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ELECTROCHEMICAL BEHAVIOR OF COPPER IN CHLORIDE MEDIUM IN THE PRESENCE OF PINE CONE MACERATE

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Abstract
The article presents the results of the study of the electrochemical behavior of copper during oxidation in a 0.5 mol/dm^3 NaCl solution in the absence and presence of pine cone macerate of different concentrations. The electrochemical behavior of copper was investigated using the cyclic voltammetry method and the potentiostatic method. The results of cyclic voltammetry show that three current peaks appear on the anodic polarization curves, which correspond to the formation of copper chloride and copper oxide. Potentiostatic polarization was performed at 0.5 mV vs. SCE for 100 s and at 25°C. Potentiostatic curves show that the steady-state currents decrease with increasing concentration of macerate in the electrolyte. Microscopic images confirm that a protective layer has formed on the copper surface in the presence of the pine cone macerate, which prevents the corrosion process.

***Keywords**: electrochemical behavior, copper, chloride medium, pine cone macerate*

1. INTRODUCTION

Corrosion of copper and its alloys is a major problem because it causes considerable material and financial losses. To protect against corrosion, it is important to investigate the effect of various potential inhibitors in different environments. So far, a large number of potential inhibitors have been investigated. Research should be focussed on the application of ecological - "green" inhibitors, with the main criterion for application being their ecological compatibility. Research into plant extracts has recently been of great interest when it comes to corrosion inhibitors [1,2]. They are also natural antioxidants that are cheap and have no negative impact on the environment. The inhibitory effect of some plant extracts is achieved by the presence of tannins in their composition. In perennial herbaceous plants, the underground organs (rhizomes and roots) are richest in tannins, while in woody plants the bark of roots, stems and thicker branches, leaves, fruits, etc. are richest in tannins [3].

This paper presents the results of the investigation of the influence of pine cone macerate on the corrosion behaviour of copper in 0.5 mol/dm^3 NaCl.

2. EXPERIMENTAL

To prepare a solution of 0.5 mol/dm^3 NaCl, NaCl produced by d.d.."Zorka Pharma" Šabac was used. The solution was prepared with chemicals of p.a purity and distilled water. The working solutions were prepared by pouring 10, 20, 30 and 40 mL of pine cone macerate (Pinophyta) into volumetric flasks of 100 mL each and then adding a solution of 0.5 mol/dm^3 NaCl, always

maintaining the concentration of sodium chloride in the solution. The macerate of pine cones was prepared as follows: first, 1000 mL of distilled water was heated up to 60 °C and then 100 g of crushed sporophylls of pine cones were added. The process to obtain the macerate takes 4 hours, mixing with a magnetic stirrer at 400 min^{-1}. After 4 hours, the resulting macerate is filtered in a Bichner apparatus and stored in a refrigerator.

The experiments were carried out using a system consisting of an electrochemical cell with three electrodes (working, reference and auxiliary electrode), hardware (PC, Burr-Brown PCI-20428W, AD/DA converter and an analogue interface developed at the Faculty of Engineering in Bor) [4]. The study of the electrochemical behaviour of copper in 0.5 mol/dm^3 NaCl solution in the absence and presence of pinecone macerate was carried out by recording the anodic polarization curves. The curves were recorded in the potential range from -0.4 V vs. SCE to 1 V vs. SCE with a scan rate of 20 mV/s. The potentiostatic curves were recorded at 0.5 V vs. SCE for 100 s. Optical microscopy was used to characterize the electrode surface after potentiostatic oxidation.

3. RESULTS AND DISCUSSION

Figure 1 shows the anodic polarization curves for pure copper in 0.5 mol/dm^3 NaCl solution with and without pine cone macerate.

