U.P.B. Sci. Bull., Series B, Vol. 68, No. 1, 2006

TEMPERATURE AND CORROSION INHIBITORS INFLUENCE ON PITTING CORROSION OF AlMn1 ALLOY USED IN THE AUTOMOTIVE INDUSTRY

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Au fost utilizate metode electrochimice de analiză, în special voltametria ciclică, pentru a studia sensibilitatea la coroziunea localizată a aliajului pe bază de aluminiu 3003 (AlMn1) în lichidele antigel folosite la radiatoarele automobilelor. A fost studiată influența a doi inhibitori de coroziune din lichidele de răcire glaceol A şi glaceol D, a temperaturii şi a apei de distribuție asupra comportamentului la coroziunea localizată. Suprafața curbelor de voltametrie ciclică şi diferența dintre potentialul "pitting" şi cel de repasivare au fost utilizate pentru a evalua capacitatea inhibitoare a inhibitorilor de coroziune

Modern electrochemical methods, especially the cyclic voltammetry, have been used to investigate the sensitivity to pitting corrosion of aluminum 3003 (AlMn1alloy) in specific cooling liquids in the automotive industry. The influence of two corrosion inhibitors specific to the cooling liquids glaceol A and glaceol D has been studied. Other factors such as temperature and addition of distribution water have also been investigated. The surface of the cyclic voltamperograme curves and the difference between the pitting potential and the repassivation potential have been used to evaluate the inhibitory capacity of the corrosion inhibitors.

Keywords: pitting corrosion, corrosion inhibitors, cyclic voltammetry, antifreezing liquids, Al-Mn alloys

Introduction

Several challenges which favor the use of aluminium. [1,2] are currently present in the car industry (such as weight reduction of the vehicle, diminished fuel consumption, reduced pollution,). Among the many car components made of aluminium alloys, the heating radiator made of the low manganese AlMn1 alloy (also designated 3003) is one of the most severely stressed by corrosion .

This paper is intended to investigate the behaviour of this alloy to localized corrosion (pitting corrosion) in conditions simulating the chemical

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environment and temperature action to which the radiator tubes are subject in service. The research was mainly focussed on the influence of the corrosion inhibitors added to the cooling liquids currently in use for the Renault and Renault-Dacia automobiles, namely glaceol D (containing an organic inhibitor) and glaceol A (containing an inorganic inhibitor), respectively.

1. Materials and methods

The glaceol D and glaceol A cooling liquids used as corroding medium in the present research contain the same basic component with antifreeze vocation, namely the monoethylen glycol (MEG) . The organic corrosion inhibitor used in glaceol D consisted of a derivative azole namely TTA 5-(p-tolyl)-1,3,4-triazole. The inorganic inhibitor used in glaceol A was the sodium tetraborate $Na_2 B_4 O_7 .5H_2 O$ (borax).

The properties of the inhibiting film have been characterized by electrochemical techniques [3, 4]. The method used was cyclic voltammetry which provides information on the thermodynamics and kinetics of the investigated electrochemical system. A potential E variable in time is applied on the electrode and the curve i-E is recorded directly [5] with possibility to reverse the direction of variation of the sweeping potential back to its initial value. At the instant of the passive layer failure the electrical answer will correspond to the potential of pitting (E_{pit}). Once a given potential reached, one carries out the way reverses until the stopping of the progression of the pitting in the studied medium. This edge will be reached when the response to the current is null and it represents the potential of repassivation (E_{rep}). The area of the curves of cyclic voltammetry and the difference between the pitting potential and repassivation potential characterize the sensitivity to localized corrosion. A small surface between the ascending and downward curves will be the sign of a weak pitting corrosive capacity [6].

All the voltamperogrammes in this paper have been obtained at a 0,2 mV/s sweeping speed.

2. Results and Discussion

A. Influence of the type of inhibitor in the cooling liquids

As seen in Fig.1 the voltamperogrammes obtained in the mediums containing MEG, glaceol A, glaceol D mixed with 50% distilled water without preliminary immersion show a very low sensitivity to localized corrosion for glaceol D. In this case the passive field is very important; at the time of sweeping return there is a weak tendency to repassivation . The behavior of glaceol A is similar to that of MEG (Fig.1)

