anodic one and back in 0.5 M NaCl solution. Cycles: *a* – first, *b* – second, *c* – third. The exposure time at $E = -0.5$ V in the beginning of every cycle is 1 h. The arrows parallel to the horizontal axis show: the upper ones with the index “exp” – the potential of electrode exposure in the cathodic region; the lower ones – E_{cor} . The arrows on the curves show the polarization direction.

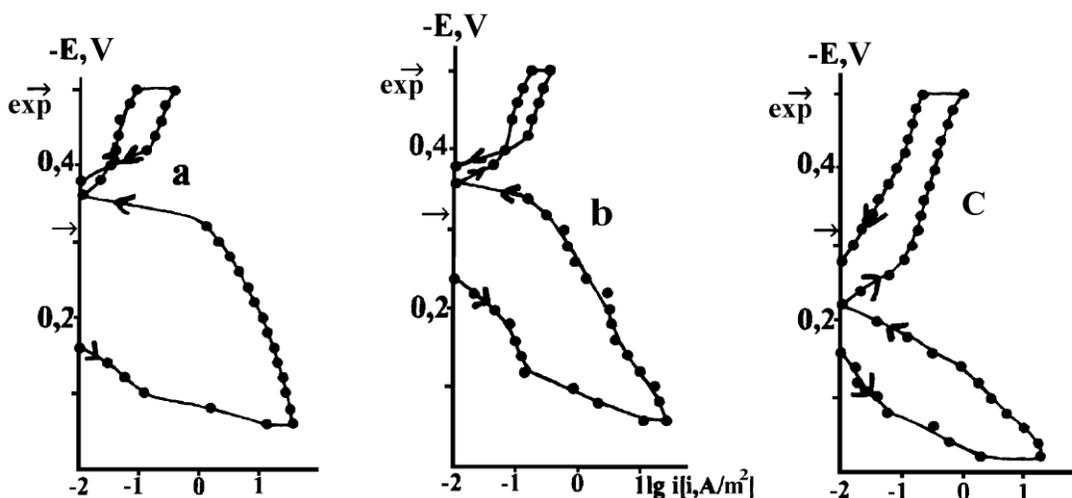


Fig. 7. Polarization of steel electrode covered by a protective film based on $n\text{-C}_{10}\text{H}_{22}$ alkane and $\text{C}_{16}\text{H}_{33}\text{NH}_2$ amine from the cathodic region to the anodic one and back in 0.5 M NaCl solution. Cycles: *a* – first, *b* – second, *c* – third. The exposure time at $E = -0.5$ V in the beginning of every cycle is 1 h. The rest of the designations are the same as in Fig. 6.

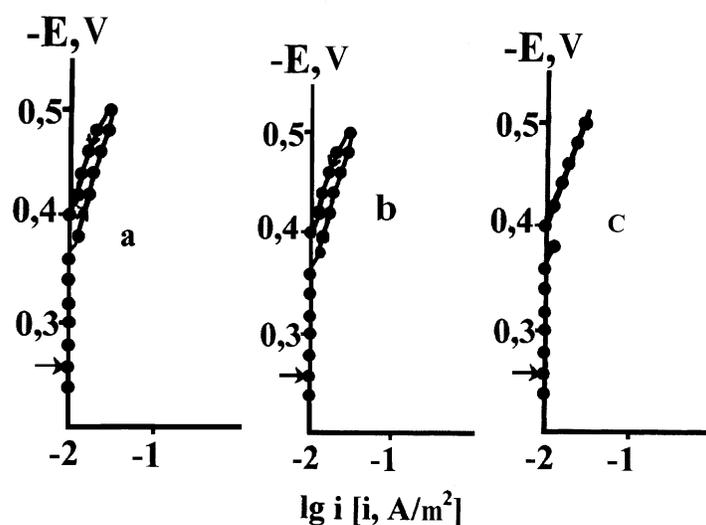


Fig. 8. Polarization of steel electrode covered by a protective film based on $n\text{-C}_{15}\text{H}_{32}$ alkane and $\text{C}_{16}\text{H}_{33}\text{NH}_2$ amine from the cathodic region to the anodic one and back in 0.5 M NaCl solution. Cycles: *a* – first, *b* – second, *c* – third. The exposure time at $E = -0.5$ V in the beginning of every cycle is: *b* – 5 min; *c* – 1 h. The rest of the designations are the same as in Fig. 3.

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