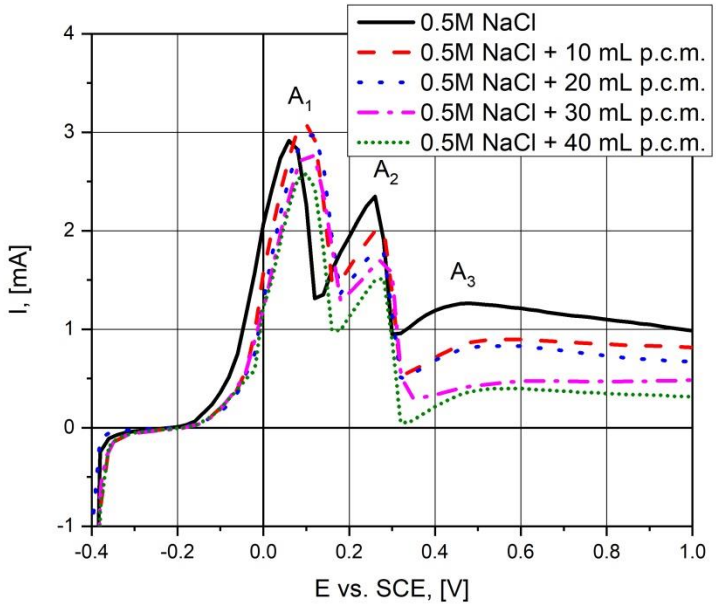


Figure 1. Anodic polarization curves for copper with a scan rate of 20 mV/s in 0.5 mol/dm^3 NaCl with and without the addition of pine cone macerate (p.c.m.- pine cone macerate)

Three current peaks corresponding to the formation of chloride (current peaks A_1 and A_2) and copper oxide (current peak A_3) appear on the anodic polarization curve obtained in 0.5 mol/dm^3 NaCl [5,6]. With the addition of 10 mL and 20 mL of pine cone macerate, the current strength values for current peak A_1 are higher compared to the current strength value without the addition of pine cone macerate, while the current strength values with the addition of 30 mL and 40 mL of pine cone macerate are lower compared to the current strength value without the addition of macerate. In the area of the potential where the current peaks A_2 and A_3 occur, the values of the current strength of the current peaks in the presence of pine cone macerate are lower than the value of the current strength without the addition of pine cone macerate at all macerate concentrations. From the polarization curves obtained, it can be concluded that pine cone macerate slows down

the process of copper chloride and oxide formation on the copper surface and that pine cone macerate acts as an anodic inhibitor of copper corrosion in 0.5 mol/dm^3 NaCl.

Figure 2 shows the potentiostatic curves after potentiostatic treatment of copper for 100 s in 0.5 mol/dm^3 NaCl solution without and with pine cone macerate.

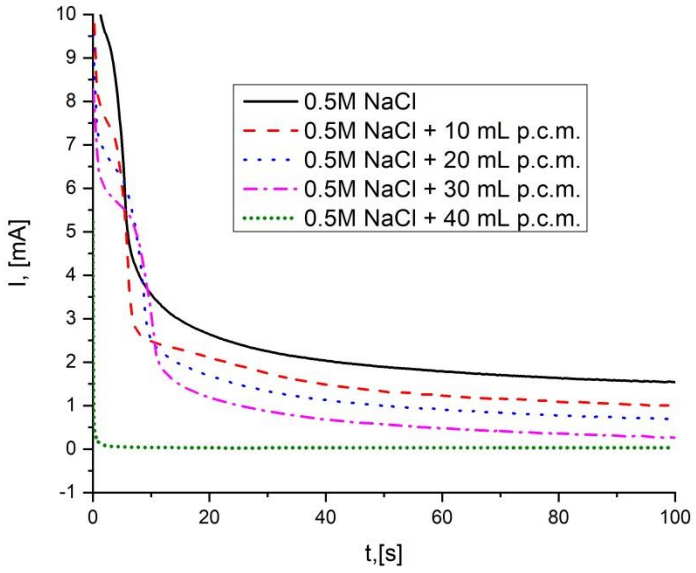
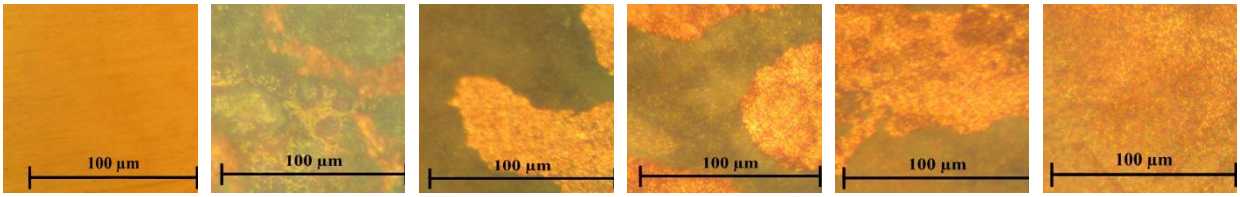