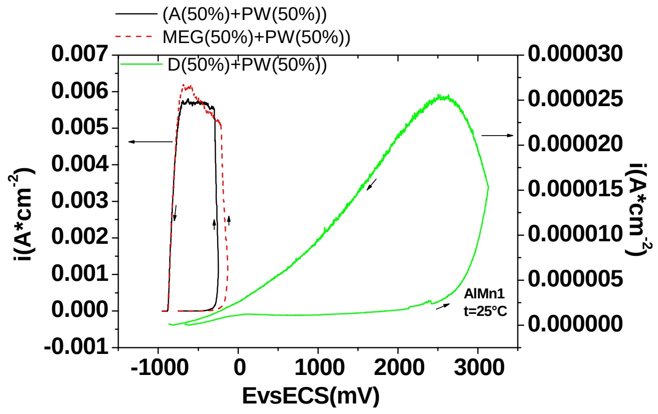

Fig.1. Cyclic voltammetry curves for the AlMn1 alloy in the presence of various inhibitors

The main characteristics of the voltamperogrammes in Fig.1 are indicated in Table 1

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Table 1.

Characteristics of the curves of cyclic voltammetry obtained for the AlMn1 alloy in the presence of different inhibitors (% volume - DW = distilled water).

Medium	$E_{pitting}$	$E_{repassivation}$	$E=E_{pit}-E_{rep}$
MEG(50%)+DW(50%)+NaCl(50mg/L)	-200mV	-880mV	680mV
A(50%)+DW(50%)+NaCl(50mg/L)	-250mV	-880mV	530mV
D(50%)+DW(50%)+NaCl(50mg/L)	2780mV	-200mV	2580mV

B. Influence of the distribution water

Water from the distribution network is sometimes added to the antifreezing liquid instead of distilled water. The distribution water may change the corrosive action of the medium on account of its limestone content (24^{o} French degrees). The results obtained by cyclic voltammetry are presented in Fig. 2 and Fig.3 when distilled water and distribution water, respectively, were added to glaceol D and glaceol A

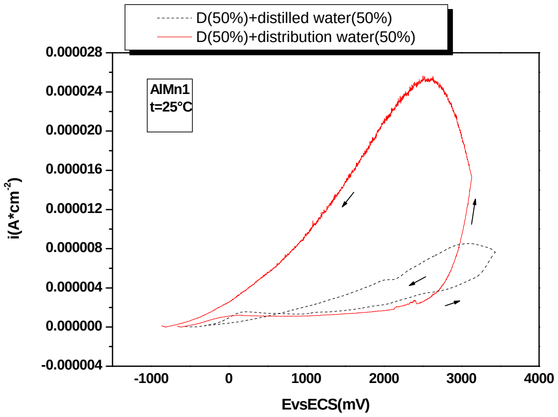

Fig.2 . Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol D with distilled water and distribution water

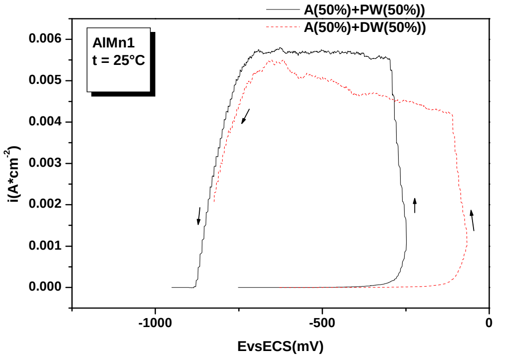

Fig. 3. Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol A with distilled water and distribution water

Fig.2 points to a very good stability for glaceol D. In the case of glaceol A (Fig.3) the distribution water has not a major influence on the sensitivity to localized corrosion but nevertheless glaceol A seems to be more sensitive than glaceol D to the addition of distribution water. The surface obtained between the ascending and downward curve is larger in the presence of distribution than in the case of distilled water, but as shown in Table 2 the difference between E_{pit} and E_{rep} is smaller in the case of of distribution water.

Table 2.

Characteristics of the voltamperogrames obtained relating to the behavior of the AlMn1 alloy in the mediums without and with distribution water (PW = distilled water ; DW = distribution water).

Medium	$E_{pitting}$	$E_{repassivation}$	$E=E_{pit}-E_{rep}$
A (50%)+PW(50%)+NaCl(50mg/L)	-260mV	-860mV	600mV
A(50%)+DW(50%)+NaCl(50mg/L)	-100mV	-860mV	760mV
D(50%)+PW(50%)+NaCl(50mg/L)	2720mV	-770mV	3490mV
D(50%)+DW(50%)+NaCl(50mg/L)	2990mV	-510mV	3500mV

The cyclic voltammetry curves obtained in the three mediums: glaceol A, MEG, glaceol D mixed with distribution water are presented together in Fig.4. They point to a better stability in the case of glaceol D, whereas in the case of glaceol A we observe the greatest sensitivity.