Figure 2. Potentiostatic curves for copper in 0.5 mol/dm^3 NaCl without and with the addition of pine cone macerate (p.c.m.- pine cone macerate) at 0.5 V vs. SCE

The potentiostatic curve obtained for copper with the addition of 10 mL of pine cone macerate drops sharply in the first 7 seconds, then the curve decreases monotonically until about 90 seconds when it stabilizes and the value of the steady-state current is 1 mA. The potentiostatic curve obtained for copper with the addition of 20 mL of pine cone macerate drops sharply in the first 10 seconds and then continues to decrease slowly until it stabilizes after about 80 seconds and the value of the steady-state current is 1.6 mA. The potentiostatic curve obtained for copper with the addition of 30 mL of macerate drops sharply in the first 10 seconds, then continues to decrease slightly and stabilizes at around 90 seconds, with the value of the steady-state current being 0.3 mA. When 40 mL of pine cone macerate is added, stabilization occurs in the first few seconds and the value of the steady-state current is 0 mA. This means that the pine cone macerate protects the copper surface well against corrosion. Figure 3a shows a photomicrograph of untreated copper. Figures 3b, 3c, 3d, 3e and 3f show microphotographs of the copper surface after potentiostatic treatment in 0.5 mol/dm^3 NaCl without and with the addition of pine cone macerate.



a) b) c) d) e) f)

Figure 3. Microphotographs of the copper surface after potentiostatic treatment on the potential of 0 V vs. SCE during 100 s: a) untreated surface; b) in 0,5mol/dm^3 NaCl; c) in 0,5mol/dm^3 NaCl + 10 mL pine cone macerate; d) in 0,5mol/dm^3 NaCl + 20 mL pine cone macerate; e) in 0,5mol/dm^3 NaCl + 30 mL pine cone macerate; f) in 0,5mol/dm^3 NaCl + 40 mL pine cone macerate

4. CONCLUSION

Increasing concern for the protection of the environment has led to stricter regulations on the use of chemicals that can have a harmful effect on the environment. This has resulted in the use of a number of very effective inhibitors being reduced or discontinued.

Based on the experiments carried out, the following conclusions can be drawn:

- When investigating the electrochemical behavior of copper using the cyclic voltammetry method in 0.5 mol/dm^3 NaCl, it was found that three current peaks appear on the anodic polarization curve. The current peaks A_1 and A_2 correspond to the formation of copper chloride, while the current peak A_3 corresponds to the formation of copper oxide on the surface. In the presence of pine cone macerate, the inhibitory effect of the macerate is achieved in the area of potential A_1 with the addition of more than 20 mL, while in the area of potential A_2 and A_3 the pine cone macerate has an inhibitory effect at all investigated concentrations of pine cone macerate.

- The results of the potentiostatic measurement show that stabilization is achieved more quickly in the presence of pine cone macerate. The values of the steady-state current in the 0.5 mol/dm^3 NaCl solution in the presence of macerate are lower than the value of the steady-state current without the presence of macerate. This indicates that a protective film forms on the copper surface in the presence of the macerate, which slows down the copper oxidation process.

- Photomicrographs after potentiostatic treatment of copper in a 0.5 mol/dm^3 NaCl solution clearly show the presence of a green phase, representing copper chloride, and a black phase, representing copper oxide. When pine cone macerate is added, the photomicrographs show green and black phases on a smaller scale. This indicates that pine cone macerate acts as a copper corrosion inhibitor.

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