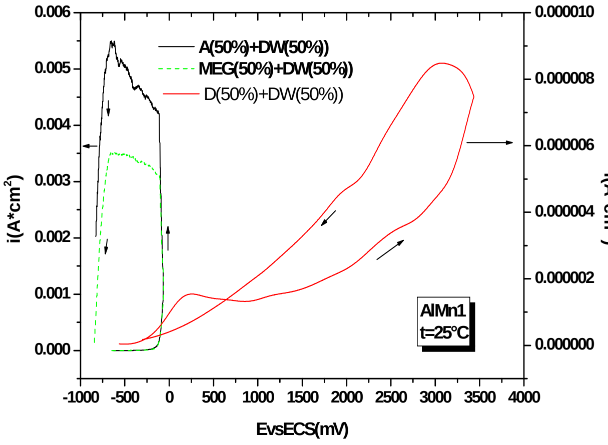

Fig. 4. Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol A, glaceol D and MEG with distribution water

The characteristics of the above voltamperogrammes are gathered in Table 3. One can observe the same difference between E_{pit} and E_{rep} for MEG and glaceol A, but the surface between the ascending and downward curve in the case of glaceol A is larger than in the case of MEG.

Table 3.

Characteristics of the voltamperogrames relating o the behavior of the AlMn1 alloy in the mediums containing MEG, glaceolA, glaceol D with distribution water (vol% - DW = distribution water).

Medium	$E_{piquration}$	$E_{repassivation}$	$E=E_{piq}-E_{rep}$
MEG(50%)+DW(50%)+NaCl(50mg/L)	-100mV	-700mV	600mV
A(50%)+DW(50%)+NaCl(50mg/L)	-100mV	-70mV	600mV
D(50%)+DW(50%)+NaCl(50mg/L)	2990mV	-510mV	3500mV

C. Influence of the corrosive water on the inhibiting capacity of the inhibitors

The behavior of each type of inhibitor when slightly salted water was added to the cooling liquid was investigated by following the evolution of the resistance of polarization and by plotting the curves of cyclic voltammetry.

The evolution of the resistance of polarization in the slightly salted mediums for MEG, glaceol A, glaceol D and as well as in corrosive water is presented in Fig.5. In the case of glaceol D (which contains the organic inhibitor) the resistance of polarization increases during time and its values are definitely higher than the values obtained in all the other cases. The evolution of the resistance of polarization for glaceol A (which contains the inorganic inhibitor) indicates an important decrease of the resistance to corrosion in the slightly salted mediums.

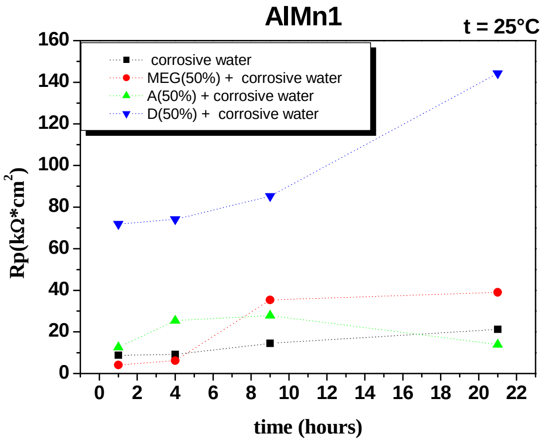

Fig. 5. Evolution of the resistance of polarization during 21 hours of immersion of the alloy AlMn1 in the mediums: - glaceol D(50%) + corrosive water; glaceol A(50%) + corrosive water; MEG(50%) + corrosive water

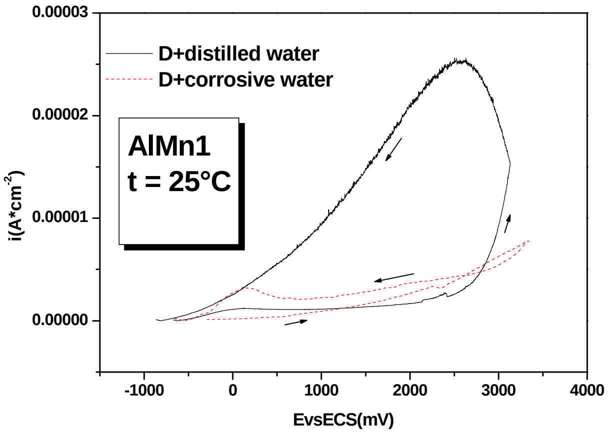

Fig. 6. Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol D with distilled water and with corrosive water.

The voltamperogrammes obtained in the slightly salted mediums are given in Figures 6, 7, 8. and their main characteristics are indicated in Table 4.

These results point to a better stability for glaceol D. Glaceol A maintains the same behavior as before, which is similar to that of the basic component MEG.

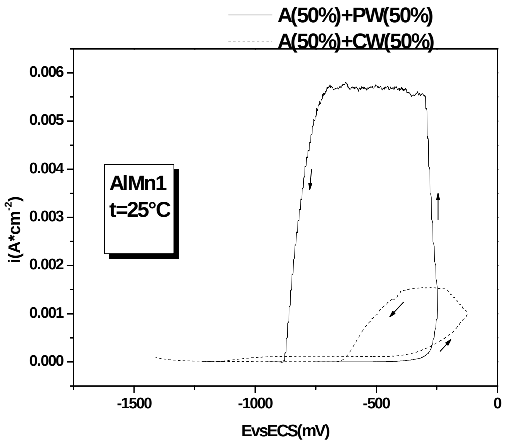

Fig.7. Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol A with permuted water (PW) and corrosive water

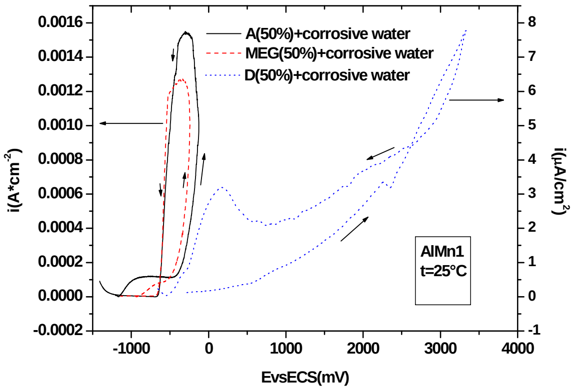

Fig. 8. Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol A, D and MEG with corrosive water

Table 4.

Characteristics of the voltamperogrames obtained for the AlMn1 alloy in the mediums without and with corrosive water (PW = distilled water; CW = corrosive water).

Medium	$E_{piquration}$	$E_{repassivation}$	$E=E_{piq}-E_{rep}$
D (50%)+PW0%)	-2780mV	-770mV	3550mV
D(50%)+CW50%)	1700mV	-300mV	2000mV
A(50%)+PW50%)	-250mV	-880mV	530mV
A(50%)+CW50%)	2780mV	-200mV	2580mV

D. Influence of the inhibitor content on the inhibiting capacity

The influence exerted by the content of inhibitor was studied for glaceol D comprising the organic inhibitor. To this purpose the antifreezing liquid glaceol D was diluted with distilled water in various proportions (20%, 50% and 80%).

The obtained cyclic voltammetry curves are presented in Fig.9. They clearly show that the increase in the inhibitor concentration results in a reduction in the sensitivity to localized corrosion.

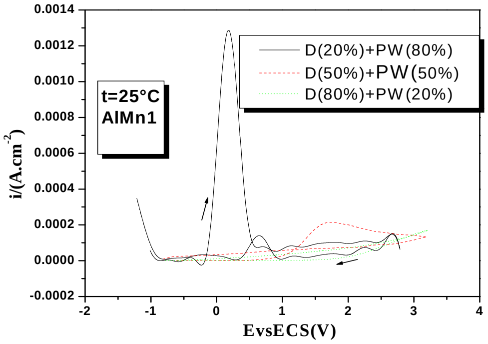

Fig.9. Voltamperogrammes obtained for the AlMn1 alloy in solution of glaceol D and distilled water with various concentrations (20%, 50% and 80%) at t=25°C after 48 hours of immersion

D. Influence of temperature on the inhibiting capacity of the inhibitors

The behavior to localized corrosion in function of temperature for the mediums with inhibitor and without inhibitor was investigated after 21 hours of immersion. The curves of cyclic voltammetry were obtained at 25°C, 50°C and 80°C and they are given in Fig.10, 11, 12, and 13.

The main characteristics of the voltamperogrammes in Fig.10,11,12 and 13 are indicated in Tables 5,6,7 and 8.

These experimental results clearly show that temperature does not have a major influence on the behavior to localized corrosion for all investigated mediums. Glaceol D remains definitely stable compared to glaceol A whatever the temperature.

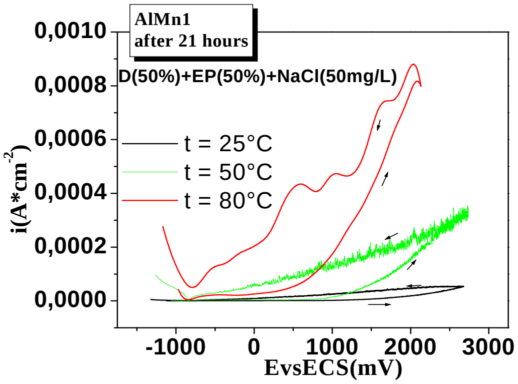

Fig.10. Curves of cyclic voltammetry obtained for the AlMn1 alloy in glaceol medium D(50%), distilled water and NaCl 50mg/L at various temperatures after 21 hours of immersion

Table 5.

Characteristics of the curves of cyclic voltammetry obtained for the AlMn1 alloy in the medium: glaceol D(50%), distilled water and NaCl 50mg/L at various temperatures after 21 hours of immersion

Temperature	$E_{pitting}$	$E_{repassivation}$	$E=E_{pit}-E_{rep}$
25°C	1750mV	-846mV	2450mV
50°C	1250mV	-700mV	1950mV
80°C	625mV	-857mV	1472mV

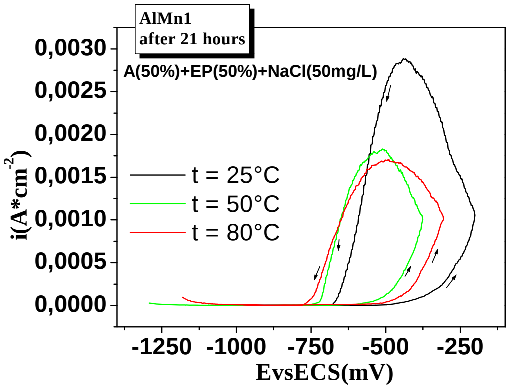

Fig.11. Curves of cyclic voltammetry obtained for the AlMn1 alloy in the medium: glaceol A(50%), distilled water and NaCl 50mg/L at various temperatures after 21 hours of immersion

Table 6.

Characteristics of the curves of cyclic voltammetry obtained for the AlMn1 alloy in the medium: glaceol A(50%), distilled water and NaCl 50mg/L after 21 hours of immersion

Temperature	$E_{pitting}$	$E_{repassivation}$	$E=E_{pit}-E_{rep}$
25°C	-280mV	-650mV	370mV
50°C	-430mV	-750mV	320mV
80°C	-480mV	-720mV	240mV

Table 7.

Characteristics of the curves of cyclic voltammetry obtained for the AlMn1 alloy in the mediums: MEG, glaceol A and glaceol D mixed with distilled water (EP) at t=25°C after 21 hours of immersion (% volume).

Medium	$E_{pitting}$	$E_{repassivation}$	$E=E_{pit}-E_{rep}$
MEG(50%)+EP(50%)+NaCl(50mg/L)	-280mV	-700mV	420mV
A(50%)+EP(50%)+NaCl(50mg/L)	-325mV	-650mV	325mV
D(50%)+EP(50%)+NaCl(50mg/L)	1360mV	-190mV	1550mV

Table 8.

Characteristics of the curves of cyclic voltammetry obtained for the AlMn1 alloy in the mediums based on MEG, glaceol A and glaceol D mixed with distilled water (EP) at t=25°C after 21 hours of immersion (% volume).

Medium	$E_{pitting}$	$E_{repassivity}$	$E=E_{pit}-E_{rep}$
MEG(50%)+EP(50%)+NaCl(50mg/L)	-680mV	-700mV	20mV
A(50%)+EP(50%)+NaCl(50mg/L)	-500mV	-700mV	200mV
D(50%)+EP(50%)+NaCl(50mg/L)	1300mV	-800mV	2100mV

Table 9.

Characteristics of the curves of cyclic voltammetry obtained for the AlMn1 alloy in the mediums based on MEG, glaceol A and glaceol D mixed with distilled water (EP) at t=80°C after 21 hours of immersion (%volume).

Medium	$E_{pitting}$	$E_{repassivation}$	$E=E_{pit}-E_{rep}$
MEG(50%)+EP(50%)+NaCl(50mg/L)	-330mV	-760mV	330mV
A(50%)+EP(50%)+NaCl(50mg/L)	-390mV	-745mV	355mV
D(50%)+EP(50%)+NaCl(50mg/L)	700mV	-800mV	1500mV

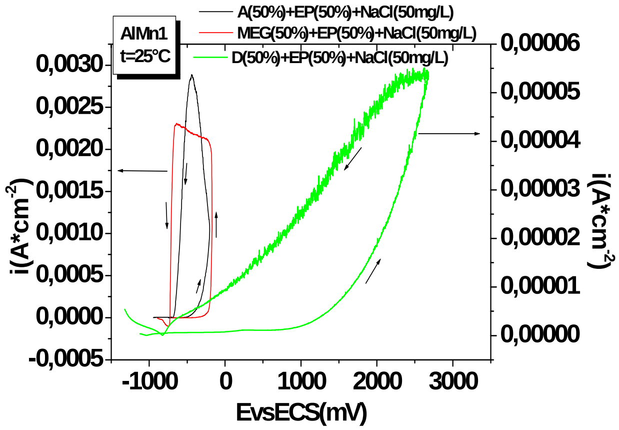

Fig.12. Curves of cyclic voltammetry obtained for the AlMn1 alloy in mediums: glaceol A, glaceol D and MEG mixed with distilled water at=25°C after 21 hours of immersion

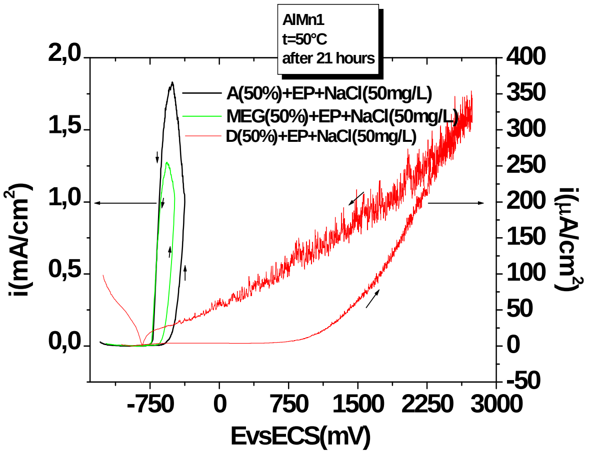

Fig.13. Curves of cyclic voltammetry obtained for the AlMn1 alloy in solution of glaceol A, glaceol D and MEG mixed with permuted water at t=50°C after 21 hours of immersion

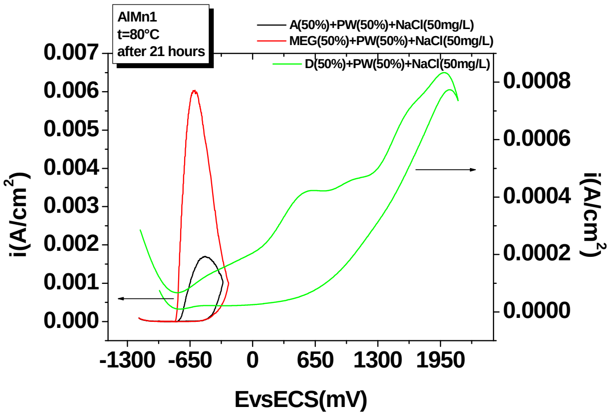

Fig.14 Curves of cyclic voltammetry obtained for the AlMn1 alloy in solution of glaceol A, glaceol D and MEG mixed with distilled water at t=80°C after 21 hours of immersion

The curves of cyclic volatammetry obtained at 80ºC for the three mediums based on: MEG, glaceol A and glaceol D are presented in Fig. 14. They clearly show a very good stability for the cooling liquid based on the organic inhibitor.

Conclusions

The AlMn1 alloy is very slightly sensitive to localized corrosion in the antifreezing liquid consisting of glaceol D that comprises the organic inhibitor

The behavior to localized corrosion in glaceol A that comprises the inorganic inhibitor resembles that in the basic medium (mono ethylene glycol) with no corrosion inhibitor;

Raising the temperature does not result in an increase of the sensibility to localized corrosion for the two types of inhibitors used;

The difference $\Delta E = E_{pit} - E_{rep}$ obtained for the organic inhibitor is definitely higher than the values obtained for the inorganic inhibitor and this fact points to a very good inhibiting capacity to localized corrosion.

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